The Regularized Resolvent Transform for Quantum Dynamics Calculations[†,‡]

Vladimir A. Mandelshtam[§]

Chemistry Department, University of California, Irvine, California 92697-2025

Received: October 5, 2000

A recently introduced numerical expression for spectral estimation, called the regularized resolvent transform (RRT) (*J. Magn. Reson.* **2000**, *147*, 129), is shown to be very useful in a number of applications in quantum dynamics calculations. RRT has emerged from the filter diagonalization method (FDM), although it is based on a different linear algebraic algorithm and, therefore, has different numerical properties, such as stability, robustness, speed, etc. Given a time signal $c(t)$, RRT provides a direct estimate of its infinite time Fourier spectrum $I(s)$. Replacement of the argument s in the RRT expression by $-iE$ leads to a very useful formula to estimate the inverse Laplace transform of $c(t)$. Two applications of RRT are discussed in detail: the calculation of *all* **S**-matrix elements using a *single* wave packet propagation and the problem of estimating the microcanonical quantities, such as the density of states, from the canonical cross-correlation functions.

I. Introduction

In this paper we are concerned with signal processing problems arising in quantum dynamics calculations. A commonly implemented scheme consists of the two general steps: (i) the signal generation, where the "signal" is not necessarily the ultimate quantity of interest, and (ii) the *signal processing*, when the physically interesting information is extracted from the signal by, for example, solving an *inverse problem*. In particular, we will consider two inverse problems, the spectral estimation from truncated cross-correlated time signals and estimation of the inverse Laplace transform. Such problems may arise in the context of time-dependent and/or path-integral approaches. An intelligent signal processing not only provides a higher accuracy for the quantities of interest but sometimes allows one to access the information that is hardly available otherwise.

One example is the calculation of resonance parameters of molecules with high number and density of states by harmonic inversion of damped Chebyshev correlation functions.[1,2] Although, for isolated resonances, the relevant information can be obtained by Fourier transformation of the same Chebyshev signal, to achieve a similar spectral resolution, one would need to use a substantially longer Chebyshev propagation.

Other examples include accurate calculation of *very* broad poles of the Green's function by harmonic inversion of time cross-correlation functions[3], or tunneling splittings calculations from semiclassical real-time cross-correlation functions,[4] or semiclassical quantization using the Gutzwiller cross-correlated periodic orbit sums.[5] Apparently, in the conventional Fourier spectral analysis of time signals this dynamical information about the underlying system is hardly available.

In ref 6 we pointed out that the commonly used strategy to compute the scattering matrix using the time-dependent approach, where each column of the **S**-matrix is computed by propagating a wave packet with specific initial characteristics[7−10] is not necessarily the optimal. In such calculations a lot of information contained in the computed time cross-correlation functions is wasted. A much more economical approach could use propagation of a *single* initial wave packet: any **S**-matrix element (or a general transition matrix element) could be computed by processing cross-correlation functions of the propagated state with the appropriate initial and final states. It was also pointed out that this approach would be most suitable for the case of resonance-dominated scattering, while it could be unstable otherwise. We will revisit this problem in the present paper.

We will also consider the problem of estimating the density of states $\rho(E)$ from the imaginary-time-correlation function $c(\beta)$.[11] The latter can be computed using the path-integral techniques. The two quantities are related via the Laplace transform,

$$c(\beta) = \int_0^\infty \rho(E) \mathrm{e}^{-\beta E}\, \mathrm{d}E \tag{1}$$

However, $\rho(E)$ cannot be computed directly from $c(\beta)$ as the signal $c(\beta)$ is not available for the complex-valued argument β. Estimation of the inverse Laplace transform is a perfect example of a very ill-defined inverse problem.

The spectral estimation technique to be used and extended here is the *regularized resolvent transform* (RRT).[12] It has recently emerged as a variant of the *filter diagonalization method* (FDM)[13,1] (see also the review[14] and references therein). FDM solves the *harmonic inversion problem*, namely, it fits a finite discrete-time signal $c(n\tau)$, $n = 0, ..., N - 1$, by the form

$$c(n\tau) = \sum_{k=1}^{K} d_k \mathrm{e}^{-\mathrm{i}n\tau\omega_k} \tag{2}$$

with the unknown complex frequencies ω_k and amplitudes d_k by diagonalizing an effective evolution operator $\hat{U} = \mathrm{e}^{-i\tau\hat{\Omega}}$. The RRT is designed to directly estimate the infinite-time discrete

[†] Part of the special issue "William H. Miller Festschrift". This work is dedicated to W. H. Miller on his 60th birthday.

[‡] Important notations. A linear operator is identified by a cap: $\hat{U}$. The round brackets are used for the symmetric (not Hermitian) inner product: $(\Psi|\Phi) = (\Phi|\Psi)$. Bold characters, as **U** or **C**, are used for matrix representations of linear operators or vectors. Their elements are then defined using the following notations: $[\mathbf{U}]_{mn}$ or $[\mathbf{C}]_n$. $\mathbf{U}^{\mathrm{T}}$ is a transpose of matrix **U**, while $\mathbf{U}^{\dagger}$ is its adjoint (transposed and complex conjugated) matrix.

[§] Corresponding author. E-mail: mandelsh@uci.edu.

10.1021/jp0036689 CCC: $20.00
Published on Web 02/22/2001

Fourier transform, defined as

$$I(s) = \sum_{n=0}^{\infty} c(n\tau) e^{in\tau s}(1 - \delta_{n0}/2) \tag{3}$$

by directly evaluating a resolvent matrix element of the same evolution operator $\hat{U}$. The term $(1 - \delta_{n0}/2)$ in eq 3 multiplies $c(0)$ by $^1/_2$ to correct the error introduced by the discrete sum approximation of the continuous half-line Fourier integral.

Interestingly, $I(s)$ can be analytically continued by simply replacing the real frequency argument s by $-iE$ in the RRT formula (see below) without creating any instability, thus, leading to a very useful expression to estimate the inverse Laplace transform of $c(n\tau)$.

Even though FDM and RRT are very much related, the linear algebraic algorithms involved in the two methods are quite different as well as their numerical properties, such as stability, speed, etc. $I(s)$ can, in principle, be estimated by FDM using the set of d_k and ω_k. However, numerical fit by the form of eq 2 may, sometimes, encounter difficulties, for instance, in the case of noisy signal and/or the presence of nonlocalized spectral features (background spectrum) resulting in an unreliable spectral estimate.[15] In RRT $I(s)$ is evaluated directly by avoiding the calculation of d_k and ω_k and the said instability does not occur.

The rest of the paper is organized as follows. In section II we derive the RRT expression. In section III RRT is adapted for processing the Chebyshev cross-correlation functions to compute all S-matrix elements from a single wave packet propagation. In section IV we analytically continue the RRT expression for the problem of estimating the inverse Laplace transform. In section V this method is extended further by considering an imaginary-time cross-correlation matrix. Section VI concludes.

II. Derivation of the Resolvent Formulas

To derive a linear algebraic expression for spectral estimation, we use the quantum ansatz of Wall and Neuhauser,[13] in which $c(n\tau)$ is associated with a time autocorrelation function of a fictitious quantum system for some fictitious initial state Φ,

$$c(n\tau) = (\Phi|\hat{U}^n|\Phi) \tag{4}$$

where the round brackets define the complex symmetric (not Hermitian) inner product. The effective evolution operator $\hat{U}$ may be nonunitary but is assumed to be symmetric with respect to the inner product, i.e., $(\hat{U}\Psi|\Phi) = (\Psi|\hat{U}\Phi) = (\Psi|\hat{U}|\Phi)$.

(Note that the assumption that the evolution operator $\hat{U}$ has a finite rank K is equivalent to the assumption of eq 2, which could be used for rigorous proofs.) Substituting eq 4 into eq 3 and evaluating the geometric sum analytically, we obtain

$$I(s) = \left(\Phi\left|\left\{\frac{1}{1 - e^{i\tau s}\hat{U}} - \frac{1}{2}\right\}\right|\Phi\right) \tag{5}$$

Equation 5 cannot be used directly for calculating $I(s)$, as we still need to obtain a matrix representation of the auxiliary objects $\hat{U}$ and Φ in terms of the known data $c(n\tau)$. To do so, as in ref 1, we introduce an auxiliary (Krylov) basis,

$$\Phi(n) = \hat{U}^n\Phi\ ,\ n = 0, 1, \ldots, M - 1 \tag{6}$$

According to our assumption, the rank of $\hat{U}$ is K, so that the $M \leq K$ Krylov vectors $\Phi(n)$ are generally linearly independent and we can rewrite eq 5 by evaluating everything in this basis:

$$I(s) = \mathbf{C}^{\mathrm{T}}\mathbf{R}(s)^{-1}\mathbf{C} - c(0)/2 \tag{7}$$

with $\mathbf{R}(s) = \mathbf{U}_0 - e^{i\tau s}\mathbf{U}_1$, where the evolution operator and the overlap matrix elements are defined as, respectively, $[\mathbf{U}_1]_{nn'} = (\Phi(n)|\hat{U}\Phi(n'))$, $[\mathbf{U}_0]_{nn'} = (\Phi(n)|\Phi(n'))$, and the coefficients of the $1 \times M$ column vector $\mathbf{C}$ are $[\mathbf{C}]_n = (\Phi(n)|\Phi)$. It is not hard to see[1] that $\mathbf{U}_1$, $\mathbf{U}_0$ and $\mathbf{C}$ are all representable in terms of the signal data points $c(n\tau)$ as

$$[\mathbf{U}_p]_{nn'} = c[(n + n' + p)\tau], \qquad p = 0, 1$$
$$[\mathbf{C}]_n = c(n\tau) \tag{8}$$

Rather surprisingly, eq 7 is a working expression. In the case eq 2 is exactly satisfied and if we choose $M = K$, it yields the exact infinite time Fourier spectrum,

$$\mathrm{I(s)} = \sum_{k=1}^{K} \frac{d_k}{1 - e^{i\tau(s-\omega k)}} - \frac{c(0)}{2} \tag{9}$$

even though only a finite part of the signal $c(n\tau)$ *of size* $N = 2M$ is used and the spectral parameters ω_k *and* d_k *are not computed.* The result is also exact if $M > K$, although in this case the set of vectors $\Phi(n)$ is linearly dependent, requiring evaluation of a pseudo-inverse of the singular $M \times M$ matrix $\mathbf{R}(s)$. For example, the singular value decomposition (SVD) of $\mathbf{R}(s)$ could be used. Typically, the matrices are not exactly singular due to noise, although they could still be very ill-conditioned, implying that some kind of regularization will often be advantageous. We will revisit this issue later in the paper.

Unfortunately, eq 7 is numerically very expensive for long (e.g., $N > 1000$) signals; however, just like in FDM[13,1] this problem can be ameliorated by performing the spectral analysis locally in the frequency domain using a Fourier transformation of the Krylov basis $\{\Phi(n)\}$,

$$\tilde{\Phi}_j = \sum_{n=0}^{M-1} e^{in\tau\varphi_j}\Phi(n), \qquad j = 1,2, \ldots, K_{\mathrm{win}} \tag{10}$$

where here and throughout the rest of the paper the tilde identifies the use of the Fourier basis. The values φ_j could be evenly spaced using

$$\Delta\varphi = \frac{2\pi}{\aleph M\tau} \tag{11}$$

For $\aleph = 1$ and $K_{\mathrm{win}} = M$ the transformation from the Krylov basis $\{\Phi(n)\}$, to the Fourier basis $\{\tilde{\Phi}_j\}$ is unitary. However, as argued first in ref 13 and later in ref 1, it is advantageous to use a local basis of small size $K_{\mathrm{win}} \ll M$ with $\aleph > 1$ (e.g., $\aleph = 1.1$). It could be even more efficient to use *multiscale basis*[15] corresponding to a nonuniform distribution of φ_j's with j-dependent Fourier length $M = M_j$ in eq 10, which describes a very narrow frequency window in high resolution and the rest of the spectrum, in low resolution, while having minimal overall size.

One can now use the new Fourier basis (10) to reevaluate the matrices in eq 8, which after some manipulation[1] leads for $j \neq j'$ to

$$[\tilde{\mathbf{U}}_p]_{jj'} = \hat{S} \sum_{\sigma=0,1} \frac{e^{i\sigma[\tau M(\varphi_j'-\varphi_j)+\pi]}}{1 - e^{i\tau(\varphi_j'-\varphi_j)}} \sum_{n=\sigma M}^{(\sigma+1)(M-1)} e^{in\tau\varphi_j} c[(n+p)\tau] \tag{12}$$

where $\hat{S}$ defines the symmetrization operator over the variables φ_j and $\varphi_{j'}$,

$$\hat{S}g(\varphi_j,\varphi_{j'}) = g(\varphi_j,\varphi_{j'}) + g(\varphi_{j'},\varphi_j) \tag{13}$$

For $j = j'$ we have

$$[\tilde{\mathbf{U}}_p]_{jj} = \sum_{n=0}^{2M-2} e^{in\tau\varphi_j}(M - |M - n - 1|)c[(n+p)\tau] \tag{14}$$

Now by evaluating $\mathbf{C}$ in the Fourier basis,

$$[\tilde{\mathbf{C}}]_j \equiv (\Phi|\tilde{\Phi}_j) = \sum_{n=0}^{M-1} e^{in\tau\varphi_j} c(n\tau) \tag{15}$$

we can rewrite eq 7 as

$$I(s) = \tilde{\mathbf{C}}^{\mathrm{T}}\tilde{\mathbf{R}}(s)^{-1}\tilde{\mathbf{C}} - c(0)/2 \tag{16}$$

with

$$\tilde{\mathbf{R}}(s) = \tilde{\mathbf{U}}_0 - e^{i\tau s}\tilde{\mathbf{U}}_1 \tag{17}$$

Because of the very nature of the Fourier transformation the spectral properties around some frequency s are completely defined by a very small subspace $\{\tilde{\Phi}_j\}$ of size K_{win} (e.g., $K_{\mathrm{win}} = 10$) with $\tilde{\Phi}_j \sim s$. Therefore, only a small $K_{\mathrm{win}} \times K_{\mathrm{win}}$ matrix $\tilde{\mathbf{R}}(s)$ has to be inverted in eq 16 to yield a well-converged spectrum $I(s)$. Equation 16 can also be evaluated directly, for example, by solving the associated linear system,

$$\tilde{\mathbf{R}}(s)\tilde{\mathbf{X}}(s) = \tilde{\mathbf{C}} \tag{18}$$

and then using

$$I(s) = \tilde{\mathbf{C}}^{\mathrm{T}}\tilde{\mathbf{X}}(s) - c(0)/2 \tag{19}$$

A nonobvious issue is the stability and robustness of the algorithm. The matrix $\tilde{\mathbf{R}}$ may be very ill-conditioned. In this case, even if the exact inverse $\tilde{\mathbf{R}}^{-1}$ exists, the exact solution of eq 18 in the form of $\tilde{\mathbf{X}} = \tilde{\mathbf{R}}^{-1}\tilde{\mathbf{C}}$ is likely to be meaningless. One explanation is that a general tiny perturbation of either $\tilde{\mathbf{C}}$ or $\tilde{\mathbf{R}}$ results in a huge variation of $\tilde{\mathbf{X}}$. A *regularization* is supposed to produce a meaningful solution that, on one hand, satisfies eq 18 only approximately within certain a priori established bounds but, on the other hand, is stable with respect to small perturbations of either $\tilde{\mathbf{C}}$ or $\tilde{\mathbf{R}}$. One possibility is to use SVD of $\tilde{\mathbf{R}}(s)$ to calculate a pseudo-inverse by either discarding the singular subspace or modifying the small singular values. However, SVD, if applied at each value of s, would be computationally quite expensive. A much less expensive regularization of the resolvent can be obtained using the Tikhonov regularization[17] obtained by modyfying the original least squares problem $||\tilde{\mathbf{R}}\tilde{\mathbf{X}} - \tilde{\mathbf{C}}||^2 \rightarrow \min$, corresponding to eq 18, by $||\tilde{\mathbf{R}}\tilde{\mathbf{X}} - \tilde{\mathbf{C}}||^2 + q^2||\tilde{\mathbf{X}}||^2 \rightarrow \min$:

$$I(s) \approx \tilde{\mathbf{C}}^{\mathrm{T}}(\tilde{\mathbf{R}}(s)^{\dagger}\tilde{\mathbf{R}}(s) + q^2)^{-1}\,\tilde{\mathbf{R}}(s)^{\dagger}\tilde{\mathbf{C}} - c(0)/2 \tag{20}$$

where the dagger means Hermitian conjugate and q is a real regularization parameter. With such a regularization the singularity in the denominator is removed as $(\tilde{\mathbf{R}}^{\dagger}\tilde{\mathbf{R}} + q^2)$ is a Hermitian and positive definite matrix. (For a much more elaborate discussion on regularization of ill-conditioned linear systems see the tutorial by Neumaier.[16])

Equation 20 can be evaluated by solving the regularized Hermitian least squares problem,

$$(\tilde{\mathbf{R}}^{\dagger}(s)\tilde{\mathbf{R}}(s) + q^2)\tilde{\mathbf{X}}(s) = \tilde{\mathbf{R}}^{\dagger}\tilde{\mathbf{C}} \tag{21}$$

and then using eq 19.

Operationally, the spectral estimation using eq 20 (or eqs 19 and 21) has a status of "transform" (like FFT), while a "method", e.g., the filter diagonalization method, would refer to a procedure that would generally be less obvious to use. More precisely, eq 20 corresponds to a direct nonlinear transformation, here called the *regularized resolvent transform* (RRT), of the time signal to the frequency domain. Unlike most other nonlinear high-resolution spectral estimators, RRT is very stable, computationally inexpensive, and has adjusting parameters that are very straightforward to use. These parameters are K_{win} and $\aleph$ defining the size and spacing of the Fourier basis in the frequency domain, and the regularization parameter q. Note that K_{win} could, in principle, be as small as 3, although a larger K_{win} generally improves the resolution, while increasing the cpu time according to the cubic scaling of a linear solver. For sufficiently large K_{win}, which is usually less than 100, the results do not change noticeably. Thus, K_{win} can be chosen according to how long one is willing to wait for the spectrum to be computed. The choice for the basis density parameter, $\aleph$, between 1.1 and 1.2 usually works well if a single-scale basis (as opposed to a multiscale basis[15]) is used. Unfortunately, there is no obvious way to estimate a priori an optimal value for the regularization parameter q, as it depends on the type of the data, level of noise, etc. Generally, there is a wide range (e.g., an order of magnitude) of acceptable parameters as the results are not very sensitive to q. An increase of q leads to a more smooth and uniform spectrum, while decreasing the resolution. Note also that this smoothing is nonlinear and has nothing to do with increasing the widths of all the peaks by shifting the poles in the complex plane by $i\Gamma$.

More detail about RRT for spectral estimation with some numerical examples can be found in refs 12 and 14. In the next sections we extend RRT to some applications in the area of quantum dynamics calculations.

III. All S Matrix Elements from a Single Wavepacket Propagation

As shown in ref 8, in the time-dependent framework, and later in ref 9, using the time-independent Green's function formulation, the $\alpha \rightarrow \alpha'$ scattering amplitude can be expressed using a matrix element of the Green's function,

$$S_{\alpha'\alpha} = i\,\frac{(\xi_{\alpha'}|\hat{G}^{+}(E)|\xi_{\alpha})}{(\xi_{\alpha}|f^{+}_{\alpha E})(|\xi_{\alpha'}|f^{+}_{\alpha' E})} \qquad \alpha \neq \alpha' \tag{22}$$

where $\hat{G}^{+}(E) = (\tilde{H} - E - i0)^{-1}$ and ξ_{α} and $\xi_{\alpha'}$ are wave packets localized in the asymptotic region corresponding to the asymptotic channels with quantum numbers α and α'. As was pointed out in ref 9 ξ_{α} and $\xi_{\alpha'}$ do not have to be purely incoming or outgoing. Moreover, even the choice of real and very narrow wave packets suffices. The only condition is that the prefactor defined by the overlap integrals between ξ_{α}, $\xi_{\alpha'}$ and the incoming asymptotic solutions $f^{+}_{\alpha E}$, $f^{+}_{\alpha' E}$ is nonzero.

The numerically challenging part in eq 22 is the Green's function matrix element. It can be evaluated using a time-dependent formulation[8] in which, e.g., the initial state ξ_{α} is propagated in time, the time correlation function $(\xi_{\alpha'}|\xi_{\alpha}(t))$ is

computed and then Fourier transformed to yield the $\alpha \rightarrow \alpha'$ transition matrix element. Similar strategies are implemented in other time-dependent approaches,[7] the obvious drawback being the need to propagate as many wave packets as there are open channels in order to evaluate the full S-matrix or to compute the cumulative reaction probability.

Our choice to evaluate eq 22 corresponds to the use of the global in energy Chebyshev[18] or better the damped Chebyshev recursion expansion[19] of the Green's function,

$$(\xi_{\alpha'}|\hat{G}^{+}(E)|\xi_{\alpha}) = \frac{2\mathrm{i}}{\sin(s)}\sum_{n=0}^{\infty}(\xi_{\alpha'}|\hat{\mathrm{T}}_n^{\gamma}|\xi_{\alpha})\mathrm{e}^{\mathrm{i}ns}(1-\delta_{n0}/2) \quad (23)$$

where $\cos(s) = E$ and the damped Chebyshev polynomials[19] satisfy the following recursion relations,

$$\hat{T}_0^{\gamma} = 1, \quad \hat{T}_1^{\gamma} = \mathrm{e}^{-\hat{\gamma}}\,\hat{H}, \quad ..., \quad \hat{T}_{n+1}^{\gamma} = \mathrm{e}^{-\hat{\gamma}}(2\hat{H}\hat{T}_n^{\gamma} - \mathrm{e}^{-\hat{\gamma}}\hat{T}_{n-1}^{\gamma}) \quad (24)$$

Here for simplicity we assumed that the Hamiltonian operator $\hat{H}$ is already rescaled so that its spectrum belongs to the interval $[-1; 1]$. The damping operator $\mathrm{e}^{-\hat{\gamma}}$ provides a correct analytic continuation of the Chebyshev propagator $\hat{T}_n$.

At first glance eq 23 requires propagation of either of the two states $\xi_{\alpha'}$ or ξ_{α}, which would conceptually be similar to the time-dependent strategies. However, as demonstrated in ref 6, one can evaluate $(\xi_{\alpha'}|\hat{G}^{+}(E)|\xi_{\alpha})$ using the three cross-correlation functions

$$c_{l0}(n) = (\xi_l|\xi_0(n)), \qquad l = 0, \alpha, \alpha' \quad (25)$$

that do not require propagation of either $\xi_{\alpha'}$ or ξ_{α}, but propagation of some auxiliary state,

$$\xi_0(n) = \hat{T}_n^{\gamma}\xi_0 \quad (26)$$

A good choice for ξ_0 could be essentially any vector with random coefficients so it would overlap with *all* system eigenstates. The same ξ_0 can then be used for any other transition amplitude.

In ref 6 $(\xi_{\alpha'}|\hat{G}^{+}(E)|\xi_{\alpha})$ was computed by harmonic inversion of the three cross-correlation functions and then by combining the results to express the Green's function matrix element in terms of its poles and residues. However, this approach is difficult to apply in case when the broad poles (direct scattering) have significant contribution to the dynamics. Here we show how RRT can be implemented avoiding the solution of the harmonic inversion problems and, thus, making the approach much more robust and stable.

The assumption of eq 4 is rewritten as

$$c_{ll'}(n) = (\Phi_l|\hat{U}^n|\Phi_{l'}) \quad (27)$$

where the rank of the effective evolution operator $\hat{U}$ is doubled compared to K, the dimensionality of the actual Hamiltonian operator $\hat{H}$. This is because each complex pole E_k of the Green's function $\hat{G}^{+}(E)$ gives rise to the two complex eigenvalues of $\hat{U}$, namely, $\mathrm{e}^{-\mathrm{i}\omega_k}$ and $\mathrm{e}^{i\omega_k^*}$ satisfying $\cos\omega_k = E_k$ (see refs 1 and 6 for more detail). So one should not confuse $\hat{U}^n$ with $\hat{T}_n$ and $\xi_l(n)$ with $\Phi_l(n)$, as they are associated with two different spaces. By analogy with eq 5 we can write

$$(\xi_{\alpha'}|\hat{G}^{+}(E)|\xi_{\alpha}) = \frac{2\mathrm{i}}{\sin(s)}\left(\Phi_{\alpha'}\left|\left\{\frac{1}{1-\mathrm{e}^{\mathrm{i}s}\hat{U}} - \frac{1}{2}\right\}\right|\Phi_{\alpha}\right) \quad (28)$$

Now evaluating everything in the Fourier basis,

$$\tilde{\Phi}_j = \sum_{n=0}^{M-1}\mathrm{e}^{\mathrm{i}n\varphi_j}\Phi_0(n) \qquad j = 1, 2, ..., K_{\mathrm{win}} \quad (29)$$

we arrive at the following regularized resolvent formula,

$$(\xi_{\alpha'}|\hat{G}^{+}(E)|\xi_{\alpha}) = \frac{2\mathrm{i}}{\sin(s)}[\tilde{\mathbf{C}}_{\alpha'}^{\mathrm{T}}(\tilde{\mathbf{R}}(s)^{\dagger}\tilde{\mathbf{R}}(s) + q^2)^{-1}\tilde{\mathbf{R}}(s)^{\dagger}\tilde{\mathbf{C}}_{\alpha} - c_{\alpha'\alpha}(0)/2] \quad (30)$$

where $\tilde{\mathbf{R}}(s)$ is defined as before using eq 17 and $c_{00}(n)$; the elements of the column vectors $\tilde{\mathbf{C}}_{\alpha}$ and $\tilde{\mathbf{C}}_{\alpha'}$ are

$$[\tilde{\mathbf{C}}_l]_j \equiv (\Phi_l|\tilde{\Phi}_j) = \sum_{n=0}^{M-1}\mathrm{e}^{\mathrm{i}n\varphi_j}c_{l0}(n) \quad (31)$$

and $c_{\alpha'\alpha}(0) = (\xi_{\alpha'}|\xi_{\alpha})$.

Equation 30 is another important new result of this paper. It implies that any $S_{\alpha'\alpha}$ could be recovered although neither of the channel states $\xi_{\alpha'}$ or ξ_{α} had to be propagated. Note that an obvious but important consequence is that the microcanonical reaction rate, which is proportional to the cumulative reaction probability, can also be computed at *all* energies from a *single* wave packet propagation, no matter how many scattering channels or transition states are involved in the reaction process. Thus, for a multichannel problem the present approach compared to those based on the conventional strategies can increase the total numerical efficiency by a factor equal to the number of channels.

Note, in addition, that once the initial wave packet ξ_0 is real, its propagation involves only real arithmetics no matter whether the final wave packets ξ_{α} are real or complex.

IV. Estimation of the Inverse Laplace Transform

As noted in a number of publications,[11] sometimes it is easier to compute the Laplace transform of an observable rather than the observable itself. One important example corresponds to the imaginary-time correlation function of the type

$$c(\beta) = \mathrm{Tr}\mathrm{e}^{-\beta\hat{H}} \quad (32)$$

which can be computed by path-integral Monte Carlo techniques. If, however, the density of states,

$$\rho(E) = \mathrm{Tr}\delta(E-\hat{H}) \equiv \frac{1}{\pi}\mathrm{Im}\left[\mathrm{Tr}\frac{1}{\hat{H}-E+\mathrm{i}0}\right] \quad (33)$$

is the quantity of interest, one could, in principle, obtain it due to the Laplace transform relationship (1). This circumstance stimulated researchers to try to develop numerical algorithms for the inverse Laplace transform. The problem is usually complicated by the fact that the function to be inverted is very short and noisy, so the inversion problem is very ill-defined and any algorithm may easily become unstable. In what follows we adapt RRT to evaluate the inverse Laplace transform for a given discrete data set $c(n\tau)$, $n = 0, 1, ..., N-1$. To do this, we assume that $c(\beta)$ satisfies eq 4, but in the present case we mean $\hat{U} = \mathrm{e}^{-\tau\hat{\Omega}}$ (rather than $\mathrm{e}^{-i\tau\hat{\Omega}}$) with a non-Hermitian, but symmetric, effective Hamiltonian operator $\hat{\Omega}$ with complex poles ω_k satisfying $\mathrm{Re}\,\omega_k > 0$ and $\mathrm{Im}\,\omega_k < 0$. Note that there is no contradiction with the fact that $\hat{H}$ in eq 32 is Hermitian, as the effective Hamiltonian $\hat{\Omega}$ does not have to coincide with $\hat{H}$. We can now define a spectral function using

$$f(E) = \left(\Phi\left|\frac{1}{\hat{\Omega} - \mathrm{E}}\right|\Phi\right) \tag{34}$$

The density of states can be obtained from $f(E)$ using

$$\rho(E) = \frac{1}{\pi}\mathrm{Im}f(E) \tag{35}$$

Thus, the problem is to estimate $f(E)$. We can further assume that $\tau(\hat{\Omega} - E)$ is small, which is reasonable, and use $\mathrm{e}^{\tau E}\hat{U} \approx 1 + \tau(E - \hat{\Omega})$ to obtain the following approximation,

$$f(E) \approx \left(\Phi\left|\left[\frac{\tau}{1 - \mathrm{e}^{\tau E}\hat{U}} - \frac{\tau}{2}\right]\right|\Phi\right) \tag{36}$$

where the $\tau/2$ has the same origin as in eq 5. Finally, the RRT expression (20) can be used directly with s replaced by $-\mathrm{i}E$,

$$f(E) \approx \tau I(-\mathrm{i}E) \tag{37}$$

with the data matrix $\mathbf{R}(-\mathrm{i}E) = \mathbf{U}_0 - \mathrm{e}^{\tau E}\mathbf{U}_1$.

Note that in the present case the data size is usually small and the need to use a Fourier basis is questionable, although if one chooses the basis with φ_j values in the vicinity of zero, there is a chance to reduce both the effect of noise and the size of the matrices to be inverted.

Equations 37 and 20 constitute an important new result that has at least three advantages: (i) it provides an accurate inverse Laplace transform in the case of a noiseless signal that can be represented by the form $c(n\tau) = \Sigma_k d_k \mathrm{e}^{-n\tau\omega_k}$; (ii) it is computationally inexpensive as it does not involve the solution of any nonlinear optimization problem; (iii) it has no intrinsic (exponential) instability problem often encountered in other approaches, based on an analytic continuation.

However, eq 37 has a limited applicability as only a limited amount of information can be extracted from $c(\beta)$, which is both noisy and severely truncated. Therefore, in the spirit of ref 13 (appendix E) and refs 3−6 it should benefit from the use of a cross-correlation matrix, rather than a single signal as in eq 32. This possibility is explored in the next section.

V. Inverse Laplace Transform by Inverting a Cross-Correlation Matrix

The idea of using a cross correlation matrix is to increase the information content of the signal for the same time length.[6] To be able to benefit from this using RRT, one needs the data to be effectively representable in the form of an $L \times L$ time-cross-correlation matrix (27) with a set of fictitious states $\{\Phi_l\}$, $l = 1, ..., L$. This can be achieved by following ref 5, i.e., consider a cross-correlation matrix,

$$c_{ll'}(\beta) = \mathrm{Tr}[\hat{A}_l \mathrm{e}^{-\beta\hat{H}}\hat{\mathrm{A}}_{l'}] \tag{38}$$

constructed using a set of linear independent operators $\{\hat{A}_l\}$, $l = 0, ..., L - 1$, that commute with $\hat{H}$ and using $\hat{A}_0 = \hat{I}$, the identity operator. An example of such a set is the set of moments of $\hat{H}$, i.e., $\hat{A}_l = \hat{H}^l$, $l = 0, ..., L - 1$. If we now assume that Y_k are the eigenfunctions of all these operators and define $\hat{U} = \mathrm{e}^{-\tau\hat{H}}$ and $\Phi_l = \Sigma_k(\mathrm{Y}_k\hat{\mathrm{A}}_l\mathrm{Y}_k)\mathrm{Y}_k$, it is not very hard to see, that eq 38 can indeed be rewritten as

$$c_{ll'}(n\tau) = (\Phi_l|\hat{U}^n|\Phi_{l'}) \tag{39}$$

Another possibility is to implement projection operators $\hat{A}_l$[20] that project an initial state Φ_0 to states $\Phi_l = \hat{A}_l\Phi_0$ dominated by certain excited states. In ref 20 the authors considered a single autocorrelation function, while here we want to use the whole $L \times L$ cross-correlation matrix

$$c_{ll'}(\beta) = (\Phi_0|\hat{A}_l \mathrm{e}^{-\beta\hat{H}}\hat{A}_{l'}|\Phi_0) \tag{40}$$

Unlike ref 20, there is no strong restriction on the choice of $\hat{A}_l$ here. This makes the approach more flexible. Clearly, $c_{ll'}(\beta)$ in eq 40, as well as in eq 38, has the form of eq 39.

To extract the spectral information from $c_{ll'}(\beta)$ satisfying eq 39, consider the superbasis $\Phi_l(n) = \hat{U}^n\Phi_l$, $n = 0, ..., M - 1$, $l = 0, ..., L - 1$, with total size $M \times L$. We can evaluate Φ_0, the overlap matrix, and the operator $\hat{U}$ in this basis by analogy with eq 8,

$$[\mathbf{U}_p]_{ln l'n'} \equiv (\Phi_l(n)|\hat{U}^p|\Phi_{l'}(n')) = c_{ll'}[(n + n' + p)\tau]$$
$$[\mathbf{C}]_{ln} \equiv (\Phi_0|\Phi_l(n)) = c_{l0}(n\tau) \tag{41}$$

The desired spectral function $f(E) = \mathrm{Tr}[(\hat{H} - E - \mathrm{i}0)^{-1}]$ can be estimated using eq 37 with the only difference that the size of the basis is here increased by a factor of L for the same signal length $N = 2M$. This implies that ideally an $L \times L$ cross-correlation-matrix contains by a factor of L more information than a single time-correlation function. This circumstance is certainly very useful, especially in the context of the imaginary-time path-integral formalism as the signals of such type decay exponentially with β and, therefore, have very strict limitations on their length. Clearly, implementation of a Fourier basis here is completely analogous to the cases considered previously (e.g., in ref 6) and in section II.

VI. Summary

The new linear algebraic formalism based on RRT offers a number of numerically efficient and computationally inexpensive ways to process the data and extract the underlying spectral information, subject to the condition that the data satisfies the form of a time-correlation or time-*cross*-correlation function.

The applications considered in this paper present a great numerical challenge and are hardly manageable by the conventional signal processing techniques.

There is a broad class of problems, particularly, in the area of quantum dynamics calculations, in which our methodology can be potentially very useful. Those will be considered in our forthcoming publications.

Acknowledgment. This work was supported by the NSF grant CHE-9807229.

References and Notes

(1) Mandelshtam, V. A.; Taylor, H. S. *J. Chem. Phys.* **1997**, *107*, 6756.
(2) Weiss, J.; Schinke, R.; Mandelshtam, V. A. *J. Chem. Phys.* **2000**, *113*, 4588.
(3) Narevicius, E.; Neuhauser, D.; Korsch, H. J.; Moiseyev, N. *Chem. Phys. Lett.* **1997**, *276*, 250.
(4) Mandelshtam, V. A.; Ovchinnikov, M. *J. Chem. Phys.* **1998**, *108*, 9206.
(5) Main, J.; Weibert, K.; Mandelshtam, V. A.; Wunner, G. *Phys. Rev. E* **1999**, *60*, 1639.
(6) Mandelshtam, V. A. *J. Chem. Phys.* **1998**, *108*, 9999.
(7) Balint-Kurti, G. G.; Dixon, R. N.; Marston, C. C. *Faraday Trans. Chem. Soc.* **1990**, *86*, 1741. Dai, J. Q.; Zhang, J. Z. H. *J. Phys. Chem.* **1996**, *100*, 6898.
(8) Tannor, D. J.; Weeks, D. E. *J. Chem. Phys.* **1993**, *98*, 3884.
(9) Kouri, D. J.; Huang, Y.; Zhu, W.; Hoffman, D. K. *J. Chem. Phys.* **1994**, *100*, 3662.
(10) Gray, S. K.; Balint-Kurti, G. G. *J. Chem. Phys.* **1998**, *108*, 950.
(11) Berne, B. J.; *Annu. Rev. Phys. Chem.* **1986**, *37*, 401. Freeman, D. L. *Adv. Chem. phys.* **1988**, *70*, 139. Thirumalai, D.; Berne, B. J. *Comput.*

Phys. Commun. **1991**, *63*, 415. Ceperley, D. M.; *Rev. Mod. Phys.* **1995**, *67*, 279. Plimak, L.; Pollak, E. *J. Chem. Phys.* **2000**, *113*, 4533.

(12) Chen, J.; Shaka, A. J.; Mandelshtam, V. A. *J. Magn. Reson.* **2000**, *147*, 129.

(13) Wall, M. R.; Neuhauser, D. *J. Chem. Phys.* **1995**, *102*, 8011.

(14) Mandelshtam, V. A. *Prog. NMR Spectrosc.* **2001**, *38*, 159.

(15) Chen, J.; Mandelshtam, V. A. *J. Chem. Phys.* **2000**, *112*, 4429.

(16) Neumaier, A. *SIAM Rev.* **1998**, *40*, 636.

(17) Tikhonov, A. *Soviet Math. Dokl.* **1963**, *4*, 1035. Golub, G. H.; van Loan, C. F. *Matrix Computations*; Johns Hopkins University Press: Baltimore, 1989.

(18) Hartke, B.; Kosloff, R.; Ruhman, S. *Chem. Phys. Lett.* **1989**, *158*, 238. Kosloff, R. *J. Phys. Chem.* **1988**, *92*, 2087. Huang, Y.; Zhu, W.; Kouri, D. J.; Hoffman, D. K. *Chem. Phys. Lett.* **1993**, *206*, 96.

(19) Mandelshtam, V. A.; Taylor, H. S. *J. Chem. Phys.* **1995**, *102*, 7390. Mandelshtam, V. A.; Taylor, H. S. *J. Chem. Phys.* **1995**, *103*, 2903.

(20) Blume, D.; Mladenovic, M.; Lewerenz, M.; Whaley, K. B. *J. Chem. Phys.* **1999**, *110*, 5789.