

Spectral Analysis of Time Correlation Function for a Dissipative Dynamical System Using Filter Diagonalization: Application to Calculation of Unimolecular Decay Rates

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The filter-diagonalization method of Wall and Neuhauser for harmonic inversion of a complex time signal, $C(t) = \sum_k d_k e^{-it\omega_k}$, is simplified by introducing a different boxlike filter and is reformulated to the case of a signal given on a sparse equidistant time grid. The method is applied to the large scale quantum dynamics problem of extracting hundreds of (narrow and overlapping) resonances of the H_3^+ molecular ion directly from a single signal, $c_n = (\Phi_0, T_n(\hat{H})\Phi_0)$, generated by the dynamical system governed by a modified Chebyshev recursion. [S0031-9007(97)03023-8]

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The knowledge of the vibrational spectra for various physical systems such as molecules, clusters, glasses, crystals, etc., can provide an important insight into their dynamics. In particular, the density of states for large species can be used to calculate their thermodynamic properties. When the system of interest is dissipative (for example, if it is a small part of a larger system considered as a bath), its spectrum can often be represented by a set of complex frequencies (energies) ω_k whose negative imaginary parts characterize the decay rates. In this context, relaxation rates of excited local modes in a large molecule or the unimolecular decay rates (resonance widths) of an excited quantum scattering system can be recalled. Such spectra can often be computed by diagonalizing the Hamiltonian matrix, say, in the case of quantum dynamics, or the Hessian matrix if the normal modes of a classical system are of interest. On the other hand, a time signal $C(t)$ generated by the underlying dynamical system often carries adequate information relevant to the spectrum of the corresponding Hamiltonian or the evolution operator. Recently, Wall and Neuhauser [1] have devised an approach, filter diagonalization, for extracting highly resolved spectra for large and complex species with high densities of states by analyzing such a signal in an efficient manner. The method has been applied to extract a limited number of resonances in molecular structure [2] and a large number of instantaneous normal modes in classical molecular dynamics simulation [3]. The time signal to be analyzed could be either measured experimentally or it could be obtained in a numerical experiment. Such calculations (measurements) can be very accurate or they can introduce some “noise” (e.g., caused by the numerical errors). Because of various theoretical or practical reasons, the signal $C(t)$ might be available only on a short time segment or on a small set of sample points $t = t_n$. This makes it impossible to use a standard Fourier analysis, which in such a case can provide one with only “low resolution” results. From an informational point of view, if the number of sample points is larger than the number of unknown frequencies ω_k and amplitudes d_k contribut-

ing to the signal

$$C(t) = \sum_k d_k e^{-it\omega_k}, \quad (1)$$

one should be able, at least in principle, to extract these unknowns. This is a fundamental problem in physics and many other diverse fields. It has a long history which we will not discuss here. The interested reader is referred to Refs. [4–7] where the various “high resolution” methods (such as Prony’s method, MUSIC, maximum entropy method, ESPRIT, etc.) of spectral analysis of time signals relevant to the present approach are discussed. In this work we formulate the filter-diagonalization method by introducing a new and simple filter so that it applies rigorously to a signal defined on a finite discrete time grid (i.e., avoiding continuous integrals over the time variable). Although the formalism is very much akin to the work of Ref. [1], we present it in detail due to the simplicity of the final formulas and to the fact that they allow us the use of a very efficient method for extracting a high number of many (narrow and overlapping) resonances in large scale quantum simulations.

The crucial idea is, following the work of Wall and Neuhauser [1], to associate the time signal $C(t)$ of the form of Eq. (1) with a time correlation function generated by a suitable dynamical system (or vice versa),

$$c_n \equiv C(t_n) = (\Phi_0, \hat{U}^n \Phi_0) \equiv (\Phi_0, e^{-in\tau\hat{\Omega}} \Phi_0), \quad (2)$$

where (\cdot, \cdot) defines a complex symmetric inner product (no complex conjugation); the complex symmetric evolution operator \hat{U} is defined implicitly by

$$\hat{U} = \sum_k u_k \Phi_k (\Phi_k, \cdot), \quad (3)$$

where the set of eigenvectors $\{\Phi_k\}$ is associated with an arbitrary orthonormal basis set, the eigenvalues of \hat{U} are $u_k \equiv e^{-i\tau\omega_k}$ (or equivalently the eigenvalues of $\hat{\Omega}$ are ω_k), and the initial wave function Φ_0 is defined by its projections $(\Phi_k, \Phi_0)^2 = d_k$. The use of the discrete dynamics instead of a continuous one allows us to analyze

a signal $c_n \equiv C(t_n)$ given on an equidistant time grid, $t_n = n\tau$, which only has to be dense enough to satisfy $\tau|\omega_k| < \pi$. The “dissipative dynamics” means that $\text{Im } \omega_k \leq 0$, which is equivalent to having all the eigenvalues of the evolution operator \hat{U} inside the unit circle in the complex plane, $|u_k| \leq 1$. According to Ref. [1], this construction establishes an equivalence between the problem of extracting spectral information from a time signal with the one of diagonalizing the evolution operator \hat{U} (or the Hamiltonian $\hat{\Omega}$) of the underlying dynamical system. To show this, let us assume for a moment that we can diagonalize the operator \hat{U}^p by (i) picking a basis set $\{\Psi_j\}$, $j = 1, 2, \dots, N_{\text{win}}$, then (ii) evaluating in this basis the matrix,

$$U_{jj'}^{(p)} = (\Psi_j, \hat{U}^p \Psi_{j'}), \quad (4)$$

and then by solving the generalized eigenvalue problem,

$$\mathbf{U}^{(p)} \mathbf{B}_k = u_k^p \mathbf{S} \mathbf{B}_k. \quad (5)$$

Here, by bold characters $\mathbf{U}^{(p)}$ and $\mathbf{S} \equiv \mathbf{U}^{(0)}$, we defined the corresponding complex symmetric matrices of the size $N_{\text{win}} \times N_{\text{win}}$. The eigenvectors \mathbf{B}_k are then the column vectors of size $N_{\text{win}} \times 1$, satisfying

$$\Phi_k = \sum_j B_{jk} \Psi_j. \quad (6)$$

$$U_{jj'}^{(p)} = \frac{1}{z_j - z_{j'}} \left[z_j \sum_{l=0}^M c_{l+p} z_j^{-l} - z_j^{-M} \sum_{l=M+1}^{2M} c_{l+p} z_j^{M-l+1} - z_{j'} \sum_{l=0}^M c_{l+p} z_{j'}^{-l} + z_{j'}^{-M} \sum_{l=M+1}^{2M} c_{l+p} z_{j'}^{M-l+1} \right],$$

$$U_{jj}^{(p)} = \sum_{l=0}^{2M} (M - |M - l| + 1) c_{l+p} z_j^{-l}. \quad (9)$$

(Note that the evaluation of $\mathbf{U}^{(p)}$ requires knowledge of c_n for $n = p, p + 1, \dots, 2M + p$.)

Equation (9) with Eq. (5) are working expressions and can be applied to a general signal c_n directly as they are. Notably and quite importantly, the matrices $\mathbf{U}^{(p)}$ have a sinlike structure with large diagonal and rapidly decaying off-diagonal terms. It is this structure which justifies the procedure of filter diagonalization. Now the eigenfrequencies ω_k in a small frequency window $\varphi_{\text{min}}/\tau < \text{Re } \omega_k < \varphi_{\text{max}}/\tau$ can be obtained by solving the generalized eigenvalue problem Eq. (5) in a basis $\{\Psi_j\}$ constructed using a small set of values $\varphi_{\text{min}} < \varphi_j < \varphi_{\text{max}}$, $j = 1, 2, \dots, N_{\text{win}}$, with N_{win} being greater than the number of eigenvalues $u_k = e^{-i\tau\omega_k}$ lying near the corresponding segment of the unit circle in the complex plane (see Fig. 1). Once we have the eigenvectors \mathbf{B}_k the amplitudes d_k can [due to Eq. (6)] be obtained using [1]

$$d_k^{1/2} = \sum_j B_{jk} (\Psi_j, \Phi_0) = \sum_j B_{jk} \sum_{n=0}^M c_n z_j^{-n}. \quad (10)$$

It has to be noted that in practice the basis $\{\Psi_j\}$ is often close to linear dependent so that the matrix \mathbf{S} has some eigenvalues which are nearly zero. When solving Eq. (5) this problem is overcome by using a singular

To realize the outlined strategy we proceed by choosing a Krylov-type basis defined as a finite-time Fourier basis,

$$\Psi_j \equiv \Psi(z_j) = \sum_{n=0}^M (\hat{U}/z_j)^n \Phi_0, \quad (7)$$

for a set of complex values $z_j \equiv e^{-i\varphi_j}$, $j = 1, 2, \dots, N_{\text{win}}$ taken on the unit circle (i.e., φ_j is real). As explained in Ref. [1], one reason for choosing a Fourier-type basis is that for any z_j the function $\Psi(z_j)$ will be dominated by the eigenvectors Φ_k whose eigenvalues u_k are close to z_j . Another important reason for choosing the form of Eq. (7) is that as in [1] all the matrices $\mathbf{U}^{(p)}$ are now functionals of only the $\{c_n\}$ sequence and do not depend explicitly on either of the auxiliary objects \hat{U} , Φ_k or Φ_0 . To show this, let us insert Eq. (7) into Eq. (4) and use the symmetry property $(\Phi', \hat{U}\Phi) = (\hat{U}\Phi', \Phi)$ and the definition of c_n , Eq. (2):

$$U_{jj'}^{(p)} = \sum_{n'=0}^M \sum_{n=0}^M (z_{j'}/z_j)^n c_{n+n'+p} z_{j'}^{-(n+n')}. \quad (8)$$

The substitution $l = n + n'$ followed by summation over n gives

value decomposition of \mathbf{S} (see, e.g., Ref. [1]). If the basis $\{\Psi_j\}$ is not complete, which is usually the case, $\mathbf{U}^{(p)} \neq \mathbf{U}^p$. Only for converged eigenvalues u_k and eigenvectors \mathbf{B}_k will Eq. (5) yield the results that are independent on the power p . In other words, identification of the converged eigenvalues can be done by solving Eq. (5) simultaneously for two different values of p (e.g., $p = 1$ and $p = -1$) and then by comparing the results for the eigenvalues u_k and the eigenvectors \mathbf{B}_k .

Quantum dissipative dynamics: calculation of unimolecular decay rates.—A quantum scattering system dominated by long lived resonance states is a perfect example of a dissipative dynamics. While, in principle, the problem of extracting resonance parameters can efficiently be solved using our older version of the filter diagonalization method [8–10], for very large systems it might become unfeasible since it could require too large a storage for the window basis functions.

In order to make the present approach applicable we need to find, for a quantum scattering system, a suitable signal c_n which (i) would be easy to produce and (ii) would contain the desired spectral information, such as the energies and widths of the resonances. It might appear that the only natural choice here, as was used in

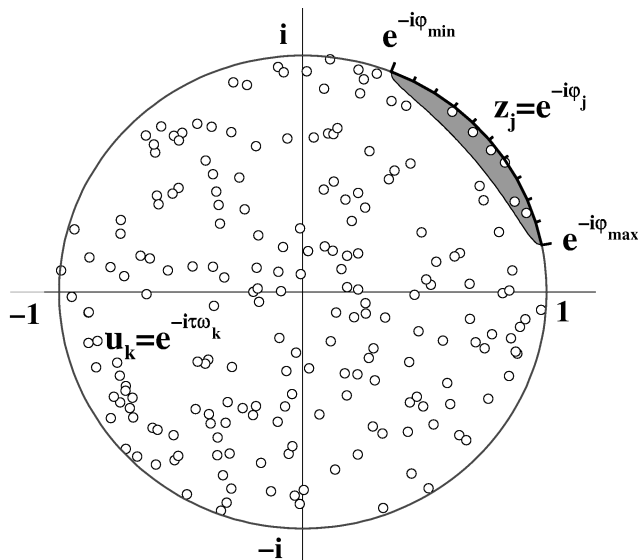


FIG. 1. A schematic plot of eigenvalues of the operator \hat{U} , a small portion of which (in the shadowed region) is extracted by the filter-diagonalization procedure.

Refs. [1,7], is the signal $c_n = C(n\tau)$ obtained from a time correlation function,

$$C(t) = (\Phi_0, e^{-it\hat{H}} \Phi_0), \quad (11)$$

where \hat{H} is the system Hamiltonian. If the quantum dynamics is governed only by bound and quasibound (resonance) states, $C(t)$ can be effectively represented by the sum over these states whose energies are taken as the complex numbers $\epsilon_k - i\Gamma_k/2$, where the widths Γ_k are associated with the decay rates,

$$C(t) \approx \sum_k d_k e^{-it(\epsilon_k - i\Gamma_k/2)}. \quad (12)$$

The coefficients d_k are then given by the overlap integrals of the initial wave packet with the resonance wave functions, $d_k = (\Phi_0, \Phi_k)^2$.

In practice, for the evaluation of $C(t)$, either the split operator method [11] or Chebyshev [12] (or modified Chebyshev [2,14]) polynomial expansion of the time evolution operator $e^{-it\hat{H}}$ can be used.

Another alternative is to use a different dynamics which is both suitable for the problem of resonances and easy to apply. An excellent example of such a dynamics, in the spirit of Refs. [13,14] is the one generated by the modified Chebyshev recursion relation itself,

$$\begin{aligned} \xi_0 &= \Phi_0, & \xi_1 &= e^{-\hat{H}} \xi_0, \dots, \\ \xi_{n+1} &= e^{-\hat{H}} (2\hat{H} \xi_n - \xi_{n-1}), \end{aligned} \quad (13)$$

with the correlation function to be analyzed,

$$c_n = (\Phi_0, T_n(\hat{H}) \Phi_0) \approx (\Phi_0, \xi_n), \quad (14)$$

where $T_n(\hat{H})$ are the Chebyshev polynomials of the Hamiltonian operator \hat{H} which is already rescaled such that its eigenvalues belong to the unit interval $[-1, 1]$.

This assures the stability of the recursion relations. The damping operator $e^{-\hat{\gamma}}$ is used to eliminate the boundary reflection effects and can be considered here as a convergence factor. For $\hat{\gamma} = 0$, Eq. (14) becomes an exact equality but is numerically inefficient because it requires very large grids. If $\gamma(r)$ is chosen properly the vectors ξ_n are localized in space, decaying rapidly in the damping region. This allows one to use finite grids extended not too far in the asymptotic region. While in Refs. [8–10,14] Eq. (13) was used to obtain an efficient recursion polynomial expansion of the Green's function $\hat{G}^+(E)$ with particular absorbing boundary conditions here we only need to satisfy Eq. (14).

To show that the signal c_n computed using Eq. (14) has the desired form of Eq. (1) let us introduce the convenient representation of the Chebyshev polynomials,

$$T_n(\hat{H}) \equiv \text{Re} e^{-in\hat{\Omega}}, \quad (15)$$

where the Hermitian operator $\hat{\Omega}$ is defined by $\hat{H} \equiv \cos \hat{\Omega}$. Now, by analogy with Eq. (12) for a real initial wave packet Φ_0 , we can write

$$c_n = \text{Re}(\Phi_0, e^{-in\hat{\Omega}} \Phi_0) \approx \frac{1}{2} \sum_k d_k e^{-in\omega_k} + d_k^* e^{in\omega_k^*}, \quad (16)$$

where $d_k = (\Phi_0, \Phi_k)^2$. The sum in Eq. (16) is taken over the same, as in Eq. (12), set of complex poles of the Green's function $\hat{G}^+(E) = (E - \hat{H} + i0)^{-1} \equiv (E - \cos \hat{\Omega} + i0)^{-1}$,

$$\epsilon_k - i\Gamma_k/2 \equiv \cos \omega_k. \quad (17)$$

Thus for a quantum scattering problem described by a Hermitian Hamiltonian \hat{H} we have found a convenient (discrete-time) signal c_n generated using a numerically simple, inexpensive, and accurate recursion procedure, Eq. (13). Relevant physical information, such as the energies and widths of resonances, can be extracted directly from c_n [i.e., avoiding construction of $C(t)$] by a high resolution spectral analysis.

Calculation of resonance states of the H_3^+ molecule.— In Ref. [10] we presented a calculation and statistical analysis of $J = 0$ bound and resonance energies of the H_3^+ molecular ion using the Meyer, Botschwina, and Burton potential energy surface of Ref. [15]. This was done using our old version of the filter-diagonalization method an effective application of which required a 500 Mbyte parallel computer. To the best of our knowledge, this was the largest (in the sense of the number and the density of states) accurate resonance calculation ever performed for open chemical systems. Here, in order to demonstrate the present approach, we apply it to the same problem. The implementation of the recursion procedure, Eq. (13), and all the basis set parameters are the same as in Ref. [10]. In particular the size of the primitive grid used was of the order of 110 000. (For more detail see this paper and references

therein.) The signal c_n , Eq. (14), was computed using $N_{\text{iter}} = 240\,000$ iterates of Eq. (13). This was necessary to converge all the bound and resonance states of H_3^+ up to $E = 41\,700\text{ cm}^{-1}$. The resonance widths as a function of energy are shown in Fig. 2. An excellent agreement (within $\sim 0.01\text{ cm}^{-1}$ for all bound and most resonance state energies) with the results of Ref. [10] was achieved for all $N_{E_s} + N_{E_a} + N_{A_1} + N_{A_2} = 604 + 604 + 358 + 256 = 1822$ bound and all $N_{E_s} + N_{E_a} + N_{A_1} + N_{A_2} = 264 + 264 + 142 + 119 = 789$ resonance states with widths $\Gamma < 100\text{ cm}^{-1}$, where E , A_1 , and A_2 correspond to irreducible representations of the $\mathbf{D}_3(\mathbf{M})$ nuclear permutation group. Note that some resonances are quite narrow but most of them (especially at higher energies) are strongly overlapping.

$N_{\text{iter}} = 240\,000$ might seem to be a large number compared to $N_{\text{iter}} = 80\,000$ used in Ref. [10]. We note, however, that all the resonances for each of the two symmetry blocks (see Ref. [10]) were obtained from a *single* signal c_n (and not window by window) using (to create the signal) ~ 31 h of the cpu time and ~ 5 Mbyte of core memory on an IBM 6000/990 work station. Extracting the spectral information from c_n takes only a few minutes.

In conclusion, implementation of the filter-diagonalization method described in this paper is quite general, numerically inexpensive, stable, and accurate. It can be routinely applied for extraction of complex spectra of

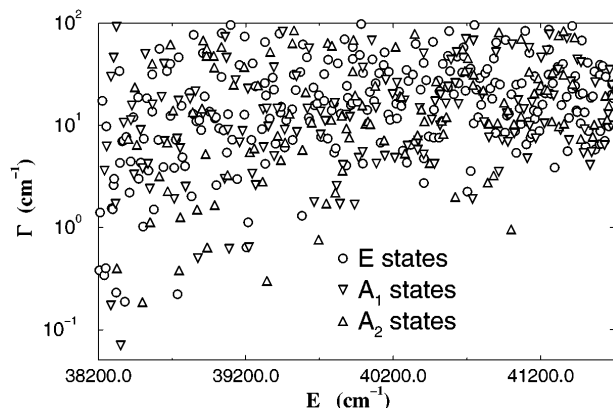


FIG. 2. The resonance widths (decay rates) of the nonrotating H_3^+ molecular ion as a function of the resonance position.

various systems using the information contained only by the time correlation function. The purpose of presenting the numerical example is to demonstrate the potential ability of the method to perform accurate resonance calculations for quantum dissipative systems that require basis sets (grids) as large as 10^{6-7} if supercomputers are used.

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