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Scattering and Bound States: A Lorentzian Function-Based Spectral Filter Approach†

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We present a Lorentzian function-based spectral filter method for computing the elements of the quantum scattering matrix (S-matrix) and molecular bound-state spectra. For computing bound-state eigenvalues in a predefined energy window, we use the Lorentzian function within the filter diagonalization framework. From the spectral filter point of view, we find that the formal theoretical structure for computing the S-matrix is the same as those of overlap and Hamiltonian matrix elements necessary for filter diagonalization, and hence, the same computational protocol can be utilized for scattering as well as bound-state studies. Furthermore, we argue that the appropriate scattering boundary conditions can be accurately built while preparing the initial wave packets. For numerical implementation, we have utilized the Lorentzian filter in two complementary series forms: (1) using Chebyshev polynomials with the Hamiltonian as its argument, which is useful for a fully quantum mechanical study; and (2) in terms of a discrete set of short-time quantum propagators, which can additionally be extended to approximate dynamical regimes. The computation of matrix elements for a filter diagonalization application and the scattering matrix requires a product of a series representation of two filter operators for which we have been able to perform a partial resummation of both the series analytically, giving thereby a very compact and rapidly convergent expression. The exponential damping term associated with the Lorentzian filter is very useful for controlling the convergence and removing unwanted features from the computed spectrum. As is true of previous discrete time expansion of the spectral density operator, the present formalism can also be utilized for inverting discrete time signals obtained from various experiments. We illustrate the validity of the present approach by test calculations on a model one-dimensional quantum scattering problem.

I. Introduction and Perspective

Quantum theory provides the most fundamental theoretical framework for a microscopic description of dynamical processes of molecular systems in the gas and condensed phases.[1] Within this framework, a molecular system is defined by an appropriate Hamiltonian, generally possessing a range of eigenstates, continuum as well as discrete, in which the system may reside. In addition, the molecular system may also be prepared in an arbitrary quantum state, which can be expressed as a linear superposition of eigenstates of the full Hamiltonian. A dynamical process is then fundamentally visualized as the transfer of the molecular system from one quantum state into another, as determined within the framework of the time-dependent Schrödinger equation. Hence, the most detailed information concerning a molecular process one can have is the eigenvalues/eigenvectors of the corresponding Hamiltonian and the transition probability amplitudes between various quantum states. Whereas the dynamical processes involving bound states of the Hamiltonian underly various laser based molecular spectroscopies,[2−4] processes involving continuum states directly relate to the conductance properties of the molecular systems[5,6] and elementary chemical reactions, wherein the quantities of prime importance are the scattering matrix (S-matrix) and reaction rates.[7,8] Clearly, a theoretical study of molecular dynamics requires an accurate and efficient computational protocol for obtaining the elements of the S-matrix and the eigenvalue−eigenvector information corresponding to molecular-bound states for a given Hamiltonian. This is the central objective of this paper. In particular, we utilize the idea of a *spectral filter*[9] to obtain a very general and compact quantum mechanical computational framework, suitable for studying molecular processes involving continuum as well as bound states, along with an additional flexibility of enabling extension of the theory to various semiclassical and mixed quantum/classical regimes in an unambiguous manner. Expressions for other experimental observables, such as conductance and thermally averaged reaction rates, can be derived by appropriately referring to the necessary equations for obtaining eigenstates and transition probability information; that is, an explicit numerical construction of eigenstates themselves may not always be required. We will address these issues in future studies. In this paper, we will concentrate only on the theory of elementary chemical reactions and molecular-bound states.

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Concerning elementary chemical reactions, there have been several theoretical formulations, with varying types of approximations and degrees of sophistication, of the relevant scattering processes with an ultimate purpose of obtaining the elements of the S-matrix.[10−48] The present approach of utilizing the notion of a spectral filter is related to the wave packet description of quantum scattering, as discussed, for example, in the treatise of Goldberger and Watson[49] and in the text by Taylor.[50] By "wave packet", we here simply mean a function that decays sufficiently rapidly, in both the position and the momentum space; that is, the function can be arbitrarily accurately approximated as band-limited with finite support. In recent years, the wave packet approach has become very popular in molecular dynamics studies because it is intuitive and offers an efficient computational protocol. In the context of chemical reaction dynamics, we particularly mention the theoretical formulations developed independently in the groups of Kouri[27−32] and Tannor,[33−36] which formally express the S-matrix element as an integral transform of an appropriate time-correlation function, and the present spectral filter approach is conceptually similar to these studies while differing significantly in the operational details. In the following, we offer a brief critique of the existing wave-packet-based approaches for computing the S-matrix, which are relevant to the present investigation.

In a series of studies, Kouri et al.[27−32] proposed and utilized the following expression for the scattering matrix (omitting the normalization and other factors)

$$S_{\beta\alpha}(E) \propto \langle \Phi^{-(\beta)} | G^{+}(E) | \Phi^{+(\alpha)} \rangle \tag{1}$$

where $|\Phi^{+(\alpha)}\rangle$ and $|\Phi^{-(\beta)}\rangle$ are wave packets, asymptotically correlating with the reactant, α, and product, β, channels, respectively, and $G^{+}(E)$ is the causal full Green's function. An expression similar to eq 1 but involving the spectral density operator, $\delta(E - \hat{H})$, in place of Green's function, has been given by Tannor et al.[33−36] Other variants of eq 1 are also available in the literature, and they have found several applications.[37−48] We first note that eq 1 is formally exact; that is, it will certainly give an exact answer if one utilizes an exact Green's function in an application. This is, unfortunately, a heavy computational burden because the construction of an exact Green's function demands either a complete diagonalization of the associated Hamiltonian or a physically equivalent quantum propagation for a sufficiently long time if one uses an integral representation of the Green's operator. Neither is feasible in a nontrivial molecular application. In a practical study, however, one almost always approximates the Green's function, usually in the form of truncating a convergent infinite series, and for an approximate Green's function, eq 1 is not the optimal prescription for obtaining the S-matrix. This is because eq 1 is fundamentally based on a certain factorization of a product of two spectral density operators, $\delta(E_1 - \hat{H})\delta(E_2 - \hat{H}) = \delta(E_1 - E_2)\delta(E_1 - \hat{H})$, which is only approximately true if one uses truncated series expansions for the relevant operators, and this significantly reduces the rate of numerical convergence.[51] The present spectral filter approach highlights and eliminates this limitation in an unambiguous manner, thereby offering a well-convergent and compact series expansion for the S-matrix. Moreover, an important feature of the present formulation is that the issue of enforcing appropriate boundary conditions, scattering as well as bound state, is directly linked to the way we prepare the initial wave packets, and no additional device (e.g., a complex absorbing potential[13,14,42,52]) is necessary for this purpose. We will elaborate these points more in the later discussion. Finally, the present formalism, like the earlier studies on this subject,[27−36] effectively retains the correlation function form of the S-matrix, and this is very important because it then easily allows one to extend the formalism into approximate dynamical regimes, which is necessary for treating large molecular systems.

As to the molecular bound-state problem, it can, in principle, be solved by direct numerical diagonalization of the relevant Hamiltonian operator expressed in some appropriate basis. But this is generally impractical because a molecular system typically involves a very large rank Hamiltonian matrix, and furthermore, one is typically interested in obtaining only a small subset of eigenvalues in a given energy range of interest. Therefore, recent research efforts have been directed toward developing various iterative methods, which generate a small basis set by a repeated application of the Hamiltonian operator on an arbitrary quantum state and use them to diagonalize the original Hamiltonian in part.[9,51,53−89] We parenthetically note that a specific numerical application usually does not require the explicit construction and storage of the basis produced by successive iterations, but only the scalar quantities entering the mathematical process by which one computes the relevant matrix elements directly.[54]

A common feature which, at present, most iterative methods share is a three-term recursion process, symbolically expressed as follows

$$f_{k+1}(\hat{H}) = (\hat{H} - \alpha_k)\, f_k(\hat{H}) - \beta_{k-1}\, f_{k-1}(\hat{H}) \tag{2}$$

where $f_k(\hat{H})$ is a k^{th} degree polynomial with the Hamiltonian, $\hat{H}$, as its argument. A notable exception is the Faber polynomial, which may be used with a recursion process involving more than three terms.[90] Various iterative methods formally differ in the choice of the polynomials and the ways of computing the unknown scalar coefficients, α_k and β_k. These coefficients are then used to construct a new matrix of much smaller rank which is therefore much easier to diagonalize. These eigenvalues progressively increase in accuracy as the recursion scheme, eq 2, proceeds. In this context, Lanczos's original prescription of implementing eq 2 and its variants[91,92] has been very popular for the last several decades. Furthermore, it is well-known that the Lanczos method tends to converge the well-separated eigenvalues preferentially. Thus, if one can dilate the spectrum of the Hamiltonian in the desired energy region using an energy-dependent "shift operator" before implementing the Lanczos method, one can substantially accelerate the eigenvalue computation.[54−59,93] Although there have been several studies exploiting this theme with varying degrees of success,[56−59] the application of an energy-dependent shift operator in a practical application remains a major computational bottleneck. On the other hand, the iterative method has gained further popularity in recent years due to the development of a filter diagonalization (FD) scheme by Neuhauser[60−66] and others.[9,51,67−86] A FD scheme involves an energy-dependent spectral filter, which acts on an arbitrary state to generate a basis set spanning a preselected energy window and uses it for the purpose of matrix diagonalization. Since the filter operator is usually expressed in a degenerate kernel infinite series[94] consisting of orthogonal polynomials (therefore satisfying a three-term recursion relation similar to eq 2), the FD scheme can also be visualized as yet another prescription for computing the coefficients, α_k and β_k, and the filtering process itself is akin to applying the "shift operator" as mentioned above. However, FD schemes differ from the Lanczos-type processes in several important ways: (1) Whereas the Lanczos method attempts to generate a strictly tridiagonal matrix, whose dimension grows with the number of recursions, the FD generates a diagonally dominant matrix of a priori fixed dimension, to be diagonalized, (2) as opposed to the Lanczos method with an energy-dependent shift operator, the recursion process in the FD is completely decoupled from the energy window of interest, solely due to the possibility of expanding the filter in a degenerate kernel series,[94] and this means the three-term recursion, eq 2, involving a matrix−vector product, which is numerically the most expensive step, need not be repeated with a change of the energy window one is interested in. (3) Although the Lanczos method is useful strictly for quantum mechanical studies, the FD-based methods can easily be extended for use in classical or semiclassical studies, which certainly are required for large molecular systems. In this paper, we thus focus our attention only on filter-based methods for molecular bound-state studies. We note that from the present spectral filter perspective, the theoretical structure of the FD method for a bound-state problem finally turns out to be similar to that of the S-matrix theory. The difference lies only in the nature of the wave packets employed in the final computation, and this is simply due to the fact that a scattering problem fundamentally differs from a bound-state one only in the nature of the boundary conditions. Hence, one can use the same computational protocol, as developed here, for both bound-state and scattering studies. We will elaborate on this theme in the later discussion.

We now briefly review the ingredients of filter theory and the scope of the present work. In spectral filter theory,[9] the quantity of central importance is the *spectral density operator* (SDO), $\delta(E - \hat{H})$, where the filter energy, E, is within the spectral range of the Hamiltonian, $\hat{H}$, of the quantum system. Because $\delta(E - \hat{H})$ is a projection onto the space of solutions of the homogeneous Schrödinger equation both for scattering and bound states, its application on an arbitrary wave function yields the eigenstates describing the bound as well as the scattering states,[95] depending on the value of E and the enforced boundary conditions. Since the SDO mathematically involves an infinite limiting process, it must be suitably approximated before it can be applied numerically. This is an important issue associated with the implementation of various spectral filter algorithms. In practical applications, it is often convenient to take the filter function to have some prelimit form (e.g., a sinc, Gaussian, Lorentzian, etc.) and express it as a degenerate-kernel infinite series[94] involving polynomials, thereby separating the dependence on the filter energy, E, from that of the Hamiltonian operator. The choice of a prelimit expression of the SDO and its series expansion necessarily determines the convergence features of the resulting algorithm, and hence, there have been several suggestions for dealing with this issue in the literature.[90,96−100] In particular, Kouri and co-workers[90,96−98] used a sinc function approximation of the SDO and obtained its series expansion in terms of Legendre and Chebyshev polynomials. A more general expansion of the SDO and Green's function in terms of Jacobi polynomials, of which Legendre and Chebyshev polynomials are special cases, has also been reported.[99] Hermite polynomials have also been used to obtain a series representation of the SDO, expressed as a Gaussian limiting process.[78] Further extension of a general complex operator-valued function, in terms of Faber polynomials, a special case of which is the Chebyshev polynomial, has also been reported by Kouri and co-workers.[90,98] In the present work, we use a Lorentzian function representation of the SDO, $\lim_{\zeta\to 0} \zeta/\pi[\zeta^2 + (E - \hat{H})^2]$, and we will explain later why this choice is better suited for numerical studies. In the first implementation approach, we expand the Lorentzian in terms of Chebyshev polynomials with a Hamiltonian argument, because it is known to provide a uniformly convergent approximating scheme.[91] Furthermore, this choice allows us to perform all relevant time integrals analytically and also facilitates certain algebraic manipulations involving series, leading to a compact, energy-separable and nicely convergent set of equations. In the second implementation approach, we express the SDO as a degenerate kernel series in terms of the short-time quantum propagator, which then allows us to express all observable quantities in terms of a discrete set of time-correlation functions. We then argue that in appropriate practical situations, one may ignore the quantum mechanical origin of the time-correlation function and obtain it by other suitable approximate dynamical schemes. That means one can easily obtain a dynamically approximate representation (for example, a semiclassical one) for the SDO. In this way, the present approach offers a unified computational framework extending from quantum to classical regimes, suitable for studying molecular bound states and scattering problems for systems ranging from small to large. It should be noted that the present suggestion of computing short-time correlation functions by approximate dynamical means has been very popular and explored by other researchers in various contexts.[10,11,48,70,71,101−105]

The organization of this paper is as follows. In Section II, we define the notion of spectral filter along with its Lorentzian function realization, in terms of both Chebyshev polynomials and discrete-time quantum propagators. In Section III, we introduce the wave packet description of quantum scattering from a filter perspective and obtain a compact set of expressions for the elements of the S-matrix. In Section IV, we elaborate on the Lorentzian function-based filter diagonalization scheme to compute a set of eigenvalues in an arbitrary energy window and also obtain an expression for the spectral intensity. We discuss numerical results for a model scattering problem in Section V, and finally, we present our conclusions and future research directions in Section VI.

II. Spectral Filters

In the present work, we are concerned with the use of an energy filter, associated with the Hamiltonian, $\hat{H}$, of the system. The general notion of a filter in quantum mechanics is directly related to the concept of "selective measurement", as discussed by Dirac,[1] and this aspect has recently been elaborated by us for the purpose of bound-state studies.[9] We first recall the salient features of the notion of a filter, which are relevant for the present investigation.

We first assume the existence of an orthogonal reference space spanned by the eigenvectors, discrete [$|\phi_m\rangle$; $m = 1, ..., N$, satisfying $\langle\phi_m|\phi_n\rangle = \delta_{mn}$] as well as continuous, [$|\phi_\epsilon\rangle$; $\epsilon = 0, \infty$, satisfying $\langle\phi_\epsilon|\phi_{\epsilon'}\rangle = \delta(\epsilon - \epsilon')$] of the system Hamiltonian. This allows us to express an arbitrary quantum state, $|\psi\rangle$, as follows:

$$|\psi\rangle = \int d\epsilon\, A(\epsilon)|\phi_\epsilon\rangle + \sum_m C_m|\phi_m\rangle \qquad (3)$$

The discrete and the continuous sectors of the eigenstates are assumed to be orthogonal. It is clear that the arbitrary state, $|\psi\rangle$, contains complete eigenstate information, provided the coefficients, $A(\epsilon)$ and C_m, are all nonzero. To extract spectral information from $|\psi\rangle$, we introduce the notion of *selective measurement* or *filtration*, in which we imagine an ideal process which selects only one of the eigenstates (discrete or continuous) from $|\psi\rangle$. Mathematically, this amounts to applying a projection operator, $\Delta(E)$, which acts on $|\psi\rangle$ and produces the eigenstate if the filter energy, E, is equal to the corresponding eigenvalue of $\hat{H}$, as is evident from the following implicit definition,

$$\Delta(E)|\psi\rangle = |\phi_E\rangle\langle\phi_E|\psi\rangle = \mathrm{A}(E)|\phi_E\rangle \qquad (4)$$

where E is either a discrete or a continuous variable. The notion of filteration in eq 4 is only formal, because it defines the projection operator in terms of the eigenstates of the Hamiltonian, which are a priori unknown; hence, it cannot be used for practical applications. For operational purposes, however, the mathematical object that satisfies the primary notion of the filter in quantum mechanics is the spectral density operator (SDO) $\delta(E - \hat{H})$, where E is the energy at which the filter process is to be carried out. By definition, then, the application of $\delta(E - \hat{H})$ on an arbitrary state, $|\psi\rangle$ selects out the eigenstate if E is an eigenvalue and the corresponding eigenstate has a finite overlap with the initial arbitrary state, $|\psi\rangle$. Whether the projected state belongs to the discrete or the continuous sector of the spectrum will depend on the energy, E, and the manner in which the $|\psi\rangle$ has been initially prepared, because the Hamiltonian portion of the SDO in itself does not possess any bias favoring a particular state vector; therefore, it does not enforce any boundary condition whatsoever. We will say more on this point later on. In any event, it is clear that the spectral filtering essentially necessitates an appropriate application of the spectral density operator. We here stress that the notion of the Dirac delta function as a filter is a very general unifying theme, which offers a convenient framework to set up various computational algorithms necessary to study molecular dynamics.

Because $\delta(E - \hat{H})$ conceptually refers to an infinite limiting process applied to an appropriate sequence of functions, it must be suitably represented before it can be applied numerically, and this is an important issue associated with the implementation of various spectral filter algorithms. The procedure we follow here is first to choose an appropriate integral representation of the following form

$$\delta(E - \hat{H}) = \lim_{\zeta\to 0} \frac{1}{2\pi\hbar}\int_{-\infty}^{\infty} \mathrm{d}t\, f(|t/\hbar|;\,\zeta)\; \mathrm{e}^{iEt/\hbar}\mathrm{e}^{-i\hat{H}t/\hbar} \qquad (5)$$

Here, different choices for the damping function, $f(|t/\hbar|; \zeta)$, will give different sequential representations for the SDO. With $f(|t/\hbar|; \zeta)$ as unity, we have the traditional prelimit sinc function approximation to the delta function. Other frequently used choices for $f(|t/\hbar|; \zeta)$ are exponential and Gaussian functions. In the present study, we shall use an exponential form for $f(|t/\hbar|; \zeta)$; the reason for this choice will become clear later (see also ref 51). The choice of an exponential function for $f(|t/\hbar|; \zeta)$ is equivalent to approximating $\delta(E - \hat{H})$ by a Lorentzian function. A finite value of the parameter ζ, having units of energy, ensures that the integral in eq 5 is convergent and gives a finite width to the otherwise sharp delta function. This is very useful for practical calculations. Thus, for a finite ζ, we have the following Lorentzian representation of the SDO,

$$\delta(E - \hat{H}) = -\frac{1}{\pi}\mathrm{Im}G^{+} = \lim_{\zeta\to 0}\frac{1}{\pi}\frac{\zeta}{\zeta^2 + (E - \hat{H})^2} = \lim_{\zeta\to 0}\frac{1}{\pi\hbar}Re\int_0^{\infty} \mathrm{d}t\; \mathrm{e}^{i(E+i\zeta)t/\hbar}\mathrm{e}^{-i\hat{H}t/\hbar} \qquad (6)$$

where $G^{+} = (E - \hat{H} + i\zeta)^{-1}$ is the well-known causal Green's function. Notably, eq 6 shows the SDO to be the real part of a Laplace transform of the quantum time propagator, $\mathrm{e}^{-i\hat{H}t/\hbar}$. Thus, our next problem is to obtain an appropriate representation of the time propagator, for which we here consider two possibilities: (1) a series expansion in terms of some choice of orthogonal polynomials, and (2) an iterative solution in short-time steps. As we will later see, although the polynomial expansion is useful for a fully quantum mechanical treatment, the latter can additionally be implemented with a semiclassical or a mixed quantum/classical form of the time propagator. There are excellent short-time dynamical schemes, valid in the quantum, semiclassical, and mixed-quantum/classical regimes, available in the literature, which can be employed for this purpose.[10,101−103,106−115]

We first consider the orthogonal polynomial representation of the time propagator, for which there have been several studies in the past.[97,99,100,107−110] In the case of a real and time-independent $\hat{H}$, a general expression for the time propagator in the form of ultraspherical polynomials has been obtained.[99] Special cases are Legendre[97] and Chebyshev[100,108] (first and second kind) polynomials. In the present study, we utilize the Chebyshev polynomials of the first kind, and therefore, the present treatment will be limited to the case in which the damping parameter, ζ in eqs 5 and 6, is coordinate-independent. Chebyshev polynomials, in addition to giving a uniformly convergent scheme for applying the quantum propagator, also possess certain algebraic properties (not shared by any other orthogonal polynomials) which allow further simplification, leading to a very compact and rapidly convergent expression for computing the elements of the scattering matrix (S-matrix) and necessary matrix elements used in the filter diagonalization algorithm for studying molecular bound states. The Chebyshev polynomial expansion of the time propagator[99,100,108] also allows the time integral in eq 6 to be performed analytically, and thus, we obtain[95,96,99]

$$\delta(E - \hat{H}) = \lim_{\zeta\to 0}\left(\frac{1}{\pi\Delta\lambda}\right)\sum_{k=0}^{\infty}(2 - \delta_{k0})Re[D(E)\,Z^k(E)]T_k(\hat{H}_{\mathrm{sc}}) \qquad (7)$$

where $D(E)^{-1} = [1 - (E_{\mathrm{sc}} + i\zeta_{\mathrm{sc}})^2]^{1/2}$, $Z(E) = [(E_{\mathrm{sc}} + i\zeta_{\mathrm{sc}}) - i\,D(E)^{-1}]$, $\zeta_{\mathrm{sc}} = \zeta/\Delta\lambda$, and $\Delta\lambda E_{\mathrm{sc}}(\hat{H}_{\mathrm{sc}}) = E(\hat{H}) - \bar{\lambda}$. Here, $\Delta\lambda$ and $\bar{\lambda}$ are parameters (with units of energy) which map the eigenvalues of $\hat{H}$ in the range $[\lambda_{\mathrm{min}}, \lambda_{\mathrm{max}}]$ into the eigenvalues of $\hat{H}_{\mathrm{sc}}$ in the range $[-1, 1]$, and render $\hat{H}_{\mathrm{sc}}$ dimensionless. This Hamiltonian renormalization is a necessity with the choice of Chebyshev polynomials, but it does not affect the generality of the overall scheme. It should be noted that in a practical calculation, the upper limit of the summation in eq 7 is truncated to some appropriate finite number, N, which is equivalent to restricting the upper limit of the integration in eq 6 to a total time, T. This incurs an additional error, which is equivalent to multiplying the Lorentzian representation of the SDO by a numerical factor. It can easily be shown that a practical calculation using eq 7 with a finite number of terms and a finite positive value of the parameter, ζ, approximates the SDO as follows,

$$\delta_T(E - \hat{H}) = \frac{1}{\pi}\frac{\zeta}{\zeta^2 + (E - \hat{H})^2} \times \left[\{1 - \mathrm{e}^{-\zeta T/\hbar}\cos(E - \hat{H})T/\hbar\} + \left(\frac{E - \hat{H}}{\zeta}\right)\mathrm{e}^{-\zeta T/\hbar}\sin(E - \hat{H})T/\hbar\right] \qquad (8)$$

where $\delta_T(E - \hat{H})$ refers to an approximate SDO. Clearly, the numerical factor multiplying the Lorentzian is equal to $(1 - \mathrm{e}^{-\zeta T/\hbar})$ at the exact location of the eigenvalue of the Hamiltonian;

that is, "the focusing power" of the Lorentzian is reduced by a small exponential factor. Now, a comment concerning the general convergence characteristics of the series in eq 7 is in order here.[51] This series is composed of terms that oscillate faster with higher k, superimposed upon a k-dependent exponential damping factor. It is easy to verify the damping factor to be $\exp(-ky)$, where y is a positive number determined from the relation, $2\cosh^2 y = (1 + E_{sc}^2 + \zeta_{sc}^2) + [(1 + E_{sc}^2 + \zeta_{sc}^2)^2 - 4E_{sc}^2]^{1/2}$. The convergence is, thus, guaranteed here due to two factors: (1) cancellation due to the summation of rapidly oscillating terms, and (2) the exponential damping.

We now consider the short-time iterative scheme for the SDO. In this scheme, we first choose a total length of time propagation, T (formally, $T \to \infty$), and discretize the total interval into N smaller steps, Δt; that is, $N\Delta t = T$. We then perform the integration in eq 6 according to the trapezoidal rule.[116] Thus, eq 6 can be approximated as follows,

$$\delta_T(E - \hat{H}) = \frac{\Delta t}{2\pi\hbar}\sum_{k=0}^{N}(1 - \delta_{k0}/2)(1 - \delta_{kN}/2) \times [\{Z(E)\}^k\hat{U}^k + \{Z(E)^*\}^k\hat{U}^{-k}] \quad (9)$$

where $\hat{U} = e^{-i\hat{H}\Delta t/\hbar}$, $Z(E) = e^{i(E+i\zeta)\Delta t/\hbar}$, and * denotes complex conjugation. We have chosen integration by the trapezoidal rule because it is known to be more accurate than the ordinary summation resulting from the rectangle integration scheme. This can be seen as follows. We first note that without the end-point correction factors, $(1 - \delta_{k0}/2)$ and $(1 - \delta_{kN}/2)$, in eq 9, the finite discrete time representation essentially amounts to the following approximation for the SDO.

$$\delta(E - \hat{H}) \approx \{[\{\sinh(\zeta\Delta t/\hbar)\{1 - e^{-\zeta T/\hbar}\cos(E - \hat{H})T/\hbar\} + e^{-\zeta T/\hbar}\sin(E - \hat{H})\Delta t/\hbar\,\sin(E - \hat{H})T/\hbar\}/\{\cosh(\zeta\Delta t/\hbar) - \cos(E - \hat{H})\Delta t/\hbar\}] + [1 + e^{-\zeta T/\hbar}\cos(E - \hat{H})T/\hbar]\}\frac{\Delta t}{2\pi\hbar} \quad (10)$$

It can then easily be shown that the end-point correction as employed in eq 9 exactly cancels the term $[1 + e^{-\zeta T/\hbar}\cos(E - \hat{H})T/\hbar]$ on the right-hand side of eq 10, which is an extra error solely due to the time discretization. Furthermore, it is easy to verify that the $\Delta t \to 0$ limit transforms eq 10 to eq 8, which is to be expected for consistency. Thus, eqs 8 and 10 clearly reveal the nature of the approximations involved in the present treatment. Of course, one could also choose even more accurate numerical integration schemes than what we use here in eq 9, the necessity of which was not felt in the present investigation. Finally, we note that no Hamiltonian renormalization is necessary for the discrete representation of the SDO as shown in eq 9, contrary to the use of Chebyshev polynomials as in eq 7; however, it may be desirable to carry out such a renormalization for certain implementations of the FD algorithm (see Discrete Time Representation).

A comment on the nature of the damping parameter, ζ, in eqs 6−10 is in order here. That is, one may choose ζ to be coordinate-dependent after passing the SDO to the integral or the discrete summation form, in which case this will act as an absorbing potential and render the Hamiltonian of the system to be non-Hermitian. Even though a non-Hermitian Hamiltonian carries its own set of disadvantages, the use of absorbing potentials has found many useful applications in earlier molecular scattering studies and it has also been highlighted as a convenient device that may be used to enforce an outgoing wave boundary condition in scattering studies.[13,14,42,52] If one so desires, the present formulation can easily be extended to such situations with only minor modifications. The present study, however, uses a coordinate-independent ζ and handles the scattering boundary conditions by appropriately constructing initial wave packets (vide infra). That is, one does not necessarily have to make the Hamiltonian a non-Hermitian one just for the purpose of enforcing boundary conditions.

III. Quantum Scattering

Here we follow a general quantum mechanical wave packet approach to the scattering process of a molecular system with internal degrees of freedom, with the objective of computing the so-called scattering matrix. The present theoretical treatment of quantum scattering is similar to the time-dependent method discussed by Taylor[50] and Goldberger and Watson,[49] modern implementations of which have appeared in the research of Tannor et al.[33−36] and Kouri and co-workers.[27−32] In the following, we first briefly define the notion of a scattering process and obtain a general expression for the elements of the S-matrix in terms of reactant and product wave packets, using the idea of spectral filters as discussed in the previous section.

A general molecular scattering process is characterized by an interaction region (in the position space, for example), in which the interaction between molecular fragments is nonzero, and asymptotic regions in which the interaction vanishes asymptotically (in the reactant and product arrangement channels). The complete scattering dynamics itself is governed by the Hamiltonian, $\hat{H}$, of the total molecular system, consisting of asymptotic Hamiltonian plus the interaction. As an example, we consider a general bimolecular collision,

$$\mathrm{A - B + C - D \to A - C + B - D} \quad (11)$$

and denote the molecular system in the reactant (A − B + C − D) and product (A − C + B − D) arrangement channels by the symbols α and β, respectively. For notational simplicity, we specify the translational degree of freedom by x and suppress the set of quantum numbers needed to specify the various internal degrees of freedom of the fragmented systems in their respective asymptotic arrangement channels. We now assume the existence of a complete set of energy eigenstates for each asymptotic arrangement channel, $\hat{H}^{\alpha}\phi^{(\alpha)}(E) = E\phi^{(\alpha)}(E)$, where $\hat{H}^{\alpha}$ is the asymptotic α-arrangement channel Hamiltonian. For example, the energy eigenstate for the α^{th} arrangement channel is given as

$$|\phi^{(\alpha)}(E)\rangle = |\mathrm{ro - vibration}\rangle_{\mathrm{A-B}} \otimes |\mathrm{ro - vibration}\rangle_{\mathrm{C-D}} \otimes |\mathrm{ro - translation}\rangle_{\mathrm{R(AB-CD)}} \quad (12)$$

Here, the total energy is given as, $E = E_{AB} + E_{CD} + E_x$, where E_{AB} and E_{CD} are the rotational−vibrational energies of the fragments, and E_x is the energy in the relative rotational and translational degrees of freedom (scattering energy). Ideally, a molecular scattering experiment would prepare the system in one of the channel eigenstates; in practice, this may not be feasible.

Now, the energy is a conserved quantity in a physical process, and therefore, we use this as a basis for our discussion of the molecular scattering process here. For every value of energy E in the molecular continuum, the scattering eigenstate, $\chi(E)$, consists of degenerate components, which differ in the direction of the associated quantum flux. In one dimension, for example, $\chi(x, E) = \chi^{+}(x, E) + \chi^{-}(x, E)$, where the flux associated with

χ^+ and χ^- points in the positive and negative directions, respectively. We can thus define the scattering eigenstate as follows:

$$\hat{H}\,\chi^{\pm(\alpha)}(E) = E\,\chi^{\pm(\alpha)}(E) \tag{13}$$

$$\hat{H}\,\chi^{\pm(\beta)}(E') = E'\,\chi^{\pm(\beta)}(E') \tag{14}$$

Here, $\chi^{\pm(\alpha)}(E)$ and $\chi^{\pm(\beta)}(E')$ are globally defined in the representation space, and they asymptotically correlate with the eigenstate of the Hamiltonian in the reactant channel (α-arrangement) of the energy E, $\phi^{\pm(\alpha)}(E)$ and the product channel (β-arrangement) of the energy E', $\phi^{\pm(\beta)}(E')$, respectively. The existence of such asymptotic correlations is motivated on the physical ground that the Hamiltonian, $\hat{H}$, takes the form of channel Hamiltonians ($\hat{H}^{\alpha}$ and $\hat{H}^{\beta}$) as the molecular interaction vanishes.

Now, all scattering eigenstates within both positive and negative flux sectors are mutually orthogonal and normalized in the delta function sense, as shown below.

$$\langle\chi^{\pm(\alpha)}(E)\,|\chi^{\pm(\alpha)}(E')\rangle = \delta(E - E') \tag{15}$$

$$\langle\chi^{\pm(\beta)}(E)\,|\chi^{\pm(\beta)}(E')\rangle = \delta(E - E') \tag{16}$$

The overlap between the positive and the negative flux components, which correlate with the respective asymptotic scattering channels, defines the elements of the on-shell S-matrix, as shown below.

$$\langle\chi^{-(\beta)}(E')\,|\chi^{+(\alpha)}(E)\rangle = S_{\beta,\alpha}(E)\,\delta(E - E') \tag{17}$$

This completes the definition of the scattering matrix, and our next problem is to provide a procedure to compute the scattering states, as required in eq 17.

We now use the idea of the spectral filter to obtain the scattering eigenstates from known (but to an extent, arbitrary) wave packets, $\Phi^{+(\alpha)}$ and $\Phi^{-(\beta)}$, located in the appropriate asymptotic channels in the position space, as follows,

$$\chi^{+(\alpha)}(E) = \frac{1}{A_{\alpha}^{+}(E)}\,\delta(E - \hat{H})\,\Phi^{+(\alpha)} \tag{18}$$

$$\chi^{-(\beta)}(E') = \frac{1}{A_{\beta}^{-}(E')}\,\delta(E' - \hat{H})\,\Phi^{-(\beta)} \tag{19}$$

where $A_{\alpha}^{+}(E)$ and $A_{\beta}^{-}(E')$ are, in general, nonzero complex numbers, denoting the contribution of scattering eigenstates $\chi^{+(\alpha)}(E)$ and $\chi^{-(\beta)}(E')$ to the wave packets $\Phi^{+(\alpha)}$ and $\Phi^{-(\beta)}$, respectively. In particular, eqs 18 and 19 easily lead to the following definitions.

$$A_{\alpha}^{+}(E) = \langle\chi^{+(\alpha)}(E)|\Phi^{+(\alpha)}\rangle$$

and

$$A_{\beta}^{-}(E') = \langle\chi^{-(\beta)}(E')|\Phi^{-(\beta)}\rangle \tag{20}$$

and

$$|A_{\alpha}^{+}(E)|^2 = \langle\Phi^{+(\alpha)}\,|\delta(E - \hat{H})|\Phi^{+(\alpha)}\rangle$$

and

$$|A_{\beta}^{-}(E')|^2 = \langle\Phi^{-(\beta)}|\delta(E' - \hat{H})|\Phi^{-(\beta)}\rangle \tag{21}$$

Eq 21 defines the quantity that is generally known as the spectral intensity, and it is clearly seen here to be the Fourier transform of the autocorrelation function. An important question, however, which remains here is: How does one ensure that the filtering process satisfies the appropriate boundary conditions? That is, eq 18, for example, produces the state with *only* positive flux from the reactant side directed toward the scattering region so that the coefficient computed using eq 21 belongs *only* to the incident wave. Enforcing such scattering boundary conditions is known to be a nontrivial issue as an arbitrarily prepared wave packet in an asymptotic channel produces quantum flux both in the positive and negative directions. As we explain in the following, it is possible to make the negative flux component negligible by a proper choice of the wave packets in eqs 18 and 19 so that eq 21 remains accurate for the numerical purpose.

We first note that $\Phi^{+(\alpha)}$ and $\Phi^{-(\beta)}$ in eqs 18 and 19 are the moving wave packets, which we obtain by choosing an arbitrary function, $\Phi^{(\alpha)}$, that has a sufficiently rapid decay both in the coordinate space and in the Fourier space (one may select a real Gaussian function, for example), and multiplying by a momentum eigenfunction as follows,

$$\Phi^{+(\alpha)} = e^{iK_0x}\,\Phi^{(\alpha)}$$

and similarly,

$$\Phi^{-(\beta)} = e^{-iK_0x}\,\Phi^{(\beta)} \tag{22}$$

where $K_0 = +\sqrt{2\mu E_0}/\hbar$ and E_0 is an arbitrary (preferably large) energy. Thus, we can express $\Phi^{+(\alpha)}$ in the integral representation as follows,

$$\begin{aligned}\Phi^{+(\alpha)}(x) &= \int_0^\infty d\epsilon\,[A(\epsilon)\,e^{i(K_0+K_\epsilon)x} + B(\epsilon)\,e^{i(K_0-K_\epsilon)x}]\\ &= \int_0^\infty d\epsilon\,A(\epsilon)\,e^{i(K_0+K_\epsilon)x} + \int_0^{E_0} d\epsilon\,B(\epsilon)\,e^{i(K_0-K_\epsilon)x} +\\ &\qquad \int_{E_0}^\infty d\epsilon\,B(\epsilon)\,e^{-i(K_\epsilon-K_0)x}\\ &\equiv \int_0^\infty d\epsilon\,A^{+}(\epsilon)\,e^{i\tilde{K}x} + \int_{E_0}^\infty d\epsilon\,B(\epsilon)\,e^{-i(K_\epsilon-K_0)x}\end{aligned} \tag{23}$$

where $K_\epsilon = \sqrt{2\mu\epsilon}/\hbar$ and $\tilde{K}$ is a function of ϵ and E_0. The last step in eq 23 is symbolic, where we have explicitly shown that the state $\Phi^{+(\alpha)}$ consists of components moving in the positive (first term) and negative (second term) directions and, thus, produces flux in both directions, toward as well as away from the interaction region. But we know that the original function, $\Phi^{(\alpha)}$, is rapidly decaying in the Fourier space, and this means the coefficients, $A(\epsilon)$ and $B(\epsilon)$, must rapidly go to zero as we increase ϵ. Thus, the contribution from the second term in eq 23 can be made arbitrarily small if we choose E_0 to be sufficiently large, which is in any case arbitrary. Thus, the above construction effectively gives the following results.

$$\Phi^{+(\alpha)}(x) = \int_0^\infty d\epsilon\,A_{\alpha}^{+}(\epsilon)\,e^{i\tilde{K}x} \tag{24}$$

Similarly,

$$\Phi^{-(\beta)}(x) = \int_0^\infty d\epsilon\,A_{\beta}^{-}(\epsilon)e^{-i\tilde{K}x} \tag{25}$$

In this manner, we can ensure that the states filtered from the packets, $\Phi^{+(\alpha)}(x)$ and $\Phi^{-(\beta)}(x)$, satisfy the appropriate incident and scattered wave boundary conditions. For example, we can easily verify that the result of filtering in eq 18 in the reactant (α-arrangement) channel is indeed only the incoming wave,

$$\delta(E - \hat{H})\, \Phi^{+(\alpha)}(x) = \frac{1}{\hbar}\sqrt{\frac{\mu}{2E}} \int_0^\infty \mathrm{d}\epsilon\, A_\alpha^+(\epsilon) \times [\delta(K_E + \hat{k}) + \delta(K_E - \hat{k})]\, \mathrm{e}^{i\tilde{\mathrm{K}}x} = A_\alpha^+(E)\, \mathrm{e}^{iK_E x} \tag{26}$$

where $K_E = \sqrt{2\mu E}/\hbar$ and $\hbar\hat{k}$ is the momentum operator. In eq 26, we have utilized the fact that the Hamiltonian in the reactant channel is simply the kinetic energy operator. There is certainly no denying the fact that there is always an error, controllably small, in the above prescription of preparing wave packets. This is because the second term in eq 23 is always finite, but it can be made arbitrarily small. As we will later see from the numerical evidence, this prescription is very accurate for computing scattering probabilities, and they are independent of E_0. Thus, the scattering boundary conditions will be fulfilled from the nature of the initially prepared wave packets, which are localized in the asymptotic reactant and product channels and spatially separated. No additional device is, therefore, needed to enforce the boundary conditions in the wave packet-based scattering calculations.

Using eqs 17−19, the S-matrix can now be expressed as follows:

$$S_{\beta,\alpha}(E)\, \delta(E - E') = \frac{\langle \Phi^{-(\beta)} | \delta(E' - \hat{H})\, \delta(E - \hat{H}) | \Phi^{+(\alpha)} \rangle}{[A_\beta^-(E')]^*\, A_\alpha^+(E)} \tag{27}$$

At this stage, we could, in principle, factorize the product of two delta functions in eq 27 as

$$\delta(E - \hat{H})\, \delta(E' - \hat{H}) = \delta(E - E')\, \delta(E - \hat{H}) \tag{28}$$

and obtain the expression for the on-shell S-matrix as follows.

$$S_{\beta,\alpha}(E) = \frac{\langle \Phi^{-(\beta)} | \delta(E - \hat{H}) | \Phi^{+(\alpha)} \rangle}{[A_\beta^-(E)]^*\, A_\alpha^+(E)} \tag{29}$$

Equation 29, which essentially defines the on-shell S-matrix elements as the Fourier transformation of an appropriate correlation function, was obtained by Tannor and co-workers.[33−36] In addition, an expression for the on-shell S-matrix, which is similar to eq 29 but involves a causal full Green's function, $G^+(E)$, in place of the delta function, was independently obtained by Kouri and co-workers.[27−32] Notably, the presence of the anticausal Green's function, $G^-(E)$, in the numerator of eq 29 does not contribute anything significant if the wave packet, $\Phi^{+(\alpha)}$, contains predominantly positive flux (vide supra). In this sense, the two formulations are essentially equivalent.[31,32,117] In any event, we note that the above factorization of the product of two delta functions mathematically holds only in the exact limit. This means that $N \to \infty$ and $\zeta \to 0$, if one uses a series representation for the delta function, for example, as given by eqs 7 and 9. In a practical calculation, N (and also ζ) is *always* finite, and for a finite N, this factorization introduces some additional error, which diminishes only slowly as N increases. This is due to the fact that a truncated series gives a finite width to the delta function (which can, of course, be made as small as one wishes by simply increasing N), and this width is symmetrically distributed between the bra and ket in eq 27. This symmetry is clearly lost when one goes to eq 29. This assertion can easily be verified by examining the identity in eq 28 with the use of any integral representation of the delta function, wherein one notices that the direction of double integration resulting from two delta functions gets rotated as one goes from the left-hand side to the right-hand side. Additionally, with an appropriate truncated series representation for each of the delta functions, eq 27 defines both the on-shell and the off-shell S-matrix elements, which information is lost in the factorization process. Therefore, we shall not use this factorization in the present work. Instead, we will make an additional, exact algebraic manipulation with eq 27 to obtain a compact series expression for the S-matrix elements. Our strategy is as follows.

We first select an appropriate truncated series representation for the SDO (see Section II). Because eq 27 contains a product of two SDOs, we will have a corresponding finite double series. It then turns out that a partial, analytically exact, resummation of the resulting double series can be accomplished in certain situations, resulting in a single series, which is advantageous for the most efficient numerical implementation. Finally, we substitute $E = E'$ to obtain the expression for the elements of on-shell S-matrix. Thus, the modulus square of the S-matrix element is given as follows,

$$|S_{\beta,\alpha}(E)|^2 = \frac{\left| \left\langle \Phi^{-(\beta)} \middle| \frac{\delta_T(E - \hat{H})\, \delta_T(E - \hat{H})}{\delta_T(E - E)} \middle| \Phi^{+(\alpha)} \right\rangle \right|^2}{|A_\beta^-(E)|^2 |A_\alpha^+(E)|^2} \tag{30}$$

where δ_T in eq 30 refers to an approximation to the spectral density operator that would be obtained by truncating the series after N terms in eqs 7 and 9 for a finite and positive ζ. Equation 30 is a central object for which we obtain series representations in the following sections.

We parenthetically note that eq 29 in conjunction with eq 7 or 9 for the spectral density operator will remain accurate in situations when the associated time cross-correlation functions decay sufficiently rapidly. If, however, there are long-lived scattering resonances in the system and the time evolution of wave packets contains the feature of multiple revivals, the associated time-correlation functions will have a practically inaccessible long time tail, and therefore, the convergence of the scattering probabilities will be slow with eq 29.

Short-Time Iterative Implementation. Here, we obtain a compact expression for the elements of the on-shell S-matrix as a sum involving a discrete series of short-time correlation function. First of all, the spectral intensity, $|A_\alpha^+(E)|^2$, as required in eq 30 can be obtained using eqs 9 and 21 as follows

$$|A_\alpha^+(E)|^2 = \frac{\Delta t}{2\pi\hbar} \sum_{k=0}^{N} (1 - \delta_{k0}/2)(1 - \delta_{kN}/2) \times [\{Z(E)\}^k C_k^{(\alpha,\alpha)} + \{Z(E)^*\}^k C_{-k}^{(\alpha,\alpha)}] = \frac{\Delta t}{\pi\hbar} \sum_{k=0}^{N} (1 - \delta_{k0}/2)(1 - \delta_{kN}/2)\, Re[\{Z(E)\}^k C_k^{(\alpha,\alpha)}] \tag{31}$$

where $C_{\pm k}^{(\alpha,\alpha)} = \langle \Phi^{+(\alpha)} | \hat{U}^{\pm k} | \Phi^{+(\alpha)} \rangle$ is the short-time autocorrelation function. In eq 31, we used the fact that the packet $\Phi^{+(\alpha)}$ is initially localized in the asymptotic channel, and therefore, the autocorrelation function in eq 31 will decay very rapidly and also satisfy the time reversal symmetry, $C_{-k}^{(\alpha,\alpha)} = [C_k^{(\alpha,\alpha)}]^*$. There will be a similar expression for $|A_\beta^-(E)|^2$ because the above analysis holds equally for $\Phi^{-(\beta)}$.

The expression for $\delta_T(E - E)$, on the other hand, can easily be obtained by substituting $E = \hat{H}$ in eq 10, which gives the following result,

$$\delta_T(E - E) = \left(\frac{\Delta t}{2\pi\hbar}\right)\left[\frac{\sinh(\zeta\Delta t/\hbar)\,\{1 - \mathrm{e}^{-\zeta T/\hbar}\}}{\cosh(\zeta\Delta t/\hbar) - 1}\right] \quad (32)$$

where $T = N\Delta t$ is the total length of time propagation.

Now, using eq 9 for the SDO and results from Appendix A, we obtain the following result

$$\langle\Phi^{-(\beta)}|\delta_T(E - \hat{H})\,\delta_T(E - \hat{H})|\Phi^{+(\alpha)}\rangle = \sum_{k=0}^{2N} F_k(Z)\,C_k^{(\alpha,\beta)} + [F_k(Z)]^*\,C_{-k}^{(\alpha,\beta)} \quad (33)$$

where

$$F_k(Z) = \begin{cases} \left(\dfrac{\Delta t}{2\pi\hbar}\right)^2\left[k + \left(1 - \dfrac{\delta_{k,0}}{2}\right) \times \left\{\dfrac{\mathrm{e}^{-x} + 1}{\mathrm{e}^{-x} - 1}(\mathrm{e}^{(k-N)x} - 1) - \dfrac{\delta_{k,0}}{2}\mathrm{e}^{(k-N)x}\right\}\right]Z^k & (0 \le k \le N) \\ \left(\dfrac{\Delta t}{2\pi\hbar}\right)^2\left[(2N - k) + \dfrac{\delta_{k,2N}}{4}\right]Z^k & (N + 1 \le k \le 2N) \end{cases} \quad (34)$$

where $Z = \mathrm{e}^{i(E+i\zeta)t/\hbar}$, $x = 2\zeta\Delta t/\hbar$ and $C_{\pm k}^{(\alpha,\beta)} = \langle\Phi^{-(\beta)}|\hat{U}^{\pm k}|\Phi^{+(\alpha)}\rangle$ is the short-time cross-correlation function. An important point to note here is that for a general scattering problem, $[C_k^{(\alpha,\beta)}]^* \neq C_{-k}^{(\alpha,\beta)}$, but in the expression for the correlation function, $C_{\pm k}^{(\alpha,\beta)}$, we notice that the wave packet $\Phi^{+(\alpha)}$ is initially located in the asymptotic reactant arrangement channel and by construction produces predominantly positive quantum flux. Therefore, the operator $\hat{U}^{-k}$ will primarily move this packet *away* from the interaction region. Thus, the contribution from the backward time propagation, $C_{-k}^{(\alpha,\beta)}$, will be controllably small for the scattering process.[117] In fact, this contribution can be made negligible in a practical calculation by using the form of the wave packet as discussed earlier and using various devices to keep the wave packet narrow until it reaches the interaction region. We can therefore drop the term containing $C_{-k}^{(\alpha,\beta)}$ from eq 33 without significant numerical error. This is equivalent to removing the contribution of the anticausal Green's function from eq 30.

We can now substitute eqs 31−34 in eq 30 to obtain the desired scattering probabilities. Notably, eqs 31 and 33 remain in the energy-separable form; hence, one needs to compute the correlation functions only once and use them for different energies.

We now discuss further simplifications of eq 33 that are possible by taking some appropriate limits, valid under specific situations. First of all, the factor, $x = 2\zeta\Delta t/\hbar$ is expected to be small; therefore, we can safely take the limit $x \to 0$. In this limit, we substitute $\mathrm{e}^x = 1 + x$, $\sinh(x) = x$, and $\cosh(x) = 1 + x^2/2$. As a result, $\delta_T(E - E)$ in eq 32 reduces to $(N\Delta t/\pi\hbar)$, and eq 34 takes the following simple form:

$$F_k(Z) = \left(\frac{\Delta t}{2\pi\hbar}\right)^2\left[(2N - k) - \delta_{k,0}(N - k + 1/4) + \frac{\delta_{k,2N}}{4}\right]Z^k \qquad (0 \le k \le 2N) \quad (35)$$

Now, using eqs 32, 33, and 35, it is straightforward to obtain the following result.

$$\left\langle\Phi^{-(\beta)}\left|\frac{\delta_T(E - \hat{H})\,\delta_T(E - \hat{H})}{\delta_T(E - E)}\right|\Phi^{+(\alpha)}\right\rangle = \frac{\Delta t}{2\pi\hbar}\sum_{k=0}^{2N}\left[\left(1 - \frac{\delta_{k,0}}{2}\right) - \frac{k}{2N} + \frac{1}{8N}(\delta_{k,2N} - \delta_{k,0})\right]Z^k C_k^{(\alpha,\beta)} \quad (36)$$

In eq 36, we have dropped the term containing $C_{-k}^{(\alpha,\beta)}$ for the reason discussed above. Now, eq 36 can be further simplified if the nature of the correlation function, $C_k^{(\alpha,\beta)}$, is such that it remains finite only for a "short" time and then falls off rapidly, at least at a rate faster than $1/N$. In such a situation, the summation in eq 36 would be practically restricted to a finite $2N$; hence, taking the limit $N \to \infty$ would not add anything significant. Moreover, $C_k^{(\alpha,\beta)}$ is expected to be 0 for $k = 0$ as well as for $k = N$, where $N \to \infty$. As a result, the end-point corrections no longer matter here, and we can drop terms containing $\delta_{k,0}$ and $\delta_{k,2N}$ from eq 36. Thus, eq 36 reduces to the following simple form.

$$\left\langle\Phi^{-(\beta)}\left|\frac{\delta_T(E - \hat{H})\,\delta_T(E - \hat{H})}{\delta_T(E - E)}\right|\Phi^{+(\alpha)}\right\rangle = \frac{\Delta t}{2\pi\hbar}\sum_{k=0}^{\infty} Z^k C_k^{(\alpha,\beta)} \quad (37)$$

In the numerical implementation of eq 36 or 37, we can explicitly take the limit $\zeta \to 0$ in the expression for Z without any difficulty as we have already taken the limit $x \to 0$. That means Z would simply be $\mathrm{e}^{iE\Delta t/\hbar}$, and the implementation would be free from the width parameter of the Lorentzian filter. We emphasize that the nature of simplifications leading to eq 37 is specific only for certain scattering situations. As we will see later, such simplifications are not possible for filter diagonalization-based bound states studies.

How does the present implementation of the S-matrix differ from those of earlier studies,[27−36] which utilized eq 29 as their starting point? In fact, if we use eq 9 for the SDO in conjunction with eq 29 and follow the arguments advanced above, we will obtain eq 37 with $Z = \mathrm{e}^{i(E+i\zeta)\Delta t/\hbar}$. This is not surprising, but the present analysis clearly reveals the limiting process $[x(= 2\zeta\Delta t/\hbar) \to 0$, and hence, $\zeta \to 0]$ and clarifies the approximations that are made in the direct implementation of eq 29. Thus, if the cross-correlation function decays sufficiently rapidly, at least faster than $1/N$, the present implementation does not differ from earlier studies.[27−36] We advocate the use of eq 37 in that case. This observation is important and provides a posteriori justification for the use of the factorization of a product of two delta functions (eq 28), which is numerically accurate only in certain situations, as discussed above. However, if the cross-correlation function does contain long time features, such as scattering resonances, wave packet revivals, etc., one will practically have access to only limited information on $C_k^{(\alpha,\beta)}$. In such a situation, the use of eq 33 or 36 is expected to be more accurate.

It is now clear that the computation of the S-matrix requires the input of short-time auto- and cross-correlation functions, $C_k^{(\alpha,\alpha)}$ and $C_k^{(\alpha,\beta)}$, respectively. At this stage, we may choose to ignore their quantum mechanical origin and compute them by a semiclassical,[10,101,103,115] mixed-quantum/classical,[101,102,114] or simply by a classical method. This opens a way to extend the filter approach of quantum scattering to various approximate dynamical regimes. This idea has been successfully utilized by Tannor and co-workers.[36]

Chebyshev Polynomial Representation. Here, we obtain a compact expression for the elements of the on-shell S-matrix as a series involving the Chebyshev polynomials with a

Hamiltonian operator as its argument. Using eq 7 for the SDO and results from Appendix B, we can easily obtain the following:

$$\langle \Phi^{-(\beta)} | \delta_T(E - \hat{H})\, \delta_T(E - \hat{H}) | \Phi^{+(\alpha)} \rangle = \frac{1}{(\pi \Delta\lambda)^2} \sum_{k=0}^{N} (G_k^{(1)} C_k^{(\alpha,\beta)} + G_k^{(2)} C_{k+N}^{(\alpha,\beta)}) \quad (38)$$

where $G_k^{(1),(2)} = Re\{A_k^{(1),(2)}[Z(\tilde{E}), D(\tilde{E}); Z(\tilde{E}), D(\tilde{E})] + A_k^{(1),(2)}[Z(\tilde{E}), D(\tilde{E}); Z^*(\tilde{E}), D^*(\tilde{E})]\}$ and $C_k^{(\alpha,\beta)} = \langle \Phi^{-(\beta)} | T_k(\hat{H}_{sc}) | \Phi^{+(\alpha)} \rangle$. The coefficients $A_k^{(1)}$ and $A_k^{(2)}$ have been defined in Appendix B (see eqs B-6−B-10).

Using eqs 7 and 21, we can obtain the following expression for $|A_\alpha^+(E)|^2$, as required in eq 30 for the S-matrix,

$$|A_\alpha^+(E)|^2 = \left(\frac{1}{\pi \Delta\lambda}\right) \sum_{k=0}^{N} (2 - \delta_{k0}) Re[D(E)\, Z^k(E)] C_k^{(\alpha,\alpha)} \quad (39)$$

where $C_k^{(\alpha,\alpha)} = \langle \Phi^{+(\alpha)} | T_k(\hat{H}_{sc}) | \Phi^{+(\alpha)} \rangle$. The expression for $|A_\beta^-(E)|^2$ will be the same as given in eq 39, but one has to replace $C_k^{(\alpha,\alpha)}$ with $C_k^{(\beta,\beta)} = \langle \Phi^{-(\beta)} | T_k(\hat{H}_{sc}) | \Phi^{-(\beta)} \rangle$. Finally, we need to substitute $E = \hat{H}$ in eq 7, truncated to N terms, to obtain the volume factor $\delta_T(E - E)$ to be used in eq 30. In a general situation, the expression for $\delta_T(E - E)$ remains in the series form. As a result, the division of eq 38 by $\delta_T(E - E)$ could not be performed analytically, unlike the case of short-time iterative implementation in Section III. A. It is, however, anticipated that such a division would be possible if we explicitly take the $\zeta \to 0$ limit, which we have not attempted here. In any case, the computation of $\delta_T(E - E)$ from the series in eq 7 does not incur significant numerical effort. We can now substitute eqs 38 and 39 in eq 30 to obtain the desired scattering probabilities.

It is important to notice that eqs 38 and 39 are in the energy-separable form. This means the coefficients $C_k^{(\alpha,\alpha)}$ and $C_k^{(\alpha,\beta)}$, which are computationally most expensive to obtain, have to be computed only once and stored, and they then can be used to obtain the S-matrix elements for all scattering energies of interest. We also note that if one chooses $\Phi^{(\alpha)}$ and $\Phi^{(\beta)}$ to be the same, then one can compute $2N$ C_k's by performing only N Chebyshev recursions by using a special property of Chebyshev polynomials, $2T_kT_{k'} = T_{|k+k'|} + T_{|k-k'|}$, not satisfied by other classical orthogonal polynomials. This is one of the reasons why we choose Chebyshev polynomials for such filter applications.

Again, we consider how the present implementation of the on-shell S-matrix is different from the direct use of eq 29 in conjunction with eq 7 for the Chebyshev expansion of the SDO, as is implicit in the previous studies?[27−36] First of all, the expression for the Chebyshev correlation functions, $C_k^{(\alpha,\alpha)}$ and $C_k^{(\alpha,\beta)}$ remains the same; so are the coefficients, $|A_\alpha^+(E)|^2$ and $|A_\beta^+(E)|^2$. It is, however, clear that the coefficients, $G_k^{(1)}$ and $G_k^{(2)}$, in eq 38 are different from what one would obtain from the direct use of eq 7 into eq 29. In addition, we know that the SDO is by definition a sum of anticausal and causal Green's functions, and therefore, the contribution of the former, which leads to a backward time propagation of the wave packet, can be removed from eq 29 very easily. In the present formulation, on the other hand, it is no longer possible to identify the anticausal Green's function part in eq 38 in a simple manner, contrary to what we could accomplish in the discrete time iterative implementation (see Short-Time Iterative Implementation). This is of no concern because we know that the initial wave packet in the reactant channel is constructed such that it produces predominantly positive flux (vide supra). Moreover, we have not found a physically appropriate analytical limiting process which could transform the coefficients $G_k^{(1)}$ and $G_k^{(2)}$ in eq 38 into what one would obtain from the direct use of eq 7 into eq 29. Hence, in this case, we do not know the exact physical situation in which the use of the factorization of a product of two delta functions (eq 28) will remain numerically valid here, hence, giving a posteriori justification of the use of eq 29 as suggested in earlier studies.[27−36]

IV. Bound States

In this section, we present our implementation of the Lorentzian function-based spectral filter method for computing the eigenvalues and spectral intensities, corresponding to the bound states of a molecular Hamiltonian, in an arbitrary energy range. The central quantity in this procedure again is the spectral density operator (SDO), for which we again consider both the Lorentzian-function-based Chebyshev polynomial and discrete time representations.

Spectral Intensities. Let us consider a finite dimensional Hamiltonian, $\hat{H}$, representing a bound molecular system, which supports a set of eigenstates, $|\phi_m\rangle$, $m = 1, N$,

$$\hat{H}\, |\phi_m\rangle = \epsilon_m |\phi_m\rangle \quad (40)$$

where ϵ_m is the m^{th} eigenvalue. As discussed in Section II, an arbitrary quantum state, $|\psi\rangle$ (which could be an experimentally prepared wave packet) can be expressed as a linear combination of the eigenstates of $\hat{H}$,

$$|\psi\rangle = \sum_{m=1}^{N} I_m |\phi_m\rangle \quad (41)$$

where $|I_m|^2 = |\langle \phi_m | \psi \rangle|^2$ is called the spectral intensity for the m^{th} eigenstate, and it defines the relative weight with which each eigenstate contributes to form the initial wave packet, $|\psi\rangle$. It is an important quantity, since this is what is typically observed in various spectroscopic measurements.

Now, using the idea of the spectral filter, we can easily obtain the following general expression for $|I_m|^2$.

$$|I(E)|^2 = \langle \psi | \delta(E - \hat{H}) | \psi \rangle \quad (42)$$

On substituting eq 7 for the SDO in eq 42, we obtain

$$|I(E)|^2 = \frac{1}{\pi \Delta\lambda} \sum_{k=0}^{N} (2 - \delta_{k,0})\, Re[D(E)\, Z^k(E)] C_k \quad (43)$$

where $C_k = \langle \psi | T_k(\hat{H}_{sc}) | \psi \rangle$ is the so-called Chebyshev correlation function. Similarly, on substituting eq 9 for the SDO, we obtain

$$|I(E)|^2 = \frac{\Delta t}{\pi \hbar} \sum_{k=0}^{N} \left(1 - \frac{\delta_{k,0}}{2}\right)\left(1 - \frac{\delta_{k,N}}{2}\right) Re[Z^k(E)\, D_k] \quad (44)$$

where, $D_k = \langle \psi | e^{-i\hat{H}k\Delta t/\hbar} | \psi \rangle$ is the short-time autocorrelation function.

In eqs 43 and 44, the correlation functions C_k and D_k have to be obtained only once, and they can then be used to compute the intensity for any arbitrary energy. We note that the plot of $|I(E)|^2$ as a function of E will show, by definition, a set of Lorentzian profiles with peaks falling on the exact eigenvalue locations. Therefore, the location of eigenvalues can be obtained, in principle, by finding the zeroes of $(d/dE)I(E)$. It should, however, be kept in mind that in practical situations, less intense peaks may not be very easy to distinguish, and therefore, this procedure will not always be practically convenient for such states. In fact, the exact location of eigenvalue positions is easily obtained by theFD technique, which we discuss in the following. In fact, it will also be possible in a practical study to combine the spectral intensity information with the FD method to make the FD numerically more efficient, because the former faithfully reveals the energy region where eigenvalues are located.

Eigenvalues: Filter Diagonalization. Filter diagonalization methods have been extensively discussed in the literature, and the underlying principle is now well-understood.[51,60−86] Therefore, we do not go into detail here, and in the following, we give the minimum necessary details for the purpose of explaining the current implementation, which utilizes the Lorentzian function-based spectral filter. A preliminary report of this implementation involving Chebyshev polynomials has recently been published.[51]

For a given Hamiltonian, $\hat{H}$, a FD method involves construction of a set of basis states by applying a spectral filter in a preselected energy window, on an arbitrary wave packet, $|\psi\rangle$, and using them as a basis to diagonalize the Hamiltonian. Conceptually, a filter operator corresponds to the SDO, which in an ideal situation will select out the eigenstate itself. However, the operation with an approximate representation of the SDO (a finite sum in eqs 7 and 9, for example) on an arbitrary wave packet will produce not an eigenstate, but it yields a superposition of eigenstates which are concentrated over a range of eigen energies located near the filter energy, E, and a set of such selected states (obtained by applying $\delta_T(E - \hat{H})$ to more than one packet or using the same packet but changing the value of E) may serve as a good basis for eventual diagonalization of the Hamiltonian. This is the basic principle of the FD method. We denote these filtered states by $|\varphi_l\rangle$, $l = 1, L$, where L is the number of energies in a given range at which the filteration has been carried out. We note that an actual implementation of the FD method does not require us to construct $|\varphi_l\rangle$ explicitly. Instead, one just needs a prescription to compute the necessary matrix elements over the basis of a set of $|\varphi_l\rangle$ directly. This is what we will elaborate on in the following discussion. There are several choices for an approximate representation of the SDO, but as discussed in section II, the Lorentzian function representation currently seems to offer an optimum choice for a practical application;[51] this is what we suggest to use here. In the following, we give a brief description of the computational tools required to perform the FD applications.

In FD applications, we first set up the following generalized eigenvalue problem,

$$HB = SBE \tag{45}$$

where the matrix B is defined by the linear relation between the filtered states, $|\varphi_l\rangle$ and the eigenstates, $|\phi_m\rangle$, as follows:

$$|\phi_m\rangle = \sum_{l=0}^{L} B_{l,m}\,|\varphi_l\rangle \tag{46}$$

Here, H and S are the Hamiltonian and overlap matrices, respectively, represented in the basis of filtered states, as shown below,

$$\begin{aligned} A^{(p)}_{m,n} &= \langle\varphi_m|(\hat{H})^p|\varphi_n\rangle \qquad (m, n = 1, L) \\ &= \langle\psi|\delta_T(E_m - \hat{H})(\hat{H})^p\,\delta_T(E_n - \hat{H})|\psi\rangle \end{aligned} \tag{47}$$

where $|\psi\rangle$ is an arbitrary "seed" state, which is chosen randomly for the purpose of the eigenvalue problem. Here $p = 0$ and 1 give the overlap and Hamiltonian matrices, respectively. In practical studies, the overlap matrix, S, may be nearly singular, and therefore, eq 45 must be solved by employing the singular value decomposition method which diagonalizes the overlap matrix and removes "small" eigenvalues, if any. This technique is well-discussed in the literature.[118] In any event, some of the computed energies will eventually converge to the eigenvalues, ϵ_m, of the original Hamiltonian. In the FD method, it is also possible to obtain an a priori error estimate for each eigenvalue by computing, for example, the following quantity,[63]

$$\begin{aligned} \Delta(E_m)^2 &= |\langle\phi_m|(E_m - \hat{H})^2|\phi_m\rangle| \\ &= |(B^t H^{(2)} B)_{m,m} - E_m^2 (B^t S B)_{m,m}| \end{aligned} \tag{48}$$

where B^{t} is the transpose of B and $H^{(2)}_{m,n} = A^{(2)}_{m,n}$. This error estimate is a useful guideline that mostly serves the purpose of identifying the spurious eigenvalues. The formalism presented here, however, is sufficiently general to allow other more elaborate treatments for the error estimate.[83] From the above discussion, it is clear that the central quantity one needs to compute is $A^{(p)}_{m,n}$, defined in eq 47, for which we discuss the Chebyshev polynomial and discrete time representations in the following sections. Notably, we do not factorize the product of two delta functions in eq 47 for the reasons explained earlier.

Chebyshev Polynomial Representation. Using eq 7 for the SDO in eq 47 and results from Appendix B, we can easily obtain the following expression for the overlap, S, and Hamiltonian, H, matrix element using $A^{(p)}_{m,n}$ for $p = 0$ and 1,

$$S_{m,n} = \langle\psi|\delta_T(E_m - \hat{H})\,\delta_T(E_n - \hat{H})|\psi\rangle = \frac{1}{(\pi\Delta\lambda)^2}\sum_{k=0}^{2N}[G^{(1)}_k C^{(0)}_k + G^{(2)}_k C^{(0)}_{k+N}] \tag{49}$$

where, $C^{(p)}_k = (1/2)[C^{(0)}_{|k+\mathrm{p}|} + C^{(0)}_{|k-p|}]$ and $C^{(0)}_k = \langle\psi|T_k(\hat{H}_{sc})|\psi\rangle$. The coefficients $G^{(1)}_k$ and $G^{(2)}_k$ are defined in Appendix B. Similarly, it is straightforward to show that

$$H_{m,n} = \langle\psi|\delta_T(E_m - \hat{H})\hat{H}\,\delta_T(E_n - \hat{H})|\psi\rangle = \bar{\lambda}S_{m,n} + \Delta\lambda\tilde{H}_{m,n} \tag{50}$$

$$H^{(2)}_{m,n} = \langle\psi|\delta_T(E_m - \hat{H})\hat{H}^2\,\delta_T(E_n - \hat{H})|\psi\rangle = \left[\frac{\Delta\lambda^2}{2} - (\bar{\lambda})^2\right]S_{m,n} + 2\bar{\lambda}H_{m,n} + \frac{\Delta\lambda^2}{2}\tilde{H}^{(2)}_{m,n} \tag{51}$$

where $\tilde{H}_{m,n}$ and $\hat{H}^{(2)}_{m,n}$ are defined as follows:

$$H_{m,n} = \frac{\Delta\lambda}{(\pi\Delta\lambda)^2}\sum_{k=0}^{2N}[G^{(1)}_k C^{(1)}_k + G^{(2)}_k C^{(1)}_{k+N}] \tag{52}$$

$$\tilde{H}^{(2)}_{m,n} = \frac{(\Delta\lambda)^2}{2}\sum_{k=0}^{2N}[G^{(1)}_k C^{(2)}_k + G^{(2)}_k C^{(2)}_{k+N}] \tag{53}$$

We can now use eqs 49−51 in conjunction with eq 45 and obtain eigenvalues of the Hamiltonian in an arbitrary energy window.

Discrete Time Representation. In this section, we discuss a computational implementation of the FD algorithm, which is based on the discrete-time auto-correlation function, characterizing the dynamical behavior of the molecular system. In what follows, we describe two approaches, one which requires scaling the spectral range of the Hamiltonian (similar to that employed in the Chebyshev polynomial-based FD method), and the other approach which allows the use of a spectrally unscaled Hamiltonian operator.

With the unscaled Hamiltonian, we first split the operator, $\hat{H}^p$, in eq 47 symmetrically between the two delta functions and then use the following identity,

$$(\hat{H})^p\,\delta(E-\hat{H}) = (E)^p\,\delta(E-\hat{H}) \tag{54}$$

to obtain the following expression for the matrix element.

$$A^{(p)}_{m,n} = (\sqrt{E_m E_n})^p \langle\psi|\delta_T(E_m-\hat{H})\delta_T(E_n-\hat{H})|\psi\rangle \tag{55}$$

It is important to note that although eq 54 is formally an exact identity, it contains an error of the order $(E-\hat{H})^p\,\delta(E-\hat{H})$, which is small but finite, because we use an approximate delta function in practical applications. This is why we have symmetrically distributed the power of the Hamiltonian between the bra and the ket, thereby obtaining eq 55. Now, using results from Appendix A, we can easily express the matrix element as follows:

$$A^{(p)}_{m,n} = (E_m\,E_n)^{p/2}\sum_{k=0}^{2N}\mathrm{Re}[F_k(Z_m, Z_n)\,C_k] \tag{56}$$

where $C_k = \langle\psi|\hat{U}^k|\psi\rangle$ is the discrete-time auto-correlation function. To pass from eq 55 to 56, we have used the fact $C_{-k} = C^*_k$, which is valid for the auto-correlation function. Now, eq 56 being in an energy-separable form can be used efficiently to obtain the necessary matrix elements for FD applications.

We now consider a spectrally scaled Hamiltonian, an approach used in earlier studies on this subject.[9,68] We first explain the rationale behind such a choice, even though its use is not mandatory. It is well-known that the time discretization enforces a basic limitation on the physical system; that is, from the time-energy uncertainty principle, a discretization of the time axis in terms of Δt suggests that the Hamiltonian can be represented faithfully at best in the spectral range, $\lambda_{\min} \le E \le \lambda_{\max}$, where$(\lambda_{\max}-\lambda_{\min}) = 2\Delta\lambda = (\pi\hbar/\Delta t)$. This means Δt is not completely arbitrary. Thus, it makes sense to build this physically attainable limit directly into the computational apparatus. To this end, we propose to compute the eigenvalues of a function of the Hamiltonian operator in place of the original Hamiltonian, $\hat{H}$. This is defined as follows,

$$f(\hat{H}) = \sin\Big[(\hat{H}-\bar{\lambda})\frac{\Delta t}{\hbar}\Big] = \sin\Big[\Big(\frac{\hat{H}-\bar{\lambda}}{\Delta\lambda}\Big)\frac{\pi}{2}\Big] = \sin\Big(\frac{\pi}{2}\tilde{H}\Big) \tag{57}$$

where $\bar{\lambda} = (1/2)\,(\lambda_{\max}+\lambda_{\min})$ is the offset parameter with units of energy, which helps to map the spectral range of the Hamiltonian $\lambda_{\min} \le \hat{H} \le \lambda_{\max}$ onto the range $-1 \le \tilde{H} \le +1$ and renders $\tilde{H}$ dimensionless so that the latter can be used as an argument of the sine function, and the eigenvalues of $f(\hat{H})$ fall between $-(\pi/2)$ and $(\pi/2)$. It is then easy to verify that if we compute the eigenvalue, $f(\epsilon_m)$ of $f(\hat{H})$ as defined in eq 57, the eigenvalue, ϵ_m of the original Hamiltonian, $\hat{H}$ can be obtained by the following relation.

$$\epsilon_m = \frac{\hbar}{\Delta t}\arcsin[f(\epsilon_m)] + \bar{\lambda} = \frac{2\Delta\lambda}{\pi}\arcsin[f(\epsilon_m)] + \bar{\lambda} \tag{58}$$

The reason behind the above choice of the function of $\hat{H}$ is that it allows keeping the algebraic structure of the theory completely in the time correlation function form, thereby leading to a compact expression for the matrix elements as required in the FD algorithm. Admittedly, other choices are also possible,[9,68] which if one desires can be implemented without any difficulty by following the derivation presented here. We now use eq 57 to obtain the following identity,

$$[f(\hat{H})]^p = \frac{1}{2p}\sum_{s=0}^{p}\binom{p}{s}[i\mathrm{e}^{-i\bar{\lambda}\Delta t/\hbar}\hat{U}]^{p-2s} \tag{59}$$

where $\binom{p}{s}$ is the binomial coefficient and $\hat{U} = \mathrm{e}^{-i\hat{H}\Delta t/\hbar}$ is the quantum propagator for a time step Δt. We next substitute eq 59 in eq 47 to obtain

$$A^{(p)}_{m,n} = \frac{1}{2p}\sum_{s=0}^{p}\binom{p}{s}[i\mathrm{e}^{-i\bar{\lambda}\Delta t}]^{p-2s} \times \langle\psi|\delta_T(E_m-\hat{H})\hat{U}^{p-2s}\delta_T(E_n-\hat{H})|\psi\rangle \tag{60}$$

We now use the results for the product of two SDOs from Appendix A in eq 60 to finally obtain the following expression for the matrix element.

$$A^{(p)}_{m,n} = \frac{1}{2p}\sum_{s=0}^{p}\binom{p}{s}[i\mathrm{e}^{-i\bar{\lambda}\Delta t}]^{p-2s} \times \sum_{k=0}^{2N}[F_k(Z_m, Z_n)C_{k+p-2s} + F^*_k(Z_m, Z_n)C_{-k+p-2s}] \tag{61}$$

where $C_k = \langle\psi|\hat{U}^k|\psi\rangle$ is the autocorrelation function, and the coefficient F_k has been defined in Appendix A.

V. Results and Discussion

Here, we present preliminary results of our benchmark studies on the performance of the present spectral filter implementation of the S-matrix. As a first step, we have made an extensive test of the short-time iterative algorithm as discussed in Section III, Short-Time Iterative Implementation. Our model numerical study constitutes a one-dimensional scattering of a quantum particle through the Eckart's barrier as defined below,

$$V(x) = \frac{V_0}{\cosh^2(ax)} \tag{62}$$

where V_0 and a are the maximum height and the thickness parameter of the barrier and their numerical values used here are 1.03644 eV and 2.0 Å^{-1}, respectively. The analytical expression for the transmission probability as a function of incident energy, E, that is used for comparison is well-known to be[119]

$$P(E) = \frac{\cosh\Big(\frac{2\pi}{\hbar}\frac{\sqrt{2\mu E}}{a}\Big) - 1}{\cosh\Big(\frac{2\pi}{\hbar}\frac{\sqrt{2\mu E}}{a}\Big) + \cosh\Big(\pi\sqrt{\frac{8\mu V_0}{a^2p^2} - 1}\Big)} \tag{63}$$

where μ is the mass of the particle, which we have chosen to be 1.0 amu. The scattering configuration of our numerical study is shown in Figure 1. The reactant channel, α, lies at the left of the barrier, and the product channel, β, is at the right side of the barrier. The simplicity of the present model and the scattering configuration allow us to choose the reactant and product wave packets to be of the same functional form. For this purpose, we

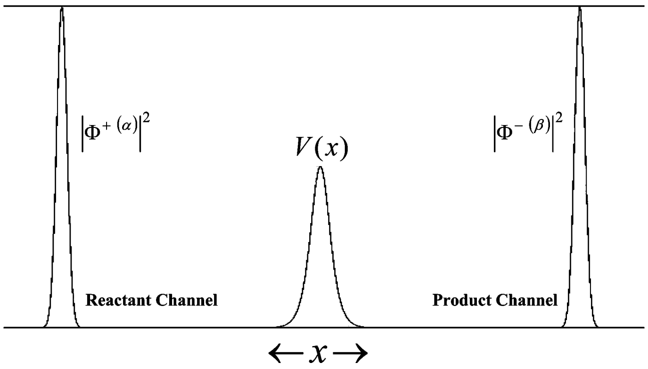

Figure 1. Scattering configuration of the present numerical study.

have taken a normalized Gaussian wave packet, which is multiplied with the eigenfunction of the momentum operator with a large momentum eigenvalue, as shown below

$$\Phi^{+(\alpha)}(x) = \Phi^{-(\beta)}(x) = \left[\frac{1}{2\pi\sigma^2}\right]^{1/4} e^{i((2\mu E_0)^{(1/2)}/\hbar)}x \exp\left[-\left(\frac{x - x_0^{\alpha \text{ or } \beta}}{2\sigma}\right)^2\right] \quad (64)$$

where σ is the width parameter of the wave packet, which has been taken to be 0.2 Å. In eq 64, E_0 is an essentially arbitrary but large energy, and its value is taken to be 0.836 04 eV. The factor $e^{i((2\mu E_0)^{(1/2)}/\hbar)x}$ in eq 64 helps to enforce appropriate boundary conditions in the calculation as, discussed earlier (Short-Time Iterative Implementation). Initially, one wave packet is centered at $x = x_0^{\alpha}$ in the α channel (left of the barrier) and the other at $x = x_0^{\beta}$ in the β channel (right of the barrier), as shown in Figure 1. To compute the time correlation functions $C_k^{(\alpha,\alpha)}$ and $C_k^{(\alpha,\beta)}$ to be used in eqs 31−37, we have represented the wave packets on an uniformly spaced x grid with Δx = 0.039 062 5 Å and evaluated the kinetic energy operator part of the Hamiltonian by the standard fast Fourier transform method.[120] The time evolution has been accomplished in steps of Δt = 0.2 fs by the standard Chebyshev polynomial-based quantum propagator.[99,100,108] The maximum kinetic energy represented on the grid with a spacing of 0.039 062 5 Å used here is estimated to be $(1/2\mu)((\pi\hbar/\Delta x))^2 \equiv 13$ eV, and therefore, both $\Delta\lambda$ and $\bar{\lambda}$ parameters, which are required to rescale the Hamiltonian so that it becomes suitable to be used as an argument of the Chebyshev polynomial, are 6.997 eV. For representing the wave function and its derivatives, we have used a rather large grid (1024 points) and propagated the wave packet for 50 fs. Because this is aimed solely at demonstrating the validity of our approach, we have not attempted to optimize the method of function representation, time propagation, and other numerical issues involved here.

In Figures 2 and 3, we show the computed correlation functions $C_k^{(\alpha,\alpha)}$ and $C_k^{(\alpha,\beta)}$ as a function of time, which we have used to compute the transmission probabilities at a number of energies. As expected, the autocorrelation function, $C_k^{(\alpha,\alpha)} = C_k^{(\beta,\beta)}$, falls off very rapidly, and as a result, we need very few terms in eq 31 to compute the normalization factors, $|A_\alpha^+(E)|^2$ and $|A_\beta^-(E)|^2$. We note that the normalization factors $|A_\alpha^+(E)|^2$ and $|A_\beta^-(E)|^2$ may also be obtained directly by projecting the initial wave packet, eq 64, on the channel eigenstates (in the present situation, they are just the planewaves), in which case, one has to include the appropriate channel momentum factor, $\sqrt{2E/\mu}$, as follows,

$$|A_\alpha^+(E)|^2 = \sqrt{\frac{2E}{\mu}}\left|\sqrt{\frac{\mu}{2E}}\int_{-\infty}^{\infty} dx\, e^{-i((2\mu E)^{(1/2)}/\hbar)x}\, \Phi^{+(\alpha)}(x)\right|^2$$
$$= \frac{1}{\sqrt{\pi}}\frac{\Delta x}{\hbar}\sqrt{\frac{\mu}{E}} \exp\left[-8\left(\frac{\Delta x}{\hbar}\right)^2 \mu\{E + E_0 - 2\sqrt{EE_0}\}\right] \quad (65)$$

where we have used eq 64 for $\Phi^{+(\alpha)}(x)$. Equation 65 is certainly the exact expression for the normalization factor here. However, if one computes the normalization factor using the autocorre-

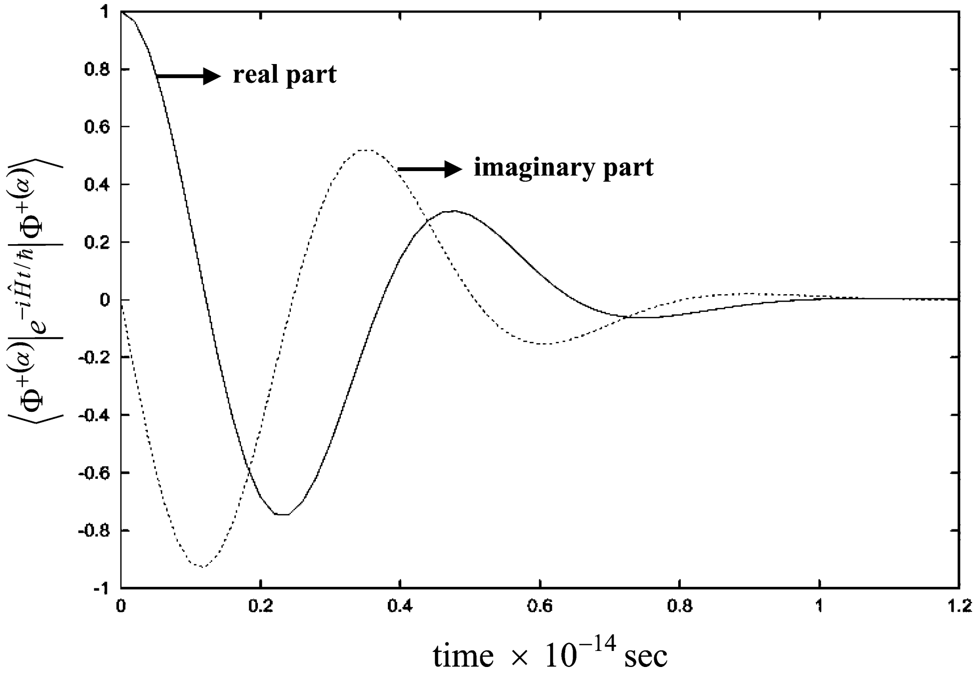

Figure 2. Computed autocorrelation function, $C_k^{(\alpha,\alpha)}$, of the reactant wave packet. The solid line refers to the real part, and the dotted line refers to the imaginary part of the function. The autocorrelation function becomes negligibly small before the wave packet reaches the interaction region. The product wave packet has the identical features in the present study.

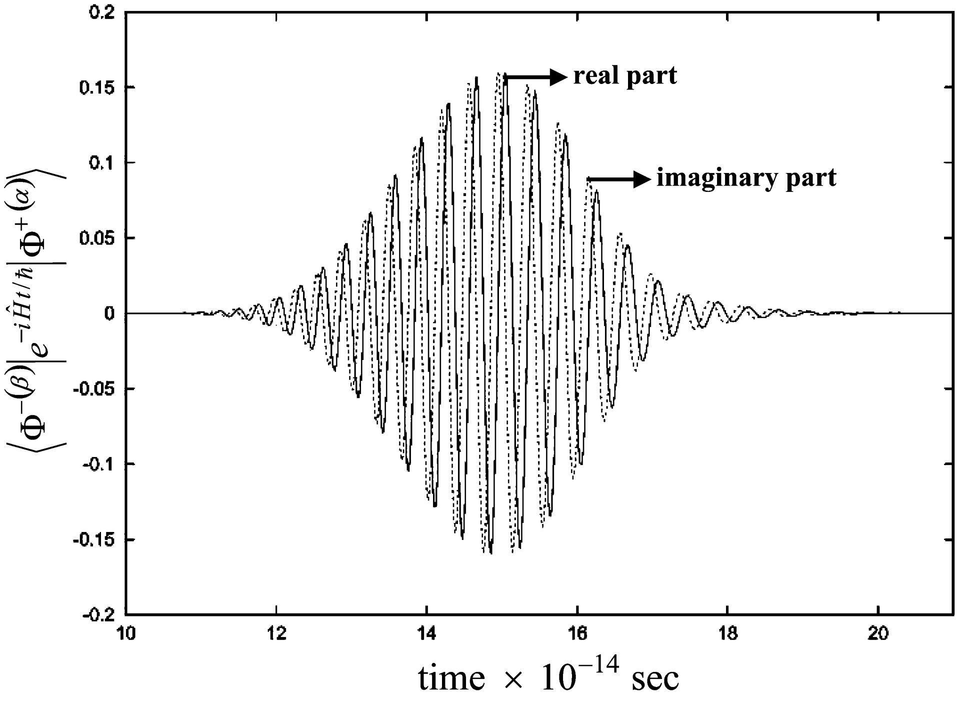

Figure 3. The cross-correlation function between the reactant and the product wave packets, $C_k^{(\alpha,\beta)}$. The solid line refers to the real part, and the dotted line refers to the imaginary part of the function. In the present study, the cross-correlation function is negligibly small outside the time range shown in the figure.

TABLE 1: A Comparison of the Computed Scattering Probabilities as a Function of Energy with Their Exact Values

			$\lvert S_{\beta,\alpha}(E)\rvert^2$	
energy (eV)	$\lvert A_\alpha^+\rvert^2 = \lvert A_\beta^-\rvert^2$	$\lvert\langle\Phi^{-(\beta)}\rvert(\delta(E-\hat{H})\ \delta(E-\hat{H})/\delta(E-E))\rvert\ \Phi^{+(\alpha)}\rangle\rvert^2$	calcd	exact
0.1244	$0.292\ 163 \times 10^{-4}$	$0.112\ 804 \times 10^{-28}$	$0.132\ 152 \times 10^{-19}$	$0.148\ 945 \times 10^{-19}$
0.1347	$0.517\ 257 \times 10^{-4}$	$0.115\ 579 \times 10^{-27}$	$0.431\ 982 \times 10^{-19}$	$0.400\ 666 \times 10^{-19}$
0.1555	$0.146\ 450 \times 10^{-3}$	$0.554\ 173 \times 10^{-26}$	$0.258\ 385 \times 10^{-18}$	$0.260\ 199 \times 10^{-18}$
0.1658	$0.235\ 760 \times 10^{-3}$	$0.352\ 793 \times 10^{-25}$	$0.634\ 716 \times 10^{-18}$	$0.632\ 721 \times 10^{-18}$
0.1762	$0.369\ 827 \times 10^{-3}$	$0.204\ 436 \times 10^{-24}$	$0.149\ 473 \times 10^{-17}$	$0.149\ 705 \times 10^{-17}$
0.1969	$0.849\ 160 \times 10^{-3}$	$0.561\ 788 \times 10^{-23}$	$0.779\ 101 \times 10^{-17}$	$0.779\ 172 \times 10^{-17}$
0.2073	$0.124\ 739 \times 10^{-2}$	$0.267\ 737 \times 10^{-22}$	$0.172\ 069 \times 10^{-16}$	$0.172\ 058 \times 10^{-16}$
0.2280	$0.254\ 830 \times 10^{-2}$	$0.514\ 482 \times 10^{-21}$	$0.792\ 263 \times 10^{-16}$	$0.792\ 248 \times 10^{-16}$
0.2384	$0.355\ 259 \times 10^{-2}$	$0.209\ 038 \times 10^{-20}$	$0.165\ 628 \times 10^{-15}$	$0.165\ 630 \times 10^{-15}$
0.2695	$0.881\ 754 \times 10^{-2}$	$0.107\ 397 \times 10^{-18}$	$0.138\ 133 \times 10^{-14}$	$0.138\ 133 \times 10^{-14}$
0.2902	$0.151\ 484 \times 10^{-1}$	$0.121\ 854 \times 10^{-17}$	$0.531\ 016 \times 10^{-14}$	$0.531\ 015 \times 10^{-14}$
0.3213	$0.313\ 588 \times 10^{-1}$	$0.360\ 725 \times 10^{-16}$	$0.366\ 823 \times 10^{-13}$	$0.366\ 823 \times 10^{-13}$
0.3420	$0.484\ 567 \times 10^{-1}$	$0.296\ 702 \times 10^{-15}$	$0.126\ 361 \times 10^{-12}$	$0.126\ 361 \times 10^{-12}$
0.4042	$0.145\ 906 \times 10^{+00}$	$0.891\ 661 \times 10^{-13}$	$0.418\ 846 \times 10^{-11}$	$0.418\ 846 \times 10^{-11}$
0.4457	$0.263\ 417 \times 10^{+00}$	$0.258\ 591 \times 10^{-11}$	$0.372\ 669 \times 10^{-10}$	$0.372\ 669 \times 10^{-10}$
0.4975	$0.481\ 663 \times 10^{+00}$	$0.115\ 686 \times 10^{-9}$	$0.498\ 650 \times 10^{-9}$	$0.498\ 650 \times 10^{-9}$
0.5286	$0.649\ 522 \times 10^{+00}$	$0.935\ 003 \times 10^{-9}$	$0.221\ 628 \times 10^{-8}$	$0.221\ 628 \times 10^{-8}$
0.5804	$0.974\ 764 \times 10^{+00}$	$0.230\ 227 \times 10^{-7}$	$0.242\ 302 \times 10^{-7}$	$0.242\ 302 \times 10^{-7}$
0.6219	$0.125\ 202 \times 10^{+1}$	$0.238\ 548 \times 10^{-6}$	$0.152\ 180 \times 10^{-6}$	$0.152\ 180 \times 10^{-6}$
0.6530	$0.145\ 257 \times 10^{+1}$	$0.122\ 408 \times 10^{-5}$	$0.580\ 141 \times 10^{-6}$	$0.580\ 141 \times 10^{-6}$
0.6944	$0.168\ 820 \times 10^{+1}$	$0.937\ 920 \times 10^{-5}$	$0.329\ 091 \times 10^{-5}$	$0.329\ 091 \times 10^{-5}$
0.7151	$0.178\ 553 \times 10^{+1}$	$0.245\ 074 \times 10{-}4$	$0.768\ 713 \times 10{-}5$	$0.768\ 713 \times 10{-}5$
0.7462	$0.189\ 917 \times 10^{+1}$	$0.967\ 579 \times 10^{-4}$	$0.268\ 263 \times 10^{-4}$	$0.268\ 263 \times 10^{-4}$
0.7773	$0.196\ 940 \times 10^{+1}$	$0.353\ 840 \times 10^{-3}$	$0.912\ 308 \times 10^{-4}$	$0.912\ 308 \times 10^{-4}$
0.8084	$0.199\ 400 \times 10^{+1}$	$0.120\ 387 \times 10^{-2}$	$0.302\ 781 \times 10^{-3}$	$0.302\ 781 \times 10^{-3}$
0.8395	$0.197\ 390 \times 10^{+1}$	$0.382\ 503 \times 10^{-2}$	$0.981\ 712 \times 10^{-3}$	$0.981\ 712 \times 10^{-3}$
0.8706	$0.191\ 280 \times 10^{+1}$	$0.113\ 806 \times 10^{-1}$	$0.311\ 048 \times 10^{-2}$	$0.311\ 048 \times 10^{-2}$
0.9017	$0.181\ 652 \times 10^{+1}$	$0.317\ 214 \times 10^{-1}$	$0.961\ 328 \times 10^{-2}$	$0.961\ 328 \times 10^{-2}$
0.9328	$0.169\ 234 \times 10^{+1}$	$0.823\ 806 \times 10^{-1}$	$0.287\ 641 \times 10^{-1}$	$0.287\ 641 \times 10^{-1}$
0.9639	$0.154\ 816 \times 10^{+1}$	$0.195\ 298 \times 10^{+00}$	$0.814\ 823 \times 10^{-1}$	$0.814\ 823 \times 10^{-1}$
0.9742	$0.149\ 704 \times 10^{+1}$	$0.253\ 209 \times 10^{+00}$	$0.112\ 983 \times 10^{+00}$	$0.112\ 983 \times 10^{+00}$
0.9846	$0.144\ 486 \times 10^{+1}$	$0.322\ 246 \times 10^{+00}$	$0.154\ 360 \times 10^{+00}$	$0.154\ 360 \times 10^{+00}$
0.9950	$0.139\ 189 \times 10^{+1}$	$0.401\ 112 \times 10^{+00}$	$0.207\ 039 \times 10^{+00}$	$0.207\ 039 \times 10^{+00}$
1.0572	$0.107\ 134 \times 10^{+01}$	$0.783\ 705 \times 10^{+00}$	$0.682\ 805 \times 10^{+00}$	$0.682\ 805 \times 10^{+00}$
1.1504	$0.646\ 775 \times 10^{+00}$	$0.409\ 324 \times 10^{+00}$	$0.978\ 499 \times 10^{+00}$	$0.978\ 499 \times 10^{+00}$
1.2541	$0.320\ 765 \times 10^{+00}$	$0.102\ 802 \times 10^{+00}$	$0.999\ 147 \times 10^{+00}$	$0.999\ 147 \times 10^{+00}$
1.5028	$0.359\ 319 \times 10^{-1}$	$0.129\ 110 \times 10^{-2}$	$0.999\ 999 \times 10^{+00}$	$0.999\ 999 \times 10^{+00}$

lation function in eq 31, the channel momentum factors are automatically included, but it will agree with the result of eq 65, provided one has used a complete autocorrelation function and not a truncated one. In the present test calculation, both methods give the identical result. This is particularly reassuring because it gives a clear indication that the contribution from the negative flux component of the wave packet (cf. eq 23) is vanishingly small, if not completely zero; that is, the scattering boundary conditions are correctly implemented in the calculation.

In Table 1, we present the computed results for $|A_\alpha^+(E)|^2$ ($= |A_\beta^+(E)|^2$, in the present example) using eq 31, $\langle\Phi^{-(\beta)}|(\delta_T(E - \hat{H})\ \delta_T(E - \hat{H})/\delta_T(E - E))|\Phi^{+(\alpha)}\rangle$ (eqs 6 and 37), and the tunneling probabilities, $|S_{\beta,\alpha}(E)|^2$ (eq 30) at select energies and compare with the analytical values obtained using eq 63. It is gratifying to note that the present method is able to reproduce the exact result to machine accuracy for all energies considered here. This test example gives us confidence that the present approach will be useful for more complicated scattering problems we will be studying in the future.

VI. Concluding Remarks

In this paper, we have presented a detailed operational foundation of the spectral filter approach to quantum molecular dynamics, involving scattering and bound states. The philosophy underlying the present approach has been to mathematically advance the formally exact treatment of the theory as far as possible before one makes practical approximations, such as semiclassical or mixed quantum/classical mechanics. In fact, it finally turns out that the formal theoretical structure and the protocol to compute observable quantities are the same for molecular bound states and scattering problems, and the only difference lies in the way one implements the appropriate boundary conditions while computing various correlation functions. We find that the boundary conditions can be built accurately while preparing the initial wave packets, and no extra device, such as complex absorbing potential is essentially warranted. As a matter of fact, we have also been able to literally take the limit $\zeta \to 0$ (damping function in eq 5 being unity) in the final expression for the S-matrix which involves a discrete set of short-time correlation function (cf. eqs 36 and 37) without any numerical error. However, complex absorbing potentials have other useful applications, and if one so desires, the present formulation can easily be extended. We will come back to this framework in our future studies.

In the discrete time implementation, the central quantity that enters various expressions for the S-matrix and the filter diagonalization method is the time correlation function in various forms. Consistent with suggestions of earlier authors,[10,11,33−36,48] we argue that the quantum mechanical origin of these correlation functions may be ignored and obtained by other approximate dynamical schemes for large molecular systems. In this manner, the present approach offers a completely unified framework for studying molecular dynamics encompassing large as well as small systems. Moreover, the time correlation functions could also be taken as experimentally derived quantities (e.g., NMR signals[66,121]), and the present method will be useful for analyzing the underlying spectra. Further numerical studies with the present method will be performed in our future applications. Extension of the present approach toward the computation of averaged quantities, such as thermal reaction rates and molecular conductance, is envisioned here, and that will be the subject of future studies.

Appendix A. Product of Spectral Density Operators Expressed as a Discrete-Time Finite Series

Here, we present a derivation of the product of spectral density operators (chosen to be a prelimit Lorentzian function) as a degenerate kernel, discrete-time finite series. Anticipating the application in the filter eiagonalization algorithm, we will obtain a general expression for the quantity, $\delta_T(E_m - \hat{H})(\hat{U})^p\ \delta_T(E_n - \hat{H})$, where $\hat{U} = \mathrm{e}^{-i\hat{H}\Delta t/\hbar}$ and p is an arbitrary integer. Thus, using eq 9 for a truncated series representation of the spectral density operator, we can easily obtain

$$\delta_T(E_m - \hat{H})(\mathrm{e}^{-i\hat{\mathrm{H}}\Delta t/\hbar})^p\ \delta_T(E_n - \hat{H}) = \left(\frac{\Delta t}{2\pi\hbar}\right)^2 \sum_{k=0}^{N}\sum_{k'=0}^{N}\left(1 - \frac{\delta_{k,0}}{2}\right)\left(1 - \frac{\delta_{k,N}}{2}\right)\left(1 - \frac{\delta_{k',0}}{2}\right)\left(1 - \frac{\delta_{k',N}}{2}\right) \times [(Z_m)^k\,(Z_n)^{k'}\hat{U}^{k+k'+p} + (Z_m^*)^k(Z_n^*)^{k'}\hat{U}^{-(k+k'-p)} + (Z_m)^k(Z_n^*)^{k'}\hat{U}^{k-k'+p} + (Z_m^*)^k(Z_n)^{k'}\hat{U}^{-(k-k'-p)}] \quad \text{(A-1)}$$

where $Z_{m(n)} = \mathrm{e}^{i(E_{m(n)}+i\zeta)\Delta t/\hbar}$. Now, the double summation involving k and k' indices, in eq A-1 can be partially summed by utilizing a Cauchy-type expansion.[122] In this procedure, we first collect all the terms for which $|k + k'|$ and $|k - k'|$ have the same value and then perform the summation of the resulting geometrical series analytically. This summation technique has frequently been used in the filter diagonalization literature.[9,51,67,68] Let us first consider a part of the series in eq A−1, which we can expand as follows.

$$\sum_{k=0}^{N}\sum_{k'=0}^{N}\left(1 - \frac{\delta_{k,0}}{2}\right)\left(1 - \frac{\delta_{k,N}}{2}\right)\left(1 - \frac{\delta_{k',0}}{2}\right)\left(1 - \frac{\delta_{k',N}}{2}\right) \times (Z_m)^k(Z_n)^{k'}\hat{U}^{k+k'+p} = \left\{\sum_{k=0}^{N}\hat{U}^{k+p}(Z_n)^k\sum_{k'=0}^{k}\left(1 - \frac{\delta_{k',0}}{2}\right) \times \left(1 - \frac{\delta_{k',k}}{2}\right)\left(1 - \frac{\delta_{k',0}\delta_{k,N}}{2}\right)\left(1 - \frac{\delta_{k',N}\ \delta_{k,N}}{2}\right)\left(\frac{Z_m}{Z_n}\right)^{k'}\right\} + \left\{\sum_{k=N+1}^{2N}\hat{U}^{k+p}(Z_m)^{k-N}(Z_n)^N\sum_{k'=0}^{2N-k}\left(1 - \frac{\delta_{k',0}}{2}\right)\left(1 - \frac{\delta_{k',2N-k}}{2}\right)\left(\frac{Z_m}{Z_n}\right)^{k'}\right\} \quad \text{(A-2)}$$

Similarly,

$$\sum_{k=0}^{N}\sum_{k'=0}^{N}\left(1 - \frac{\delta_{k,0}}{2}\right)\left(1 - \frac{\delta_{k,N}}{2}\right)\left(1 - \frac{\delta_{k',0}}{2}\right)\left(1 - \frac{\delta_{k',N}}{2}\right) \times (Z_m)^k(Z_n)^{k'}\hat{U}^{k-k'+p} = \sum_{k=0}^{N}\left(1 - \frac{\delta_{k,0}}{2}\right)\{(Z_m)^k\hat{U}^{k+p} + (Z_n)^k\hat{U}^{-\mathrm{k}+p}\} \times \left\{\sum_{k'=0}^{N-k}\left(1 - \frac{\delta_{k',0}}{2}\right)\left(1 - \frac{\delta_{k',N-k}}{2}\right)\left(1 - \frac{\delta_{k',0}\ \delta_{k,0}}{2}\right) \times \left(1 - \frac{\delta_{k',N-k}\ \delta_{k,0}}{2}\right)(Z_mZ_n)^{k'}\right\} \quad \text{(A-3)}$$

The summations over the index k' in eqs A-2 and A-3 involve a geometric series, which we perform analytically and finally substitute the results in eq A-1). The final result is

$$\delta_T(E_m - \hat{H})(\hat{U})^p\ \delta_T(E_n - \hat{H}) = \sum_{k=0}^{2N} F_k(Z_m, Z_n)\ \hat{U}^{k+p} + F_k^*(Z_m, Z_n)\ \hat{U}^{-k+p} \quad \text{(A-4)}$$

where

$$F_k(Z_m, Z_n) = \left(\frac{\Delta t}{2\pi\hbar}\right)^2 \{\alpha_k(Z_m, Z_n) + \beta'_k(Z_m, Z_n^*) + \beta''_k(Z_m^*, Z_n)\} \tag{A-5}$$

$$F_k^*(Z_m, Z_n) = \left(\frac{\Delta t}{2\pi\hbar}\right)^2 \{\alpha_k(Z_m^*, Z_n^*) + \beta'_k(Z_m^*, Z_n) + \beta''_k(Z_m, Z_n^*)\} \tag{A-6}$$

$$\alpha_k(Z_m, Z_n) = \begin{cases} \frac{1}{2}\left[\frac{Z_m + Z_n}{Z_m - Z_n}(Z_m^k - Z_n^k) + \frac{1}{2}\{\delta_{k,0} - \delta_{k,N}(Z_m^k + Z_n^k)\}\right] & (0 \le k \le N \text{ and } Z_m \ne Z_n) \\ \frac{1}{2}(Z_mZ_n)^{k-N}\left[\frac{Z_m + Z_n}{Z_m - Z_n} \times (Z_m^{2N-k} - Z_n^{2N-k}) + \frac{\delta_{k,2N}}{2}\right] & (N + 1 \le k \le 2N \text{ and } Z_m \ne Z_n) \\ Z_m^k[(N - |N - k|) + \frac{1}{4}(\delta_{k,0} - 2\delta_{k,N} + \delta_{k,2N})] & (0 \le k \le 2N \text{ and } Z_m = Z_n) \end{cases} \tag{A-7}$$

$$\beta'_k(Z_m, Z_n) = \begin{cases} \left(1 - \frac{\delta_{k,0}}{2}\right)\frac{Z_m^k}{2}\left[\frac{Z_mZ_n + 1}{Z_mZ_n - 1}\{(Z_mZ_n)^{N-k} - 1\} + \frac{\delta_{k,N}}{2} - \frac{\delta_{k,0}}{2}\{(Z_mZ_n)^N + 1\}\right] & (Z_mZ_n \ne 1) \\ \left(1 - \frac{\delta_{k,0}}{2}\right)\left(N - k - \frac{\delta_{k,0}}{2} + \frac{\delta_{k,N}}{4}\right)Z_m^k & (Z_mZ_n = 1) \\ 0 & (k \ge N + 1) \end{cases} \tag{A-8}$$

$$\beta''_k(Z_m, Z_n) = \begin{cases} \left(1 - \frac{\delta_{k,0}}{2}\right)\frac{Z_n^k}{2}\left[\frac{Z_mZ_n + 1}{Z_mZ_n - 1}\{(Z_mZ_n)^{N-k} - 1\} + \frac{\delta_{k,N}}{2} - \frac{\delta_{k,0}}{2}\{(Z_mZ_n)^N + 1\}\right] & (Z_mZ_n \ne 1) \\ \left(1 - \frac{\delta_{k,0}}{2}\right)\left(N - k - \frac{\delta_{k,0}}{2} + \frac{\delta_{k,N}}{4}\right)Z_m^{-k} & (Z_mZ_n = 1) \\ 0 & (k \ge N + 1) \end{cases} \tag{A-9}$$

Equation A4 is the main result for an arbitrary integer, p.

Appendix B. Product of Spectral Density Operators Expressed as a Finite Series Involving Chebyshev Polynomials of the First Kind

Here, we present a derivation of the product of two spectral density operators (chosen to be a prelimit Lorentzian function), expressed as a degenerate kernel finite series, using Chebyshev polynomials with the renormalized Hamiltonian as the argument. Anticipating the application in the filter diagonalization algorithm, we will obtain a general expression for the quantity, $\delta_T(E_m - \hat{H})\hat{H}^p\, \delta_T(E_n - \hat{H})$, where p is an arbitrary positive integer. First, by using the definition of the renormalized Hamiltonian, $\Delta\lambda\hat{H}_{sc} = \hat{H} - \bar{\lambda}$, we can easily obtain the following identity,

$$\delta_T(E_m - \hat{H})\, \hat{H}^p\, \delta_T(E_n - \hat{H}) = \frac{(\bar{\lambda})^p}{(\Delta\lambda)^2}\sum_{t=0}^{p}\binom{p}{t}\left(\frac{\Delta\lambda}{\bar{\lambda}}\right)^t \delta_T(\tilde{E}_m - \hat{H}_{sc})\, (\hat{H}_{sc})^t\, \delta_T(\tilde{E}_n - \hat{H}_{sc}) \tag{B-1}$$

where $\binom{p}{k}$ is the binomial coefficient and other symbols have been explained in the main text. We now substitute eq 7 for a truncated series representation of the spectral density operator in eq B-1) to obtain

$$\delta_T(E_m - \hat{H})\hat{H}^p\, \delta_T(E_n - \hat{H}) = \frac{4}{\pi^2}\frac{(\bar{\lambda})^p}{(\Delta\lambda)^2}\sum_{k=0}^{N}\sum_{k'=0}^{N}\left(1 - \frac{\delta_{k,0}}{2}\right)\left(1 - \frac{\delta_{k',0}}{2}\right)Re[D(\tilde{E}_m)\, Z^k(\tilde{E}_m)] \times Re[D(\tilde{E}_n)\, Z^{k'}(\tilde{E}_n)]\left\{\sum_{t=0}^{p}\binom{p}{t}\left(\frac{\Delta\lambda}{\bar{\lambda}}\right)^t T_k(\hat{H}_{sc})[T_1(\hat{H}_{sc})]^t\, T_{k'}(\hat{H}_{sc})\right\} \tag{B-2}$$

where $\tilde{E}_m = (E_m - \bar{\lambda})/\Delta\lambda$. Next, we use the (unique) property of Chebyshev polynomials, $2T_m(x)T_n(x) = T_{m+n}(x) + T_{m-n}(x)$, to obtain the following identity.

$$T_k(\hat{H}_{\text{sc}})[T_1(\hat{H}_{\text{sc}})]^t\, T_{k'}(\hat{H}_{\text{sc}}) = \frac{1}{2^{t+1}}\sum_{r=0}^{t}\binom{t}{r}[T_{k+k'+t-2r}(\hat{H}_{\text{sc}}) + T_{k-k'+t-2r}(\hat{H}_{\text{sc}})] \tag{B-3}$$

On substituting eq B-3 into B-2, we obtain

$$\delta_T(E_m - \hat{H})\hat{H}^p\, \delta_T(E_n - \hat{H}) = \frac{(\bar{\lambda})^p}{(\pi\Delta\lambda)^2}\sum_{t=0}^{p}\binom{p}{t}\left(\frac{\Delta\lambda}{2\bar{\lambda}}\right)^t\sum_{r=0}^{t}\binom{t}{r}\sum_{k=0}^{N}\sum_{k'=0}^{N}\left(1 - \frac{\delta_{k,0}}{2}\right)\left(1 - \frac{\delta_{k',0}}{2}\right) \times Re\{D(\tilde{E}_m)\, D(\tilde{E}_n)\, Z^k(\tilde{E}_m)\, Z^{k'}(\tilde{E}_n) + D(\tilde{E}_m)\, D^*(\tilde{E}_n)\, Z^k(\tilde{E}_m)\, \{Z^*(\tilde{E}_n)\}^{k'}\} \times [T_{k+k'+t-2r}(\hat{H}_{\text{sc}}) + T_{k-k'+t-2r}(\hat{H}_{sc})] \tag{B-4}$$

As explained in Appendix A, we can perform a partial resummation of the double series in eq B-4 by utilizing a Cauchy-type expansion.[122] Let us first consider a part of the series in eq B-4, which we can expand, and then perform the necessary summation as follows,

$$\sum_{k=0}^{N}\sum_{k'=0}^{N}\left(1 - \frac{\delta_{k,0}}{2}\right)\left(1 - \frac{\delta_{k',0}}{2}\right)D(\tilde{E}_m)\, D(\tilde{E}_n)\, Z^k(\tilde{E}_m)\, Z^{k'}(\tilde{E}_n) \times [T_{k+k'+t-2r}(\hat{H}_{sc}) + T_{k-k'+t-2r}(\hat{H}_{sc})] = D(\tilde{E}_m)\, D(\tilde{E}_n)\sum_{k=0}^{N}\left(1 - \frac{\delta_{k,0}}{2}\right)\left[Z^k(\tilde{E}_n)\sum_{k'=0}^{k}\left\{\frac{Z(\tilde{E}_m)}{Z(\tilde{E}_n)}\right\}^{k'} + \{Z^k(\tilde{E}_m) + Z^k(\tilde{E}_n)\}\sum_{k'=1}^{N-k}\{Z(\tilde{E}_m)\, Z(\tilde{E}_n)\}^{k'}\right]T_{k+t-2r}(\hat{H}_{sc}) + D(\tilde{E}_m)\, D(\tilde{E}_n)\left[\frac{Z(\tilde{E}_n)}{Z(\tilde{E}_m)}\right]^N\sum_{k=N+1}^{2N}Z^k(\tilde{E}_m)\sum_{k'=0}^{2N-k}\left\{\frac{Z(\tilde{E}_m)}{Z(\tilde{E}_n)}\right\}^{k'}T_{k+t-2r}(\hat{H}_{sc})$$

$$= \sum_{k=0}^{N}A_k^{(1)}[Z(\tilde{E}_m), D(\tilde{E}_m); Z(\tilde{E}_n), D(\tilde{E}_n)]T_{k+t-2r}(\hat{H}_{sc}) + A_k^{(2)}[Z(\tilde{E}_m), D(\tilde{E}_m); Z(\tilde{E}_n), D(\tilde{E}_n)]T_{k+N+t-2r}(\hat{H}_{sc}) \tag{B-5}$$

where the coefficients are defined as follows

$$A_k^{(1)}[Z(\tilde{E}_m), D(\tilde{E}_m); Z(\tilde{E}_n), D(\tilde{E}_n)] =$$

$$\begin{cases} \left(1 - \dfrac{\delta_{k,0}}{2}\right) D(\tilde{E}_m)\, D(\tilde{E}_n) \left[\dfrac{Z^{k+1}(\tilde{E}_m) - Z^{k+1}(\tilde{E}_n)}{Z(\tilde{E}_m) - Z(\tilde{E}_n)} + \dfrac{Z(\tilde{E}_m)\, Z(\tilde{E}_n)}{1 - Z(\tilde{E}_m)\, Z(\tilde{E}_n)} \{Z^k(\tilde{E}_m) + Z^k(\tilde{E}_n)\} \times (1 - \{Z(\tilde{E}_m)\, Z(\tilde{E}_n)\}^{N-k}) \right] & [Z(\tilde{E}_m) \neq Z(\tilde{E}_n)] \\ \left(1 - \dfrac{\delta_{k,0}}{2}\right) \dfrac{D^2(\tilde{E}_m)}{1 - Z^2(\tilde{E}_m)} [(k+1)\, Z^k(\tilde{E}_m) - (k-1)\, Z^{k+2}(\tilde{E}_m) - 2Z^{2N-k+2}(\tilde{E}_m)] & [Z(\tilde{E}_m) = Z(\tilde{E}_n)] \end{cases} \tag{B-6}$$

$$A_k^{(2)}[Z(\tilde{E}_m), D(\tilde{E}_m); Z(\tilde{E}_n), D(\tilde{E}_n)] =$$

$$\begin{cases} (1 - \delta_{k,0}) \dfrac{D(\tilde{E}_m)\, D(\tilde{E}_n)}{Z(\tilde{E}_m) - Z(\tilde{E}_n)} \{Z^{N+1}(\tilde{E}_m)\, Z^k(\tilde{E}_n) - Z^k(\tilde{E}_m)\, Z^{N+1}(\tilde{E}_n)\} & [Z(\tilde{E}_m) \neq Z(\tilde{E}_n)] \\ (1 - \delta_{k,0})(N - k + 1)\, D^2(\tilde{E}_m)\, Z^{k+N}(\tilde{E}_m) & [Z(\tilde{E}_m) = Z(\tilde{E}_n)] \end{cases} \tag{B-7}$$

The above resummation process is valid because the series in eq 7, when applied to a wave packet, is absolutely and uniformly convergent, and it is presumed that the filtering process at a particular energy is complete after summing to N terms. Now we substitute the results from eq B-5 into eq B-4 to finally obtain

$$\delta_T(E_m - \hat{H})\hat{H}^p\, \delta_T(E_n - \hat{H}) = \frac{(\bar{\lambda})^p}{(\pi\Delta\lambda)^2} \sum_{t=0}^{p} \binom{p}{t} \left(\frac{\Delta\lambda}{2\bar{\lambda}}\right)^t \sum_{r=0}^{t} \binom{t}{r} \sum_{k=0}^{N} G_k^{(1)} T_{k+t-2r}(\hat{H}_{sc}) + G_k^{(2)} T_{k+N+t-2r}(\hat{H}_{sc}) \tag{B-8}$$

where

$$G_k^{(1)} = Re\{A_k^{(1)}[Z(\tilde{E}_m), D(\tilde{E}_m); Z(\tilde{E}_n), D(\tilde{E}_n)] + A_k^{(1)}[Z(\tilde{E}_m), D(\tilde{E}_m); Z^*(\tilde{E}_n), D^*(\tilde{E}_n)]\} \tag{B-9}$$

and

$$G_k^{(2)} = Re\{A_k^{(2)}[Z(\tilde{E}_m), D(\tilde{E}_m); Z(\tilde{E}_n), D(\tilde{E}_n)] + A_k^{(2)}[Z(\tilde{E}_m), D(\tilde{E}_m); Z^*(\tilde{E}_n), D^*(\tilde{E}_n)]\} \tag{B-10}$$

Equation B-8) is the main result, which can be used to obtain the special cases for any positive integer, p.

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