Quantum mechanical reaction probabilities with a power series Green's function

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We present a new method to compute the energy Green's function with absorbing boundary conditions for use in the calculation of quantum mechanical reaction probabilities. This is an iterative technique to compute the inverse of a complex matrix which is based on Fourier transforming time-dependent dynamics. The Hamiltonian is evaluated in a sinc-function based discrete variable representation, which we argue may often be superior to the fast Fourier transform method for reactive scattering. We apply the resulting power series Green's function to the calculation of the cumulative reaction probability for the benchmark collinear H+H$_2$ system over the energy range 0.37–1.27 eV. The convergence of the power series is found to be stable at all energies and accelerated by the use of a stronger absorbing potential.

I. INTRODUCTION

One of the central tasks in theoretical reaction dynamics is the development of computational techniques able to predict the chemistry of large molecules. The *ab initio* treatment of chemical reactions in the gas phase relies on solving the quantum reactive scattering problem. At present, exact reactive scattering calculations have been reported for three atom systems.[1,2] In extending theory to larger systems, it is important to consider developments in both exact techniques and approximate models.[3–5] The approximate methods are indispensable in determining which aspects of the underlying physics control the reactivity. On the other hand, exact calculations are required in order to calibrate the validity of various approximations. In the present study, we focus on exact calculations of chemical reaction probabilities.

The computational effort required by an exact quantum calculation grows exponentially with the size of the system. Accordingly, the amount of information obtained from a quantum calculation grows exponentially as well. The most extreme case is encountered when one studies the dynamics of a pure state in which all the relative phase information is required. It therefore seems reasonable that the treatment of mixed states, which provides less detailed dynamical information, should be less computationally demanding and thus more applicable for the study of larger chemical systems. For example, the canonical rate constant for a bimolecular chemical reaction can be expressed as

$$k(T) = \frac{1}{Q_r(T)} \int_{-\infty}^{\infty} \frac{dE}{2\pi\hbar} e^{-\beta E} N(E), \qquad (1.1)$$

where $\beta = (k_B T)^{-1}$, k_B is Boltzmann's constant, and $Q_r(T)$ is the reactant partition function including relative translational motion per unit volume. In Eq. (1.1), $N(E)$ is the microcanonical cumulative reaction probability, which in turn is defined[6] by

$$N(E) = \sum_{n_p} \sum_{n_r} |S_{n_p n_r}(E)|^2, \qquad (1.2)$$

where $[S_{n_p n_r}(E)]$ is the S matrix for total energy E. The sums in Eq. (1.2) are over all energetically allowed states of the reactants and products, denoted by quantum numbers n_r and n_p, respectively. Since the S-matrix elements contain the most detailed dynamical information, they are most computationally demanding. A formally exact approach to obtain $k(T)$ or $N(E)$ which circumvents the need to carry out exact S-matrix calculations should in principle be more economical, since the information content in the former quantities is manifestly independent of system size. Two such formulations were given in terms of the analysis of reactive flux correlation functions by Yamamoto[7] and by Miller *et al.*[8] In the present study we will use the latter formulation to calculate the cumulative reaction probability.

Considerable theoretical effort has been devoted to evaluating the thermal rate constant $k(T)$ by the flux correlation formalism of Miller *et al.*[8,9] Less attention, however, has been given to the direct calculation of the cumulative reaction probability $N(E)$.[10] The theory for directly computing $N(E)$ depends on the microcanonical density operator $\delta(E-H)$, which is formally obtained from the outgoing wave energy Green's function.[11] Recently, Seideman and Miller[12] showed how to use absorbing boundary conditions (ABC) to construct a convenient, well-behaved representation of the energy Green's function for use in $N(E)$ calculations. ABC have been used in the past, primarily in wave packet propagations, for the study of laser-induced dissociation[13] and reactive scattering.[14] In the context of a wave packet propagation, absorbing boundary conditions facilitate the use of smaller spatial grids by eliminating spurious reflection from grid boundaries. In the present context, they are used to enforce outgoing wave boundary conditions in the Green's function without explicitly constructing the outgoing waves. In fact, in their study of H+H$_2$ reaction probabilities, Seideman and

Miller were able to compute $N(E)$ by focusing only on the strong chemical interaction region, making no explicit reference to the asymptotic reactant and product states that would be necessary in a full S-matrix calculation. As such, their work represents significant progress in the search for an efficient calculation of the microcanonical cumulative reaction probability.

The calculation of $N(E)$ by an absorbing boundary condition Green's function relies on the construction and inversion of a complex Hamiltonian matrix. We first discuss efficient inversion algorithms. The most straightforward inversion technique is LU decomposition,[15] which requires storage of the Hamiltonian matrix. Iterative methods,[16] which do not necessarily require such storage, are an important alternative to LU decomposition for the solution of large systems. The Lanczos algorithm,[17] in which a Hermitian matrix is reduced to tridiagonal form, can be used to diagonalize[17(b)] or invert[17(c)] a matrix with minimal storage. This technique has been used extensively to treat chemical systems with real Hamiltonians.[18–20] Whether the Lanczos algorithm is readily applicable to complex symmetric matrices is an open question.[17(b),19(d),21] The generalized minimum residual[22] method (GMRES), however, is an algorithm applicable for the solution of arbitrary linear systems. Although it has given impressive results[23] when used with preconditioning,[24] GMRES can be memory intensive. With the intention of extending $N(E)$ calculations to larger systems, we have developed a new iterative method for matrix inversion which is especially suited for Hamiltonians with absorbing boundary conditions. The method is stable, requires very little memory (as opposed to GMRES), and can readily be preconditioned (as opposed to the SYMMLQ[17(c)] algorithm). It is based on Fourier transforming the time-dependent wave packet dynamics to obtain the energy-dependent reaction probabilities and gives, in the present implementation, a power series energy Green's function.

Forming the matrix representation of the Hamiltonian operator and manipulating the Hamiltonian matrix to obtain the observable of interest can be computationally intensive. A discrete variable representation[25] (DVR) can ameliorate both of these difficulties. That is, the construction of the Hamiltonian matrix is particularly simple in a DVR because no multidimensional integrals involving the potential function are required. Also, the resulting matrix is sparse because the potential is diagonal, which expedites an iterative solution.[19(b),19(c)] In the present research, we use a sinc-function based DVR (vide infra) first developed by Colbert and Miller[26] for use in the S-matrix version of the Kohn variational principle,[1(b),27] and used subsequently for S-matrix calculations[19(b),19(c)] in addition to $N(E)$ calculations.[12] This is a uniform grid DVR which is constructed from an infinite set of points. It is then truncated[25(f)] to the shape of the potential by deleting grid points where the wave function or Green's function is vanishingly small. The uniform distribution of grid points inherent in this DVR has demonstrated significant efficiency in treating the gross anharmonicity of potential functions in reactive scattering.

Thus, the present theory includes wave packet propagation on a grid as a basic component. McCullough and Wyatt[28] performed the first such study over 20 years ago on the $H + H_2$ system. Since then, Kosloff and co-workers[2(a)] have incorporated many improvements to augment the efficiency of exact wave packet propagations, such as the Fourier representation[29] of the kinetic energy operator. This is a uniform grid over a finite interval, as opposed to sinc-function DVR which involves a uniform grid over an infinite interval. It would be interesting to determine whether the efficiency of wave packet propagation is equivalent based on these two uniform grid representations. That is, one might ask for which physical systems would one grid method be superior to the other. We will present a qualitative analysis, concluding that sinc-function DVR is preferable for the representation of a molecular reactive scattering system when a large number of grid points, necessary for the Fourier method, can be deleted from the sinc-function DVR basis.

We perform wave packet evolution by propagating over many small time steps, where each short-time evolution is effected by matrix multiplication on a grid. For many years, matrix multiplication was deemed an inappropriate method for such propagation because of the highly oscillatory nature of the short-time coordinate propagator. This problem has been addressed by several workers[30–35] who have incorporated, in one guise or another, a filter to damp the very high frequency components in the propagator that cause numerical problems and are usually unimportant to the dynamics. For example, Coalson[33] computed real time correlation functions via matrix multiplication by adding a small imaginary part to the time. Alternatively, Makri[30] deleted momenta greater than some p_{max} from the propagator to yield a well behaved effective kernel. This approach was shown to be useful for both matrix multiplication and Monte Carlo[36] evaluation of the time evolution operator. It is interesting to note that this latter approach will turn out to be mathematically *identical* to the sinc-function DVR of the short-time coordinate propagator. Inspired by the success of this effective propagator, we will present a generalization of Makri's effective kernel which might be more useful in a path integral[37] Monte Carlo evaluation of the real time propagator.

The purpose of the present paper is to introduce the power series Green's function and to show its efficient application to the benchmark collinear $H + H_2$ reaction. In the next section, we briefly summarize how absorbing boundary conditions are incorporated into the flux correlation formalism for the cumulative reaction probability. In Sec. III, we give a detailed description of the power series Green's function, in addition to the qualitative comparison between the Fourier method and sinc-function DVR. Section IV presents the results and discussion of the convergence properties of the power series method. The final section concludes with some remarks concerning future study, including a generalization of Makri's effective propagator.

II. GENERAL METHODOLOGY

We begin the calculation of the cumulative reaction probability with an expression derived from the analysis of reactive flux correlation functions[8(b)] given by

$$N(E) = \tfrac{1}{2}(2\pi\hbar)^2 \, \text{Tr}[F\delta(E-H)F\delta(E-H)], \qquad (2.1)$$

where "Tr" denotes a quantum mechanical trace. The reactive flux operator F in Eq. (2.1) is most generally defined by

$$F = \frac{1}{i\hbar}\{h[f(\mathbf{q})],H\}, \qquad (2.2)$$

where h is the step function

$$h(\xi) = \begin{cases} 1, & \xi > 0 \\ 0, & \xi < 0 \end{cases} \qquad (2.3)$$

and $f(\mathbf{q})$ defines, via the equation $f(\mathbf{q})=0$, a dividing surface which separates reactants from products. Here $\mathbf{q}$ denotes all the internal molecular coordinates. The microcanonical density operator $\delta(E-H)$ is formally obtained from the outgoing wave energy Green's function via the relation[11]

$$\delta(E-H) = -\frac{1}{\pi}\,\text{Im}\,G^+(E), \qquad (2.4)$$

where $G^+(E)$ is defined by[38]

$$G^+(E) \equiv \lim_{\epsilon\to 0}(E+i\epsilon-H)^{-1} \qquad (2.5a)$$

$$= \lim_{\epsilon\to 0}\frac{1}{i\hbar}\int_0^\infty dt\,\exp[i(E+i\epsilon-H)t/\hbar]. \qquad (2.5b)$$

In Eq. (2.5), adding an infinitesimal imaginary part to the energy E provides the outgoing wave boundary conditions and in Eq. (2.5b) can be viewed as providing a factor which ensures the convergence of the time integral.[12(a)]

Seideman and Miller recently showed,[12] in the definition of $G^+(E)$, that subtracting a coordinate dependent operator $i\epsilon(\mathbf{q})$ from the Hamiltonian H can be equivalent to adding a constant $i\epsilon$ to the energy E, so long as $\epsilon(\mathbf{q})$ is negligible in the chemical interaction region. This technique, analogous to the use of absorbing potentials in the field of time-dependent wave packet propagation,[13,14] leads to the definition of an absorbing boundary condition (ABC) Green's function. The following alternative, but formally exact expression results for $N(E)$:

$$N(E) = \text{Tr}[G_{\text{ABC}}^{+*}(E)\Gamma_p G_{\text{ABC}}^+(E)\Gamma_r], \qquad (2.6)$$

where

$$G_{\text{ABC}}^+(E) \equiv (E+\tfrac{i}{2}\Gamma-H)^{-1} \qquad (2.7a)$$

$$= \frac{1}{i\hbar}\int_0^\infty dt\,\exp\left[i\left(E+\frac{i}{2}\Gamma-H\right)t/\hbar\right] \qquad (2.7b)$$

and

$$\Gamma_p = \Gamma h, \qquad (2.8a)$$

$$\Gamma_r = \Gamma(1-h). \qquad (2.8b)$$

Here Γ is a coordinate dependent operator and h is the coordinate dependent step function operator which defines the reactive flux in Eq. (2.2). If Eq. (2.6) is evaluated in a discrete variable representation (DVR),[12,25,26] in which case the absorbing potentials Γ_r and Γ_p are diagonal, $N(E)$ becomes

$$N(E) = \sum_{\mathbf{j}'\mathbf{j}} \Gamma_p(\mathbf{q}_{\mathbf{j}'})\,|\,G_{\text{ABC}}^+(\mathbf{q}_{\mathbf{j}'},\mathbf{q}_{\mathbf{j}};E)\,|^2\Gamma_r(\mathbf{q}_{\mathbf{j}}), \qquad (2.9)$$

where $(\mathbf{q}_{\mathbf{j}})$ are the grid points and $\mathbf{j}$ is a multidimensional grid point index. Equation (2.9) is the working formula used in the present study. In what follows, we remove the "ABC" subscript from the ABC Green's function, with $G^+(E)$ denoting the ABC Green's operator and $\mathbf{G}^+(E)$ the finite dimensional ABC Green's matrix.

The computational challenge involved in Eq. (2.9) is clearly the evaluation of the matrix elements of $\mathbf{G}^+(E)$ which connect the reactant and product regions of configuration space. In previous applications,[12] these were computed as the solution of the complex symmetric linear system

$$(E\mathbf{1}+\tfrac{i}{2}\Gamma-\mathbf{H})\mathbf{G}^+(E) = \mathbf{1} \qquad (2.10)$$

by LU decompsition.[15] We call this the *direct* method of solution. For most chemically realistic systems, direct solution would require the storage and manipulation of matrices larger than can be held in the central memory of modern computers. One of the most fruitful approaches, however, in the solution of large linear systems is the use of a grid representation for the Hamiltonian in conjunction with an *iterative* solution of the resulting sparse linear system.[16] This is because iterative methods do not require storage of the Hamiltonian and are especially rapid when used to solve sparse systems.

We now describe a new iterative procedure to compute $\mathbf{G}^+(E)$ on a grid. The method is based on Eq. (2.7b), i.e., the integral representation of the ABC Green's function.

III. POWER SERIES GREEN'S FUNCTION

We construct a power series representation of the ABC Green's function by taking a finite upper limit T for the time integral in Eq. (2.7b), and by using N evenly spaced quadrature points to evaluate the resulting integral. The former approximation is valid because the use of ABC to define the Green's function guarantees the convergence of the integral in finite time. The latter approximation generates the power series. Other representations of the ABC Green's function, which incorporate more sophisticated quadrature for the time integral, are possible and are discussed in Sec. V. These modifications to Eq. (2.7b) give the following power series Green's function (PSG):

$$G^+(E) \cong \frac{\Delta t}{i\hbar}\sum_{n=0}^N w_n M^n, \qquad (3.1)$$

where

$$\Delta t = \frac{T}{N}, \qquad (3.2a)$$

w_n=quadrature weights

(e.g., extended trapezoidal rule

$$w_n = 1 - \tfrac{1}{2}\delta_{n0} - \tfrac{1}{2}\delta_{nN}), \qquad (3.2b)$$

and

$$M = \exp[i(E + \tfrac{i}{2}\Gamma - H)\Delta t/\hbar] \equiv e^{iE\Delta t/\hbar} K(\Delta t). \qquad (3.2c)$$

In Eq. (3.2c), $K(\Delta t)$ is the propagator with absorbing boundary conditions for the duration Δt. As is common to the study of wave packet propagation, we have reduced the problem to finding the most accurate and efficient representation of the propagator.[2(a),39,40] We use a simple and flexible short-time propagator (STP) developed by Feit, Fleck, and co-workers[41] (also called[40(b)] the kinetic referenced split-operator propagator) given by

$$K(t) = K_{STP}(t) + O(t^3), \qquad (3.3a)$$

where

$$K_{STP}(t) \equiv \exp[-i(V - \tfrac{i}{2}\Gamma)t/2\hbar]e^{-iTt/\hbar}$$

$$\times \exp[-i(V - \tfrac{i}{2}\Gamma)t/2\hbar], \qquad (3.3b)$$

$$H = T + V. \qquad (3.3c)$$

This has been used[42] extensively in previous time-dependent calculations and is a second-order propagator because it incorporates second-order commutation error in the symmetrization. It has the flexibility of being able to treat a time-dependent Hamiltonian, e.g., in a mixed quantum-classical time-dependent self-consistent field[42(d),43] framework, by taking a time step small enough that the Hamiltonian is approximately constant. Some alternatives to the STP to be considered for future study will be discussed in Sec. V. We note that implementing propagators which are valid for longer times is tantamount to preconditioning[24] the system, i.e., making the Hamiltonian matrix more diagonally dominant.

We represent the STP in Eq. (3.3b) with sinc-function based DVR (SDVR) for each degree of freedom, where the sinc function is given by

$$\mathrm{sinc}(x) \equiv \frac{\sin(x)}{x}. \qquad (3.4)$$

It was first described by Colbert and Miller[26] for use in the S-matrix version of the Kohn variational principle, and used subsequently for S-matrix calculations[19(b),19(c)] in addition to $N(E)$ calculations.[12] Before giving the relevant matrix elements, we compare SDVR to the closely related Fourier grid method of Kosloff and co-workers[2(a),29] which has been used extensively in previous wave packet calculations.[2,44] Both involve uniform grids in configuration space able to represent momenta up to

$$p_{\max} = \hbar \frac{\pi}{\Delta x}, \qquad (3.5)$$

where Δx is the uniform grid spacing. In addition, both representations require roughly[45,46] $N \log_2 N$ multiplications per propagation step, where N is the size of the grid.

The two methods differ, however, in the actual manner of propagation. The Fourier method requires multidimensional fast Fourier transforms[15] (FFT) to facilitate propagation, whereas SDVR relies on sparse matrix multiplication. As such, the grid used in SDVR calculations can easily be tailored[25(f)] to the shape of the potential energy surface (PES), whereas the Fourier method requires the use of rectangular or L-shaped[47] grids in order to perform the FFT. The implication here is that the rectangular grids required for the Fourier method may waste points in unimportant or unphysical regions of configuration space, where the wave function or Green's function is vanishingly small. We conclude, therefore, that for the study of multidimensional systems where the relevant region of configuration space is approximately rectangular, the Fourier grid can be more computationally efficient. This situation can obtain, e.g., in the study of photodissociation to a single fragment arrangement, or in gas-surface scattering.[47] For the study of multidimensional systems, however, where the relevant region of configuration space is *not* rectangular, e.g., a gas phase reactive scattering system, SDVR should be more efficient if enough grid points are deleted from the basis.

We now give the sinc-function based DVR of the power series Green's function. For simplicity, we restrict our attention to a one-dimensional system. The multidimensional generalization is straightforward and will be given afterwards. Letting $|u_j\rangle$ denote the jth SDVR basis ket, the matrix power series Green's function (PSG) becomes

$$G^+(E) \cong \frac{\Delta t}{i\hbar} \sum_{n=0}^{N} w_n M^n, \qquad (3.6a)$$

where

$$(M)_{j'j} = e^{iE\Delta t/\hbar}[K_{STP}(\Delta t)]_{j'j}, \qquad (3.6b)$$

$$[K_{STP}(t)]_{j'j} = \exp[-i(V_{j'} - \tfrac{i}{2}\Gamma_{j'})t/2\hbar]\langle u_{j'}|e^{-iTt/\hbar}|u_j\rangle$$

$$\times \exp[-i(V_j - \tfrac{i}{2}\Gamma_j)t/2\hbar], \qquad (3.6c)$$

and

$$T = \frac{p^2}{2m}. \qquad (3.6d)$$

Equation (3.6c) obtains from the fact that the PES and the absorbing potential are coordinate dependent operators. In Eq. (3.6c), V_i and Γ_i correspond to the PES and the absorbing potential evaluated at the ith grid point, respectively. The SDVR of the free particle propagator is given in the fashion outlined by Colbert and Miller,[26] in which one first considers a finite particle-in-a-box DVR. With $(N-1)$ functions and grid points and a grid spacing of Δx, the free particle propagator becomes

$$(e^{-iTt/\hbar})_{j'j}^{\text{finite DVR}} = \frac{2}{N} \sum_{n=1}^{N-1} \sin(\pi n j'/N)$$

$$\times \exp\left(\frac{-i\hbar\pi^2 n^2 t}{2m\Delta x^2 N^2}\right) \sin(\pi n j/N). \quad (3.7)$$

To obtain the SDVR of the free particle propagator, one takes the infinite N limit of Eq. (3.7) keeping Δx fixed, giving[48]

$$\langle u_{j'}|e^{-iTt/\hbar}|u_j\rangle \equiv \lim_{N\to\infty} (e^{-iTt/\hbar})_{j'j}^{\text{finite DVR}}$$

$$= \int_0^1 dy \cos[\pi y(j'-j)]$$

$$\times \exp\left(\frac{-i\hbar\pi^2 y^2 t}{2m\Delta x^2}\right). \quad (3.8)$$

With the variable transformation $p=\hbar\pi y/\Delta x$, the free particle propagator in Eq. (3.8) takes on the more familiar form

$$\langle u_j|e^{-iTt/\hbar}|u_j\rangle = \int_{-p_{\max}}^{+p_{\max}} \frac{\Delta x \, dp}{2\pi\hbar} \exp(ipx_{j'}/\hbar)$$

$$\times \exp(-ip^2 t/2m\hbar)\exp(-ipx_j/\hbar), \quad (3.9)$$

where $p_{\max}$ is given in Eq. (3.5) and $x_i=i\Delta x$ for $i=j',j$.

The matrix element in Eq. (3.9) is noteworthy in three respects. First, it is the product of an integration weight and a finite grid spacing representation of the kernel. This product arises because DVR includes integration weights in the transformations. As $p_{\max}$ goes to infinity (and Δx goes to zero), the summation implied by matrix multiplication goes over into an integral, and the matrix element becomes

$$\lim_{p_{\max}\to\infty} \langle u_{j'}|e^{-iTt/\hbar}|u_j\rangle = dx\langle x_{j'}|e^{-iTt/\hbar}|x_j\rangle_{\text{exact}}, \quad (3.10)$$

recovering the kernel of the free particle propagator multiplied by the infinitesimal integration weight. Second, the SDVR of the free particle propagator is easily evaluated giving the exact kernel times a smoothing factor that results from the finite grid spacing. Equation (3.9) becomes

$$\langle u_{j'}|e^{-iTt/\hbar}|u_j\rangle = \Delta x\langle x_{j'}|e^{-iTt/\hbar}|x_j\rangle_{\text{exact}}$$

$$\times f_{\text{smooth}}(x_{j'},x_j,t;m,\Delta x), \quad (3.11a)$$

where

$$f_{\text{smooth}}(x_{j'},x_j,t;m,\Delta x)$$

$$= \frac{1}{2}\left\{ \text{erf}\left[\left(\frac{it}{2m\hbar}\right)^{1/2} \frac{\hbar\pi}{\Delta x} + \left(\frac{im}{2\hbar t}\right)^{1/2}(x_{j'}-x_j) \right] \right.$$

$$\left. + \text{erf}\left[\left(\frac{it}{2m\hbar}\right)^{1/2} \frac{\hbar\pi}{\Delta x} - \left(\frac{im}{2\hbar t}\right)^{1/2}(x_{j'}-x_j) \right] \right\}. \quad (3.11b)$$

In Eq. (3.11b), erf(z) is the error function of a complex variable.[49] The third, and perhaps most intriguing aspect of

Eqs. (3.9) and (3.11), is that they have been derived before in a completely *different* context by Makri.[30] In particular, she was seeking a well behaved (i.e., less oscillatory) representation of the short-time kernel for use in real time path integral Monte Carlo[31,39] calculations. The advantage gained from the matrix element in Eq. (3.11) derives from the asymptotic behavior of the smoothing function,[30,47] namely,

$$\lim_{\alpha\to\infty} \langle u_{j'}|e^{-iTt/\hbar}|u_j\rangle = \text{sinc}\left[\frac{\pi}{\Delta x}(x_{j'}-x_j)\right], \quad (3.12a)$$

where

$$\alpha = \frac{x_{j'}-x_j}{t} \quad (3.12b)$$

and in the above limit $p_{\max}$ (and, hence, Δx) is understood to be fixed. Thus, Makri's version of the propagator automatically includes the effect of high frequency phase cancellation that numerical quadrature and Monte Carlo algorithms have to work so hard to simulate. This cancellation is manifest in the damping of the free particle propagator matrix element for large α. In fact, Makri found this propagator to be so well behaved, that wave packet propagation by straightforward matrix multiplication was efficient and accurate. That is precisely the type of propagation being done in the present study. It is analogous to the numerical matrix multiplication scheme of Berne and co-workers[50] used to compute the canonical density matrix by a discretized path integral in imaginary time. It is interesting to note that our numerical tests indicate that without the smoothing factor, the propagation becomes unstable and numerical overflow occurs. It is also worth noting that Kouri and co-workers[32] have developed a different approximation to the free particle coordinate propagator, similar in spirit to Makri's propagator, which neglects high momentum components. Thus, the SDVR of the STP gives the *exact* position representation of the STP, which, when placed on a grid with finite spacing, automatically filters out high frequency momentum components which are unimportant and difficult to integrate.

For the multidimensional generalization of Eqs. (3.6)–(3.12), consider the F-dimensional Hamiltonian operator given by

$$H = \sum_{\alpha=1}^{F} T_\alpha + V(\mathbf{q}), \quad (3.13a)$$

where

$$T_\alpha = \frac{p_\alpha^2}{2m_\alpha} \quad (3.13b)$$

and

$$\mathbf{q} = (q^1,...,q^F) \quad (3.13c)$$

is an F-dimensional point in Cartesian space. We form an F-dimensional grid defined by

$$q_{j_\alpha}^\alpha = j_\alpha \Delta q^\alpha, \quad \text{for} \quad j_\alpha = -\infty,...,-1,0,+1,...,+\infty \quad (3.13d)$$

for each coordinate q^α and corresponding grid point index j_α. The infinite grid is then truncated by adapting it to the shape of the PES. That is, the points $\mathbf{q_j}$ are retained only if they satisfy the energy criterion[25(f)] given by

$$V(\mathbf{q_j}) \leqslant V_{\text{cut}}, \tag{3.14}$$

where V_{cut} becomes a basis set convergence parameter. The corresponding ABC-DVR power series Green's function is still given by Eq. (3.6a), where the matrix $\mathbf{M}$ is now defined by

$$(\mathbf{M})_{\mathbf{j'j}} = e^{iE\Delta t/\hbar}[\mathbf{K}_{\text{STP}}(\Delta t)]_{\mathbf{j'j}}, \tag{3.15a}$$

where

$$[\mathbf{K}_{\text{STP}}(t)]_{\mathbf{j'j}} = \exp\left[-i\left(V_{\mathbf{j'}} - \frac{i}{2}\Gamma_{\mathbf{j'}}\right)t/2\hbar\right]$$
$$\times \left[\prod_{\alpha=1}^{F} \langle u^\alpha_{j'_\alpha}|e^{(-iT_\alpha t/\hbar)}|u^\alpha_{j_\alpha}\rangle\right]$$
$$\times \exp\left[-i\left(V_{\mathbf{j}} - \frac{i}{2}\Gamma_{\mathbf{j}}\right)t/2\hbar\right] \tag{3.15b}$$

and $\mathbf{j} = (j_1,...,j_F)$ is the F-dimensional grid point index alluded to in Eq. (2.9). In Eq. (3.15b), $V_{\mathbf{j}}$ and $\Gamma_{\mathbf{j}}$ are the F-dimensional PES and absorbing potential, respectively, evaluated at $\mathbf{q_j}$. Each of the factors in the direct product free particle matrix element in Eq. (3.15b) is Eq. (3.11a) evaluated with the appropriate mass and grid spacing, i.e.,

$$\langle u^\alpha_{j'_\alpha}|\exp(-iT_\alpha t/\hbar)|u^\alpha_{j_\alpha}\rangle$$
$$= \Delta q_\alpha \langle q^\alpha_{j'_\alpha}|\exp(-iT_\alpha t/\hbar)|q^\alpha_{j_\alpha}\rangle_{\text{exact}}$$
$$\times f_{\text{smooth}}(q^\alpha_{j'_\alpha}, q^\alpha_{j_\alpha}, t; m_\alpha, \Delta q_\alpha). \tag{3.15c}$$

In multidimensional SDVR, the Hamiltonian matrix is sparse, which leads to $N(2+FN^{1/F})$ complex multiplications for each application of the matrix $\mathbf{M}$, where N is the size of the grid.[19(b),19(c)]

To conclude the description of the power series Green's function (PSG), we wish to underscore how the recursive calculation proceeds. To compute the jth column of the ABC Green's function, denoted by $\mathbf{G_j}$ with elements given by

$$(\mathbf{G_j})_{\mathbf{j'}} = G(\mathbf{q_{j'}}, \mathbf{q_j}), \tag{3.16}$$

one forms the dot product of the matrix in Eq. (3.6a) with the jth column of the identity matrix. As such, the jth column of $\mathbf{G}^+(E)$ is

$$\mathbf{G_j} = \frac{\Delta t}{i\hbar} \sum_{n=0}^{N} w_n \mathbf{a}_{n\mathbf{j}}, \tag{3.17a}$$

where

$$\mathbf{a}_{0\mathbf{j}} = \mathbf{I_j}, \tag{3.17b}$$

$$(\mathbf{I_j})_{\mathbf{j'}} = \delta_{\mathbf{j'j}} = \prod_{\alpha=1}^{F} \delta_{j'_\alpha j_\alpha}, \tag{3.17c}$$

and

$$\mathbf{a}_{n+1,\mathbf{j}} = \mathbf{M} \cdot \mathbf{a}_{n\mathbf{j}}, \quad n = 0,1,...,N-1 \tag{3.17d}$$

with $\mathbf{M}$ defined by Eq. (3.15). Equation (3.17d) is the recursion relation which defines the iterative method.

We now present a numerical application of the PSG in the study of the cumulative reaction probability for the collinear $H + H_2$ reactive scattering system.

IV. RESULTS AND DISCUSSION

We present the results of the calculation of the cumulative reaction probability for collinear $H + H_2$ over the total energy range of 0.37–1.27 eV, using the method outlined in Secs. II and III. The availability of accurate PES's and dynamics calculations makes it a good benchmark system to use to study a new method. We used the Liu–Siegbahn–Truhlar–Horowitz (LSTH)[51] PES for the study. The coordinates used for the calculations were the mass-weighted rectilinear normal modes[26,52] referenced to the transition state on the LSTH PES. We denoted the 2D coordinates by $\mathbf{q} = (x,y)$, where x is the reaction coordinate and y is the perpendicular vibrational coordinate, i.e., the antisymmetric and symmetric stretch, respectively.

A primitive DVR grid is first laid down along the coordinates $\mathbf{q}$. We choose the grid spacings in the manner suggested by Colbert and Miller.[26] That is, given a mass and energy scale for each degree of freedom, we fix the number of grid points per de Broglie wavelength, denoted by n_B. This gives the grid spacing for each degree of freedom as

$$\Delta q^\alpha = \frac{2\pi\hbar}{n_B^\alpha \sqrt{2m_\alpha E_\alpha}}. \tag{4.1}$$

For all studies at total energy E, we used $E_\alpha = E$, $m_\alpha = 1060$ a.u. (the mass-weighted system reduced mass), and $n_B^\alpha \approx 4$ points per wave for both degrees of freedom. Next, the primitive grid is truncated to yield a nondirect product grid as discussed in Eq. (3.14). To avoid an overabundance of convergence parameters for later discussion, we set the energy cutoff $V_{\text{cut}} = 3.4$ eV for all calculations, which was found to give satisfactory convergence.

The absorbing potential in the ABC Green's function simulates the effect of outgoing wave boundary conditions. It does so by absorbing completely, without back reflection, any flux from the interaction region that encounters the edge of the grid in all energetically allowed arrangements. As previously discussed by many authors,[12–14] the optimal form of the absorbing potential is one which absorbs probability as rapidly (in space) as possible without reflection. We use one of the forms suggested by Seideman and Miller,[12] a sigmoid function given by

$$\Gamma[z(\mathbf{q})] = \frac{4\lambda}{1+\exp[(z_{\text{max}}-z)/\eta]}, \tag{4.2a}$$

where

$$z(\mathbf{q}) = \max[R_a(\mathbf{q}), R_c(\mathbf{q})], \tag{4.2b}$$

$$z_{\text{max}} = R_\gamma^{\text{max}}, \quad \text{if} \quad z(\mathbf{q}) = R_\gamma(\mathbf{q}) \quad \text{for} \quad \gamma = a,c, \tag{4.2c}$$
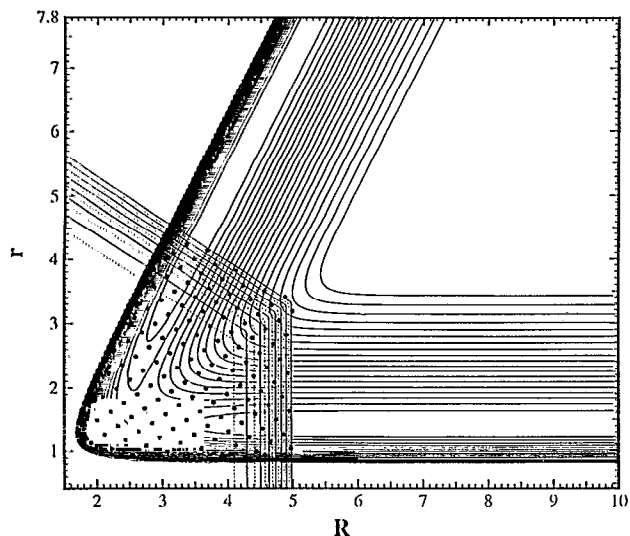
FIG. 1. The LSTH potential surface as a function of the Jacobi coordinates (R,r). The other contours show the sigmoid absorbing potential where $\lambda = 1.1$ eV and $\eta = 0.27$ a.u. The distribution of grid points shown was used for the convergence tests at $E = 0.52$ eV.

FIG. 2. The cumulative reaction probability for the collinear $H + H_2$ reaction. The circles are the R-matrix propagation results (summed over final states in Ref. 50), and the line is the power series Green's function results.

and $R_a(R_c)$ is the translational Jacobi coordinate in the reactant (product) arrangement. In the symmetric case of collinear $H + H_2$, we have $z_{max} = R_a^{max} = R_c^{max}$, where we have used $z_{max} = 5$ a.u. for most of the calculations. A typical grid is shown in Fig. 1 including the contours of the absorbing potential $\Gamma(\mathbf{q})$. The parameters λ and η are optimized by running appropriate convergence tests. For the convergence of the power series Green's function, we single out the parameter λ as being especially important. This is clear from the following analysis: We let $\Gamma(\mathbf{q}) = 2\lambda$ be a constant absorbing potential. We also assume Eq. (2.7b) for $G^+(E)$. If one takes a finite upper limit T for the time integral, the error incurred is given by

$$G^+(E)\big|_{\text{finite } T} = G^+(E)[1 - O(e^{-\lambda T/\hbar})]. \qquad (4.3)$$

Thus, we expect to see exponential convergence in the parameters λ and T. Although this analysis is complicated by the use of a coordinate-dependent absorbing potential, it seems plausible that to converge the PSG with as few iterations as possible, it may be beneficial to use larger values of λ than in previous studies. Results of this analysis will be discussed.

Before stating the results, we wish to comment briefly on the scaling of the computational expense of the PSG with respect to central memory and CPU time. For an F-dimensional system with, on average, n grid points per degree of freedom, the PSG scales as[19(b),19(c),26] $N_{RHS}N_{ITER}FnN$, where N_{RHS} is the number of reactant grid points for which a vector of $G^+(E)$ is computed and N_{ITER} is the number of iterations per RHS. From our experience, this roughly scales as FnN^3. The PSG requires only three vectors of length N for the essential recursion and summation, in addition to a very small number of vectors to enhance the speed of each iteration. Clearly *this* is where the PSG is favorable over direct methods.
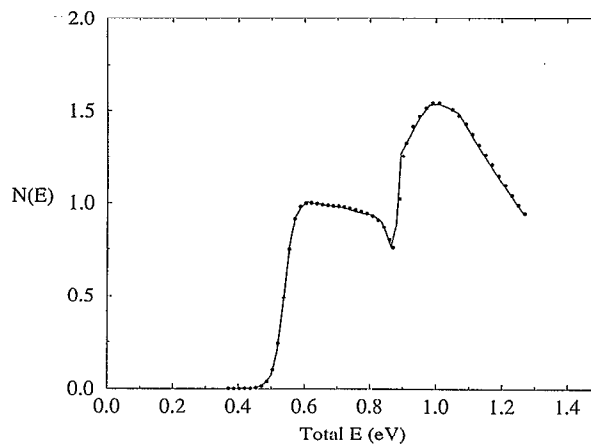
The cumulative reaction probability for collinear $H + H_2$, computed by the method outlined in Secs. II and III, is shown in Fig. 2. The circles represent the reaction probabilities computed by Bondi *et al.*[53] using R-matrix propagation on the LSTH PES. The agreement is excellent over the whole energy range. Because the cumulative reaction probability for collinear $H + H_2$ is well known, we will not discuss its physical content. In the energy range where there is only one asymptotic vibrational channel open $[E \in (0.37, 0.78 \text{ eV})]$, the error is always less than 1%. In the higher energy regime, the error is always less then 1.6%. We now present the convergence study of the PSG results.

The two important convergence parameters introduced by the power series expansion of the ABC Green's function are the total propagation time T and the time step Δt. The total time T represents the time required for reaction *and* absorption by Γ. The time step Δt is the duration in which the STP is a faithful representation of the propagator. These are both a function of the dynamics and the choice of absorbing potential. We measure Δt in units of a fundamental small time given by

$$\tau_{\text{grid}} \equiv \frac{\min \text{ grid length}}{\max \text{ grid velocity}} = \frac{m\Delta x^2}{\pi\hbar}. \qquad (4.4a)$$

That is, $\Delta t = f\tau_{\text{grid}}$, where f is some unitless number. If we choose Δx by the criterion in Eq. (4.1), we also find that

$$\tau_{\text{grid}} = \frac{2\pi\hbar}{E} \frac{1}{n_B^2} \approx \frac{2\pi\hbar}{E} \frac{1}{16}, \qquad (4.4b)$$

where n_B is defined in Eq. (4.1). Equation (4.4b) shows that this fundamental small time should, at least, be small enough to integrate the energy dependent oscillations in the time integral. Whether it is small enough for propagation, i.e., whether f is of order unity for convergence, is discussed below.

In the context of calculating $N(E)$ by the ABC-DVR approach,[12] the present work represents a new iterative

method to invert a complex matrix with less memory required than GMRES.[22,24] The overall computational framework, i.e., Eq. (2.9), is not new and is not what is being tested here. As such, we gauge the error of the power series expansion in the following way: First we converge $N(E)$ using the direct ABC-DVR method. Then, using the same Hamiltonian and grid parameters, we compute the PSG result. Relative error is therefore defined as

$$error \equiv \frac{N^{PSG}(E) - N^{direct}(E)}{N^{direct}(E)} \times 100, \qquad (4.5)$$

where the convergence of the direct result is based on the calculations of Bondi et al.[53]

First we study the convergence of $N(E)$ at $E=0.52$ eV. We use a grid and absorbing potential ($\lambda = 1.1$ eV and $\eta = 0.27$ a.u.) for which the direct ABC-DVR $N(E) = 0.242$, whereas the R-matrix propagation gives $N(E) = 0.244$. Figure 3(a) shows the percent error of $N(E)$ from the direct result as a function of the common logarithm of f, where $\tau_{grid} = 20.2$ a.u. $= 0.49$ fs. We see very well behaved, monotonic convergence to the direct result. This is remarkable for the following reason: As the time step is made smaller in Fig. 3(a), the exact STP becomes more oscillatory and hence, more difficult to integrate. However, the SDVR of the STP is sufficiently well behaved that it can be integrated with the same DVR grid while changing the time step by three orders of magnitude. Taking the first result that remains in the 1% error band as converged, $f = 0.3$ or $\Delta t = 6$ a.u. $= 0.15$ fs is the optimal time step for the STP. This time step is about 1/50 of the asymptotic H_2 ground state vibrational period, which is approximately 8 fs.[54] Such a small time step is necessary to obtain accurate results for a large value of T.

Figure 3(b) shows the convergence of $N(E)$ to the direct result for $E=0.52$ eV as a function of the total propagation time T. For the calculations in the solid curve, we set $f = 0.05$ or $\Delta t = 1$ a.u. $= 0.024$ fs. For those in the dashed curve, $f = 1$ or $\Delta t = 20.2$ a.u. $= 0.49$ fs. Both curves show the same very smooth convergence. In fact, since the rate of convergence with respect to the total time T is independent of the time step Δt, optimization of the two temporal parameters can be performed independently. Using the same 1% convergence criterion above, we see the optimal $T = 5000$ a.u. $= 121$ fs. With these parameters, the PSG required for $N(E)$ at $E=0.52$ eV converges in roughly 800 iterations.

Now we consider varying parameters in the absorbing potential to effect more rapid absorption in time. Once again, consider $E=0.52$ eV. At this energy, the ABC-DVR cumulative reaction probability is stable over a range of λ up to approximately 1.6 eV. At $\lambda = 1.5$ eV, $N(E)$ by direct ABC-DVR gives the value 0.245. In Fig. 3(c), we show the same as Fig. 3(b), except with this elevated value of λ, the absorbing potential strength parameter. In this case, convergence of $N(E)$ is obtained with a total propagation time $T = 4000$ a.u. $= 97$ fs. This calculation, requiring roughly 650 iterations, represents a modest savings in computation with fairly little effort in optimization of the absorbing potential.
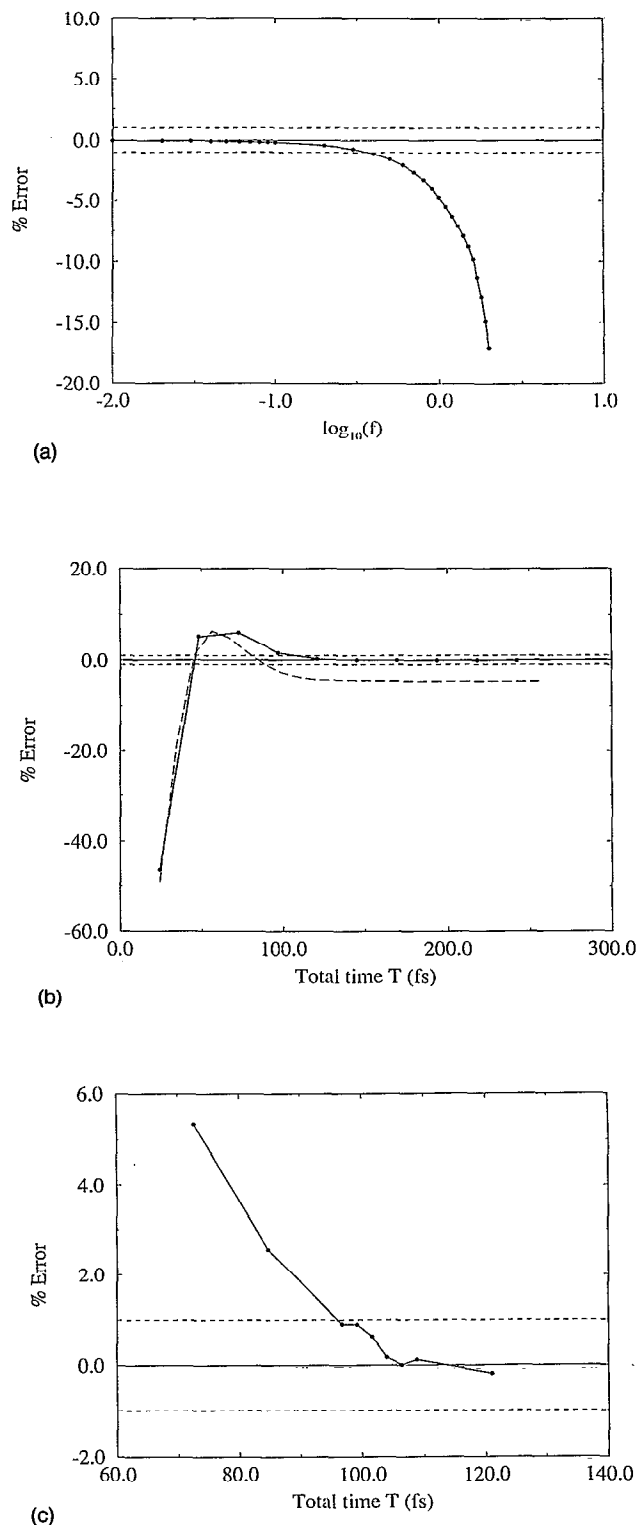

(a)

(b)

(c)

FIG. 3. Convergence of $N(E)$ at $E=0.52$ eV. (a) Convergence with respect to the split-operator time step Δt. The abscissa is $\log_{10}(f)$, where the time step is $\Delta t = f\tau_{grid}$, with $\tau_{grid} = 20.2$ a.u. $= 0.49$ fs. Note the smooth convergence obtained with a single DVR grid which results from the nonoscillatory effective propagator (Ref. 30). The optimal $\Delta t = 6$ a.u. $= 0.15$ fs. (b) Convergence with respect to total integration time T. The solid curve has $\Delta t = 1$ a.u. $= 0.024$ fs and the dashed curve has $\Delta t = 20.2$ a.u. $= 0.49$ fs. The optimal $T = 5000$ a.u. $= 121$ fs. (c) The same as Fig. 3(b), except the absorbing potential strength parameter is increased to $\lambda = 1.5$ eV. In this case, the optimal $T = 4000$ a.u. $= 97$ fs. The power series converges more rapidly with a stronger absorbing potential.

Similar convergence properties were obtained at higher energies, in which more than one asymptotic vibrational channel is open. In general, $f \approx 0.3$ is sufficient with this STP to give results accurate to about 1%. The total time T required for convergence can be easily estimated given the size of the grid and the available translational energy. In addition, grid sizes and total propagation times can be reduced by using stronger absorbing potentials.

V. CONCLUDING REMARKS

We have described a new method to compute the absorbing boundary condition energy Green's function on a sinc-function DVR grid using a power series expansion. This is an iterative procedure for inverting the complex matrix $(E1 + i\Gamma/2 - H)$, which requires very little memory. We have demonstrated the accuracy and convergence properties of the PSG method by applying it to the calculation of the cumulative reaction probability for collinear $H + H_2$. In addition, we have qualitatively discussed the numerical efficiency of SDVR relative to the FFT method. We have concluded that both approaches have their proper regime of efficient application, and in particular, that SDVR should be superior when many grid points can be deleted from the rectangular grids required for the FFT. We believe that the computation of $N(E)$ by the PSG method has the basic ingredients necessary for the realistic study of larger chemical systems. First, by computing the microcanonical reaction probability, an averaged quantity, relatively small grids can be used which focus points in the interaction region where the *chemical* dynamics takes place. Second, by using an iterative solution for the Green's function, we avoid having to store the Hamiltonian matrix and can in principle treat larger systems.

There are several avenues for future study suggested by the present results. In this section, we consider the following: first, possible improvements in the calculation of $N(E)$ by an ABC Green's function on a grid; and second, a generalization of Makri's effective free particle propagator.

The present calculation of the cumulative reaction probability uses uniform grids in space and time to integrate the Schrödinger equation. The uniform grid in space provides a simple matrix representation of the Hamiltonian operator. The uniform grid in time facilitates a power series expansion of the ABC Green's function. This is surely *not* the most sophisticated approach. We now discuss possible improvements which amount to the use of more flexible spatial and temporal quadratures.

We conjectured in Sec. III that, for the study of reactive scattering, the SDVR uniform grid would be more computationally efficient than the Fourier uniform grid because of the ease of basis truncation with SDVR. However, a nonuniform grid DVR, e.g., Gauss–Hermite DVR, would also have all the advantages that were attributed to SDVR.[25(f)] In addition, a nonuniform grid DVR might in principle be more efficient because it originates from adaptive quadrature. For example, the $H + O_2$ system, which has a deep well in the interaction region, is represented more efficiently in Gauss–Hermite DVR than in SDVR.[19(c)] A uniform grid would also be very inefficient in the case of strongly exoergic systems, e.g., the $F + H_2$ reaction. In general, treating complicated systems will require that the grid be adapted to the shape of the PES. In the case of collinear $H + H_2$, which has no deep wells and is thermoneutral, the uniform grid defined in SDVR is sufficient.

The uniform grid in time is used to construct a power series expansion of the ABC Green's function. This a simple, but primitive approach. The most sophisticated alternative would be to diagonalize the complex Hamiltonian, giving the time integral in Eq. (2.7b) in one "iteration." This is analogous to preconditioning the linear system (2.10) with the exact inverse of the Hamiltonian. Intermediate between these two extremes is the short iterative Lanczos propagator (SIL) developed by Park and Light[20(a)] and systematically tested by Leforestier et al.[40(a)] In this method, a vector ψ_0 propagated for a small duration t to yield ψ_t is given by its spectral representation

$$\psi_t \cong \{\exp[-i(H - i\Gamma/2)t/\hbar]\}_{SIL} \psi_0$$

$$\equiv \sum_{k=1}^{K} \mathbf{v}_k c_k \exp(-i\epsilon_k t/\hbar) \qquad (5.1a)$$

where

$$c_k = \mathbf{v}_k^T \cdot \psi_0 \qquad (5.1b)$$

and $(\mathbf{v}_k)$ and (ϵ_k) are the complex eigenvectors and eigenvalues, respectively, computed from diagonalizing the tridiagonal matrix obtained from K Lanczos iterations.[19(d),21] Three features of the SIL method are worth mentioning. First, if the propagation duration t is relatively small, only a handful of Lanczos iterations are required to accurately represent ψ_t.[40(a)] Second, given the initial vector ψ_0 and the number of Lanczos iterations intended, the duration t over which SIL is accurate can be predetermined.[20(a),20(b)] This last point explicitly demonstrates the adaptive nature of the SIL integrator. And third, since SIL gives the time dependence of the propagated vector analytically, the Fourier transform of the propagated vector can be trivially obtained. As such, it seems very useful for the integral representation of the ABC Green's function. Indeed, consider splitting the time integral in Eq. (2.7b) into N terms, each for a duration $\Delta t_n = t_n - t_{n-1}$, where $t_0 = 0$ and $t_N = T$ the finite upper time limit. One can show that the jth column of $G^+(E)$ becomes

$$\mathbf{G}_j(E) = \sum_{n=1}^{N} \sum_{k=1}^{K(n)} \mathbf{v}_{knj} c_{knj} f_{knj}(E), \qquad (5.2a)$$

where

$$c_{k1j} = \mathbf{v}_{k1j}^T \cdot \psi_0 = \mathbf{v}_{k1j}^T \cdot \mathbf{I}_j = (\mathbf{v}_{k1j})_j, \qquad (5.2b)$$

$$c_{knj} = \mathbf{v}_{knj}^T \cdot \psi_{t_{n-1}}, \quad \text{for} \quad n > 1, \qquad (5.2c)$$

$$f_{knj}(E) = \frac{\Delta t_n}{i\hbar} \exp[i(E - \epsilon_{knj})(t_n + t_{n-1})/2\hbar]$$

$$\times \text{sinc}[(E - \epsilon_{knj})\Delta t_n/2\hbar], \qquad (5.2d)$$

and where sinc(x) is defined in Eq. (3.4). In Eq. (5.2) $(\mathbf{v}_k)_{nj}$ and $(\epsilon_k)_{nj}$ are the complex eigenvectors and eigenvalues, respectively, for the nth time duration in the computation of the jth column of $G^+(E)$. The key for the efficiency of this method is that the propagator obtained after K Lanczos iterations is accurate for a time *longer* than $K\Delta t$, where Δt is the optimal split-operator propagation duration. Numerical tests of this approach are underway.

We consider the generalization of Makri's effective free particle kernel. For simplicity, we consider a 1D system with mass m. The success of Makri's propagator is based on the filtering of high frequency momenta which are unimportant and difficult to integrate. To this end, we denote a general momentum filter by $w(p)$ with the property that it goes to zero as $p \to \pm \infty$. This gives a generalized effective free particle kernel given by

$$\langle x' | \exp(-ip^2 t/2m\hbar) | x \rangle_{\text{eff}} \equiv \int_{-\infty}^{+\infty} \frac{dp}{2\pi\hbar} \exp(ipx'/\hbar)$$
$$\times \exp(-ip^2 t/2m\hbar)$$
$$\times \exp(-ipx/\hbar) w(p). \quad (5.3)$$

By the convolution theorem,[55] one can show that the asymptotic form of this effective kernel is given by

$$\lim_{\alpha \to \infty} \langle x' | \exp(-ip^2 t/2m\hbar) | x \rangle_{\text{eff}} = W(x'-x), \quad (5.4a)$$

where

$$\alpha = \frac{x'-x}{t} \quad (5.4b)$$

and

$$W(x) = \int_{-\infty}^{+\infty} \frac{dp}{2\pi\hbar} e^{ipx/\hbar} w(p) \quad (5.4c)$$

is the Fourier transform of the momentum filter. In the trivial case where $w(p) = 1$, i.e., no filter, then Eq. (5.3) gives the exact kernel. If we set $w(p) = 1$ if $|p| < p_{\max}$ and zero otherwise, we recover Makri's effective kernel, which we have used in a uniform grid DVR. Its asymptotic form (3.12a) is trivially obtained from Eq. (5.4). Now consider the case where $w(p)$ has a Gaussian form

$$w(p) = \exp(-p^2/2\Delta p^2). \quad (5.5a)$$

Then the effective propagator is

$$\langle x' | \exp(-ip^2 t/2m\hbar) | x \rangle_{\text{eff}}$$
$$= \langle x' | \exp(-ip^2 t/2m\hbar) | x \rangle_{\text{exact}}$$
$$\times g_{\text{smooth}}(x',x,t;m,\Delta x), \quad (5.5b)$$

where

$g_{\text{smooth}}(x',x,t;m,\Delta x)$

$$= \left\{ \exp\left[\frac{-iB^3(x'-x)^2}{A^2+B^2} \right] \exp\left[\frac{i}{2} \tan^{-1}\left(\frac{B}{A}\right) \right] \right\}$$
$$\times \left\{ \left(\frac{A^2}{A^2+B^2} \right)^{1/4} \exp\left[\frac{-AB^2(x'-x)^2}{A^2+B^2} \right] \right\},$$

$$A = \frac{1}{2\Delta x^2}, \quad B = \frac{m}{2\hbar t}, \quad (5.5c)$$

and

$$\Delta x \Delta p = \hbar. \quad (5.5d)$$

This effective propagator has three remarkable features. First, it is clear from Eq. (5.5) that the phase factor in g_{smooth} identically cancels the very rapid oscillations in the exact free particle kernel as t goes to zero, i.e., $B \gg A$. This is crucial to the stability of the effective propagator. Second, the form of the filtering function, a Maxwell–Boltzmann distribution, suggests that we are imposing an artificial temperature for which $k_B T_{\text{filter}}/2 = \Delta p^2/2m$. This is analogous to the approach of Coalson[33] in which an artificial temperature was used to compute dipole autocorrelation functions. Imposing an artificial temperature in the propagator is tantamount to propagation in complex time, which Doll[34] showed is stable even with numerical matrix multiplication (NMM). In addition, Thirumalai and Berne[35] have carried out NMM calculations of the propagator in complex time in the study of (nonartificial) temperature dependent correlation functions. Using $\Delta p = p_{\max}$ for the $N(E)$ calculations at $E = 0.52$ eV, the artificial temperature is $T_{\text{filter}} \approx 50\,000$ K. Clearly this temperature is not low enough to interfere with the microcanonical density operator, but might be low enough to filter out the high momentum components which are unimportant to the dynamics.

Finally, an approximation to the coordinate propagator containing the same real Gaussian as in Eq. (5.5c) has been previously obtained in the context of "distributed approximating functions" by Kouri, Hoffman, and co-workers.[32(c),32(d)] They were also seeking a more well behaved coordinate free particle propagator. To this end, they analytically propagated a Hermite polynomial fit to an initial wave packet and observed what effective propagator would have evolved the exact wave packet to obtain the same result. It is clear, from the present analysis, that their approach is tantamount to filtering out high frequency components in the propagator from the start, without the need to fit an initial wave packet. The intriguing aspect of this propagator, as Kouri, Hoffman, and co-workers correctly point out,[32(c),32(d)] is the possibility of performing a path integral Monte Carlo evaluation of the real time propagator using the real Gaussian in Eq. (5.5c) as the sampling distribution. However, there are some potential problems that may arise from this strategy. First, importance sampling based on free particle dynamics may require very short time slices and may not be able to anticipate the details of long-time dynamics. Second, a Gaussian filter, which is characterized by only one parameter, may not be

flexible enough to damp the high momentum components while giving the small components unit weight. Nevertheless, the possible success of this approach bears further thought and numerical testing.

ACKNOWLEDGMENTS

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