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A polynomial expansion of the quantum propagator, the Green's function, and the spectral density operator

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One of the methods for calculating time propagators in quantum mechanics uses an expansion of $e^{-i\hat{H}t/\hbar}$ in a sum of orthogonal polynomial. Equations involving Chebychev, Legendre, Laguerre, and Hermite polynomials have been used so far. We propose a new formula, in which the propagator is expressed as a sum in which each term is a Gegenbauer polynomial multiplied with a Bessel function. The equations used in previous work can be obtained from ours by giving specific values to a parameter. The expression allows analytic continuation from imaginary to real time, transforming thus results obtained by evaluating thermal averages into results pertaining to the time evolution of the system. Starting from the expression for the time propagator we derive equations for the Green's function and the density of states. To perform computations one needs to calculate how the polynomial in the Hamiltonian operator acts on a wave function. The high order polynomials can be obtained from the lower ordered ones through a three term recursion relation; this saves storage and computer time. As a numerical test, we have computed the bound state spectrum of the Morse oscillator and the transmission coefficient for tunneling through an Eckart barrier. We have also studied the evolution of a Gaussian wave packet in a Morse potential well.
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I. INTRODUCTION

To solve time dependent problems in quantum mechanics we must find an accurate and numerically efficient representation of the propagator $\hat{U}(t)=e^{-i\hat{H}t/\hbar}$. Here $\hat{H}$ is the Hamiltonian of the system, t is time and $\hbar$ is Planck's constant. There are many methods for achieving this goal.[1–44] One approach[1,2] is based on Campbell–Baker–Hausdorff[3,45,46] formula, which provides an equation for the short-time propagator $\hat{U}(\tau)$ that is easy to evaluate numerically. To obtain the wave function at the time $t=n\tau$, one applies $\hat{U}(\tau)^n$ to the initial wave function.

A second method expresses the propagator in terms of powers of the Hamiltonian, calculated by a recursion procedure that obtains $\hat{H}^n$ from $\hat{H}^{n-1}$ and $\hat{H}^{n-2}$. This recursive calculation is essential: it saves storage and diminishes the computer power needed in the calculations. Examples of such calculations are the Recursive Residue Generation Method developed in Wyatt's group[29,30] and the method of Park and Light.[16] Both use the Lanczos procedure[47] as their main computational tool.

In a third class of methods, which is the subject of our paper, the propagator is expressed in a "degenerate kernel" form,[48]

$$\hat{U}(t)=e^{-i\hat{H}t/\hbar}=\sum_{m=0}^{n} P_m(\hat{H})g_m(t). \tag{1}$$

Here $P_m(\hat{H})$ is a polynomial of order m and $g_m(t)$ is a function of time. The number n of terms in the sum depends on the polynomial used and on the length of time for which the propagator is needed. This type of formula has been used by Tal Ezer and Kosloff,[7,8] DePristo, Haug, and Metiu,[36] Kouri, Hoffmann and their co-workers,[17–27] Hu,[42] and by Vijay *et al.*[43] It has several advantages. (1) The polynomials $P_m(\hat{H})$ used in it are such that $P_m(\hat{H})$ can be calculated from $P_{m-1}(\hat{H})$ and $P_{m-2}(\hat{H})$. This saves storage and speeds up the calculation. (2) The representation of $\hat{U}(t)$ is analytic with respect to time: the propagator for real time can be obtained from the propagator for imaginary time,[7,36] if the latter is represented in the form of Eq. (1). Since imaginary time propagators can be calculated for many degrees of freedom, by Quantum Monte Carlo, this may provide a method for calculating real time propagators for systems with many degrees of freedom.[36] (3) By using Fourier transforms with respect to time, the propagator can be connected to the Green's function $G(E)=(E-\hat{H})^{-1}$ and to the density of states $\rho(E)=\delta(E-\hat{H})$. When the transform can be performed analytically, one obtains for $G(E)$ and $\rho(E)$ an expression of type Eq. (1). The methods based on Eq. (1) can also be used for the time dependent Hamiltonian if one uses an extended Hilbert space in which time is treated like a space coordinate.[11,31]

Past applications of Eq. (1) have been used for P_m Chebyshev,[8] Legendre,[23,36] Laguerre,[42] and Hermite[43] polynomials. In this paper we derive a more general formula of type Eq. (1) for $U(t)$, $G(E)$, and $\rho(E)$, in which P_m is a Gegenbauer polynomial and $g_n(t)$ is proportional to a Bessel function. The equations used in previous work can be obtained from ours by giving particular values to a parameter.

In Sec. II, we derive the new equation for the evolution operator and show how various special cases can be obtained from it. Derivations of the equations for the density of states and the Green's function are presented in Secs. III and IV, respectively. The quantum propagator in complex time is explicitly worked out in Sec. V, using Chebyshev polynomials as an example. A few simple applications are made in Sec. VI. Their purpose is to illustrate the accuracy and the convergence of the method. A summary can be found in Sec. VII.

II. TIME PROPAGATION

For a time independent Hamiltonian $\hat{H}$ the wave function $|\psi(x,t)\rangle$ at time t is obtained from the initial wave function $|\psi(x,0)\rangle$ by using

$$|\psi(x,t)\rangle = e^{-i\hat{H}t/\hbar}|\psi(x,0)\rangle, \tag{2}$$

where $e^{-i\hat{H}t/\hbar}$ is the time evolution operator in the Schrödinger representation. In what follows we are performing formal manipulations using functions of the Hamiltonian operator. All these functions are defined by the spectral decomposition,

$$f(\hat{H})|\psi,0\rangle = \sum_{n=0}^{N} |E_n\rangle f(E_n)\langle E_n|\psi(x,0)\rangle. \tag{3}$$

The ket$|E_n\rangle$ is an eigenfunction of the Hamiltonian $\hat{H}$ corresponding to the eigenvalue E_n and $|\psi(x,0)\rangle$ is the initial state of the system. Equation (3) contains only those eigenstates of the Hamiltonian that overlap with the initial wave function. This equation can be used for scattering wave functions if a box normalization is employed.

Our strategy is to find a convenient representation of $e^{-iE_nt/\hbar}$ of the form,

$$e^{-iE_nt/\hbar} = \sum_{m=0}^{\infty} g_m(t)P_m(E_n). \tag{4}$$

If we use for f in Eq. (3) $f(\hat{H}) = e^{-i\hat{H}t/\hbar}$ and in the resulting expression we replace $e^{-iE_nt/\hbar}$ with Eq. (4), we obtain

$$e^{-i\hat{H}t/\hbar} = \sum_{n=0}^{N} |E_n\rangle \sum_{m=0}^{\infty} g_m(t)P_m(E_n)\langle E_n|\psi(x,0)\rangle. \tag{5}$$

Interchanging the sums and using the definition,

$$P_m(\hat{H})|\psi,0\rangle = \sum_{n=0}^{N} |E_n\rangle P_m(E_n)\langle E_n|\psi(x,0)\rangle, \tag{6}$$

allows us to write Eq. (5) as

$$e^{-i\hat{H}t/\hbar}|\psi,0\rangle = \sum_{m=0}^{\infty} g_m(t)P_m(\hat{H})|\psi(x,0)\rangle. \tag{7}$$

The right-hand side of Eq. (7) is now well defined, since there is no ambiguity in the meaning of polynomials of the Hamiltonian. However, since we use the spectral decomposition in the derivation, we must make sure that the polynomial $P_m(E_n)$ is well defined. If we use Chebyshev or Legendre polynomials, the argument E_n must take values between -1 and 1. To ensure this, we scale the original Hamiltonian. We have already argued that because the propagator is applied to the initial state $|\psi(x,0)\rangle$ the range of values of E_n is limited. Let $E_{\max}$ be the largest value of E_n needed in the expansion of the propagator, in a formula of the type shown in Eq. (3), and $E_{\min}$ the smallest. Then, the eigenvalues $\bar{E}_n$ of the Hamiltonian $\hat{H}_{sc}$ defined by

$$\hat{H} \equiv \Delta\lambda \hat{H}_{sc} + \bar{\lambda} \tag{8}$$

take values between -1 and 1. Here $\Delta\lambda = (E_{\max} - E_{\min})/2$ and $\bar{\lambda} = (E_{\max} + E_{\min})/2$.

After this preparation we can proceed now to derive Eq. (14), which is the key formula of this paper. We first expand the evolution operator in a power series,

$$\left(\frac{t\Delta\lambda}{\hbar}\right)^{\nu} e^{\pm i\hat{H}t/\hbar} = e^{\pm i\bar{\lambda}t/\hbar} \sum_{n=0}^{\infty} \frac{(\pm i)^n(\hat{H}_{sc})^n}{n!} \left(\frac{t\Delta\lambda}{\hbar}\right)^{\nu+n}. \tag{9}$$

The reason for multiplying by the factor $(t\Delta\lambda/\hbar)^{\nu}$, where ν is an arbitrary parameter, will be clarified later. We now substitute the following Bessel function $[J_{\nu}(Z)]$ expansion of a power[49,50]

$$Z^{\mu} = 2^{\mu} \sum_{k=0}^{\infty} \frac{(\mu+2k)\Gamma(\mu+k)}{k!} J_{\mu+2k}(Z) \tag{10}$$

[where $\Gamma(\mu+k)$ is the Gamma function] in Eq. (9) to obtain,

$$\left(\frac{t\Delta\lambda}{\hbar}\right)^{\nu} e^{\pm i\hat{H}t/\hbar} = e^{\pm i\bar{\lambda}t/\hbar} \sum_{n=0}^{\infty} \sum_{k=0}^{\infty} \frac{(\pm i)^n(\hat{H}_{sc})^n}{n!} \times \frac{2^{\nu+n}(\nu+n+2k)\Gamma(\nu+n+k)}{k!} \times J_{\nu+n+2k}\left(\frac{t\Delta\lambda}{\hbar}\right). \tag{11}$$

In this expression we rearrange the double infinite summation in Eq. (11) by setting $n = m - 2k$, to obtain

$$\left(\frac{t\Delta\lambda}{\hbar}\right)^{\nu} e^{\pm i\hat{H}t/\hbar} = e^{\pm i\bar{\lambda}t/\hbar} \sum_{m=0}^{\infty} \sum_{k=0}^{m/2} \frac{(\pm i)^{m-2k}(\hat{H}_{sc})^{m-2k}}{k!(m-2k)!} \times 2^{\nu+m-2k}(\nu+m)\Gamma(\nu+m-k) \times J_{\nu+m}\left(\frac{t\Delta\lambda}{\hbar}\right). \tag{12}$$

Now the summation over the index k in Eq. (12) is identified as the coefficient of α^m in the expansion of $(1 - 2\alpha\hat{H}_{sc} + \alpha^2)^{-\nu}$ in ascending powers of α. This is also known as one of the definitions of Gegenbauer's ultraspherical polynomial, $C_m^{(\nu)}(\hat{H}_{sc})$, which, in turn, is related to the symmetric Jacobi polynomial, $P_m^{(\alpha,\alpha)}(\hat{H}_{sc})$, as given below,[50,51]

$$C_m^{(\nu)}(\hat{H}_{sc}) = \sum_{k=0}^{m/2} \frac{(-1)^k 2^{m-2k}\Gamma(\nu+m-k)(\hat{H}_{sc})^{m-2k}}{(m-2k)!k!\Gamma(\nu)} = \frac{\Gamma(m+2\nu)\Gamma(\nu+1/2)}{\Gamma(2\nu)\Gamma(m+\nu+1/2)} P_m^{(\nu-1/2,\nu-1/2)}(\hat{H}_{sc}). \tag{13}$$

Here ν is restricted to be greater than $-1/2$. We see that the introduction of the factor $(t\Delta\lambda/\hbar)^{\nu}$ in Eq. (9) helps us identify the associated orthogonal polynomial in the expansion of the propagator. The final expression for the time evolution operator, expressed in terms of ultraspherical Gegenbauer polynomials, is

$$e^{\pm i\hat{H}t/\hbar}=\left(\frac{2\hbar}{t\Delta\lambda}\right)^{\nu}e^{\pm i\bar{\lambda}t/\hbar}\Gamma(\nu)\sum_{m=0}^{\infty}(\pm i)^m(m+\nu)\times J_{m+\nu}\left(\frac{t\Delta\lambda}{\hbar}\right)C_m^{\nu}(\hat{H}_{sc}). \tag{14}$$

This is the central equation of this paper.

By using Eq. (13) we can also express the time propagator in terms of symmetric Jacobi polynomials as

$$e^{\pm i\hat{H}t/\hbar}=\sqrt{\pi}e^{\pm i\bar{\lambda}t/\hbar}\left(\frac{\hbar}{2t\Delta\lambda}\right)^{\alpha+1/2}\times\sum_{m=0}^{\infty}(\pm i)^m(2m+2\alpha+1)\frac{\Gamma(m+2\alpha+1)}{\Gamma(m+\alpha+1)}\times J_{m+\alpha+1/2}\left(\frac{t\Delta\lambda}{h}\right)P_m^{(\alpha,\alpha)}(\hat{H}_{sc}), \tag{15}$$

where $\alpha(=\nu-1/2)$ is restricted to be greater than -1. Parenthetically, we note that Eq. (14) may also be considered as an expansion of planewaves in terms of spherical harmonics in d-dimensions, where $d=2(\nu+1)$.[52]

We now briefly discuss the convergence properties of Eq. (14). It is well known[53] that the series, $\Sigma_p C_p^{(n)}(\cos\theta)\lambda^p$ is absolutely convergent if $|\lambda|\leqslant 1$; thus the series in Eq. (14) can always be made convergent by taking enough terms. As $\mu\rightarrow\infty$, $J_\mu(Z)$ behaves[54] as $1/\sqrt{2\pi\mu}(eZ/2\mu)^\mu$. Thus, $(m+\nu)$ $J_{m+\nu}(t\Delta\lambda/\hbar)$ factor in Eq. (14) can be made exponentially vanishing if $(2\pi/\nu)^{1/\nu}\nu$ is greater than $eZ/2$; that is, the coefficient of the ultraspherical polynomials in Eq. (14) can be made less than unity, when $t\Delta\lambda/\hbar$ is smaller than the order, $(m+\nu)$, of the Bessel function. We thus see that the series Eq. (14) eventually converges and the convergence is determined by the factor $t\Delta\lambda/\hbar=t(E_{\max}-E_{\min})/2\hbar$. The convergence is controlled by the difference between the highest energy and the lowest energy of the energy eigenstates contained in the initial wave function, $|\psi(x,0)\rangle$. In the numerical tests we have found that the parameter ν should not be large. We will examine the choice of ν for a model system later.

We now comment on the actual implementation of Eq. (14) or (15). We can absorb the Gamma functions and other factors appearing in Eq. (15) into the well-known three-term recursions possessed by the Jacobi polynomials,[49] $m(m+2\alpha)P_m^{(\alpha,\alpha)}(\hat{H}_{sc})=(m+\alpha)[(2m+2\alpha-1)\hat{H}_{sc}P_{m-1}^{(\alpha,\alpha)}(\hat{H}_{sc})-(m+\alpha-1)P_{m-2}^{(\alpha,\alpha)}(\hat{H}_{sc})]$. We can then conveniently write the evolution operator as follows:

$$e^{\pm i\hat{H}t/\hbar}=e^{\pm i\bar{\lambda}t/\hbar}\left(\frac{2\hbar}{t\Delta\lambda}\right)^{\alpha+1/2}\sum_{m=0}^{\infty}(\pm i)^m\times J_{m+\alpha+1/2}\left(\frac{t\Delta\lambda}{\hbar}\right)X_m^{(\alpha)}(\hat{H}_{sc}) \tag{16}$$

with the following recursion relation for $X_m^{(\alpha)}(\hat{H}_{sc})$:

$$X_m^{(\alpha)}(\hat{H}_{sc})=\frac{2m+2\alpha+1}{m}\left[\hat{H}_{sc}X_{m-1}^{(\alpha)}(\hat{H}_{sc})-\frac{m+2\alpha-1}{2m+2\alpha-3}X_{m-2}^{(\alpha)}(\hat{H}_{sc})\right], \tag{17}$$

where $X_0^{(\alpha)}(\hat{H}_{sc})=\Gamma(\alpha+3/2)$, $X_1^{(\alpha)}(\hat{H}_{sc})=2\Gamma(\alpha+5/2)\hat{H}_{sc}$, and $X_2^{(\alpha)}(\hat{H}_{sc})=2\Gamma(\alpha+7/2)\hat{H}_{sc}^2-(\alpha+5/2)\Gamma(\alpha+3/2)$. It is convenient to start the recursion from $m=3$, to avoid any artificial divergence that may occur in the second factor of the right-hand side of Eq. (17).

Now, we discuss various special cases of the general expression for the time evolution operator, as given in Eq. (14) or Eq. (15). As α in Eq. (15) is an arbitrary parameter (except that it is constrained to be greater than -1), Eq. (15) represents a family of expansions for the evolution operator. In fact, the parameter α will also dictate the final rate of convergence of Eq. (15) and we will analyze this issue by performing the numerical calculations. Furthermore, other well-known time propagators, utilizing orthogonal polynomials, can be obtained by specializing the free parameter, α in Eq. (15) as shown below.

Case 1: For $\alpha=-1/2$, Eq. (15) gives the time evolution operator expressed in terms of the Chebyshev polynomials, $T_m(\hat{H}_{sc})$. Using the known relation between symmetric Jacobi and Chebyshev polynomials,[49] $P_m^{(-1/2,-1/2)}(\hat{H}_{sc})=[(2m)!/2^{2m}(m!)^2]\ T_m(\hat{H}_{sc})$ and an identity involving Gamma functions, $\sqrt{\pi}\Gamma(2m)=2^{2m-1}\Gamma(m)\Gamma(m+1/2)$, turns Eq. (15) into

$$e^{\pm i\hat{H}t/\hbar}=e^{\pm i\bar{\lambda}t/\hbar}\sum_{m=0}^{\infty}(2-\delta_{m0})(\pm i)^m J_m\left(\frac{t\Delta\lambda}{\hbar}\right)T_m(\hat{H}_{sc}). \tag{18}$$

This was used by Tal-Ezer and Kosloff.[8] One can also obtain Eq. (18) directly from the Jacobi–Anger expansion, $\exp(iZ\cos\theta)=\Sigma_{m=-\infty}^{\infty}i^mJ_m(Z)\exp(im\theta)$, which is an expansion of a planewave in a series of cylindrical waves.[55]

Case 2: For $\alpha=0$, the Jacobi polynomial, $P_m^{(0,0)}(\hat{H}_{sc})$ in Eq. (15) is equal to the Legendre polynomial, $P_m(\hat{H}_{sc})$;[49] therefore Eq. (15) simplifies to

$$e^{\pm i\hat{H}t/\hbar}=e^{\pm i\bar{\lambda}t/\hbar}\sum_{m=0}^{\infty}(2m+1)(\pm i)^m j_m\left(\frac{t\Delta\lambda}{\hbar}\right)P_m(\hat{H}_{sc}), \tag{19}$$

where j_m is the spherical Bessel function of the first kind. This expansion of the time evolution operator has been used by DePristo, Haug, and Metiu[36] and Huang *et al.*[23] Equation (19) is also known as the expansion of plane waves in terms of spherical harmonics in three dimensions.[52]

Case 3: For $\alpha=1/2$, the propagator is expressed in terms of Chebyshev polynomials of the second kind, $U_m(\hat{H}_{sc})$, through $2\Gamma(m+3/2)U_m(\hat{H}_{sc})=(m+1)!\sqrt{\pi}P_m^{(1/2,1/2)}(\hat{H}_{sc})$.[49] This relationship simplifies to

$$e^{\pm i\hat{H}t/\hbar}=\left(\frac{2\hbar}{t\Delta\lambda}\right)e^{\pm i\bar{\lambda}t/\hbar}\sum_{m=0}^{\infty}(m+1)(\pm i)^m \times J_{m+1}\left(\frac{t\Delta\lambda}{\hbar}\right)U_m(\hat{H}_{sc}). \quad (20)$$

By changing $it/\hbar$ to $\beta=1/k_BT$, where k_B is Boltzmann's constant and T is temperature, we obtain expansions for the Boltzmann operator, $\exp(-\beta\hat{H})$. For example, making this transformation in Eq. (14) leads to

$$e^{-\beta\hat{H}}=\Gamma(\nu)e^{-\beta\bar{\lambda}}\left(\frac{2}{\beta\Delta\lambda}\right)^{\nu}\sum_{m=0}^{\infty}(-1)^m(m+\nu) \times I_{m+\nu}(\beta\Delta\lambda)C_m^{(\nu)}(\hat{H}_{sc}). \quad (21)$$

Similar expansions have been used by DePristo *et al.*[36] (who used Legendre polynomials) and by Kosloff[7] (who used Chebyshev polynomials). The equations for the Boltzmann operator, obtained from Eqs. (14) and (15) are new.

The fact that the expansion Eq. (14) can be analytically continued from imaginary time to real time can be used to calculate real time dynamics by performing imaginary time calculations and analytically continuing the result. Since the imaginary time calculations can be performed for many degrees of freedom (by Quantum Monte Carlo) this procedure offers a possibility of calculating quantum dynamics for many degrees of freedom.[36]

III. THE SPECTRAL DENSITY OPERATOR

Series representations of the density of states operator, $\rho(E)=\delta(E-\hat{H})$, in terms of Chebyshev as well as Legendre polynomials were given by Kouri and co-workers.[22–25] In the following, we obtain a more general expression for this operator from Eq. (14). The known results, that use Chebyshev or Legendre polynomials, are obtained as special cases.

Before we proceed with the derivation, it is important to realize that $\delta(E-\hat{H})$, in practical terms, only refers to a certain limiting process; there are several functions which, in specific limits, mimic the behavior of the δ function. The typical examples are $(1/2)\zeta\exp(-|E-\hat{H}|/\zeta)$, $(1/\pi)\zeta/[(E-\hat{H})^2+\zeta^2]$, $1/\zeta\sqrt{\pi}\exp[-(E-\hat{H})^2/\zeta^2]$, and $1/(\pi\zeta)\mathrm{sinc}([E-\hat{H}]/\zeta)$ [where $\mathrm{sinc}(x)=\sin(x)/x$], in the limit $\zeta\to 0$. Any one of these expressions could be utilized to derive equations for the spectral density operator.

We use the Fourier integral theorem[56] to obtain an integral representation of the approximation of the spectral density operator. We choose $1/(\pi\zeta)\mathrm{sinc}([E-\hat{H}]/\zeta)$ as an approximation because it gives the simplest integral representation, that does not involve an arbitrary damping function. Furthermore, the choice of the sinc function makes the integration over the time variable analytical. We thus have,

$$\delta(E-\hat{H})=\lim_{\zeta\to 0}\frac{1}{\pi\zeta}\mathrm{sinc}\left(\frac{E-\hat{H}}{\zeta}\right) =\lim_{T\to\infty}\frac{1}{2\pi\hbar}\int_{-T}^{T}dt\, e^{iEt/\hbar}e^{-i\hat{H}t/\hbar}. \quad (22)$$

We can now substitute Eq. (14) for the time evolution operator, $e^{-i\hat{H}t/\hbar}$, interchange the integration and the summation, and carry out the integration over the time variable, t, from $-\infty$ to ∞ analytically. By writing $E_{sc}=(E-\bar{\lambda})/\Delta\lambda$, we obtain

$$\delta(E-\hat{H})=\frac{2^{2\nu}}{2\pi\Delta\lambda}\sum_{m=0}^{\infty}(\nu+m)\frac{\Gamma(m+1)[\Gamma(\nu)]^2}{\Gamma(m+2\nu)} \times(1-E_{sc}^2)^{\nu-1/2}C_m^{(\nu)}(E_{sc})C_m^{(\nu)}(\hat{H}_{sc}). \quad (23)$$

To pass from Eq. (22) to (23), we have utilized the following known integrals:

(a) $\int_0^\infty dx x^\lambda \sin(bx)J_\mu(ax)=2^{1+\lambda}a^{-(2+\lambda)}b[\Gamma((2+\lambda+\mu)/2)/\Gamma((\mu-\lambda)/2)]F((2+\lambda+\mu)/2,(2+\lambda-\mu)/2;3/2;b^2/a^2)$, with $0<b<a$ and $(-\mathrm{Re}\,\mu-1)<1+\mathrm{Re}\,\lambda<3/2$,

(b) $\int_0^\infty dx x^\lambda \cos(bx)J_\mu(ax)=2^\lambda a^{-(1+\lambda)}[\Gamma((1+\lambda+\mu)/2)/\Gamma((\mu-\lambda+1)/2)]F((1+\lambda+\mu)/2,(1+\lambda-\mu)/2;1/2;b^2/a^2)$, with $0<b<a$ and $-\mathrm{Re}\,\mu<1+\mathrm{Re}\,\lambda<3/2$, where J, Γ, and F are the Bessel, Gamma, and hypergeometric functions, respectively, along with a known identity involving the hypergeometric functions, $F(a,b;c;z)=(1-z)^{c-a-b}F(c-a,c-b;c;z)$.[49] Finally, we have used the relations involving the hypergeometric function and the ultraspherical polynomial:

(a) $(m+\nu)B(m+1,\nu)C_{2m}^{(\nu)}(E_{sc})=(-1)^mF(-m,m+\nu;1/2;E_{sc}^2)$ and

(b) $B(m+1,\nu)C_{2m+1}^{(\nu)}(E_{sc})=(-1)^m 2E_{sc}F(-m,m+\nu+1;3/2;E_{sc}^2)$, where B is the beta function.[49]

The interchange of integration and summation is justified because in practical situations, Eq. (22) applies to a wave packet and Eq. (14) for the evolution operator is a convergent expression. This point has also been clarified by Kouri and co-workers.[27] The separation of E_{sc} and $\hat{H}_{sc}$ in Eq. (23) allows substantial computational savings when one desires results at many energies. This is because the Hamiltonian operation on a vector can be done independently and stored, and this can be used at later stages of analysis for all energies.

Other well-known expressions for the spectral density operator can be obtained by specializing the free parameter, ν, in Eq. (23). For example,

Case 1: With $\nu=0$, the limiting relation, $\lim_{\nu\to 0}(1/\nu)C_m^{(\nu)}(\hat{H}_{sc})=(2/m)T_m(\hat{H}_{sc})$, transforms Eq. (23) into the following expression involving Chebyshev polynomials:

$$\delta(E-\hat{H})=\frac{1}{\pi\Delta\lambda}\sum_{m=0}^{\infty}(2-\delta_{m0})\frac{T_m(E_{sc})}{\sqrt{1-E_{sc}^2}}T_m(\hat{H}_{sc}). \quad (24)$$

Case 2: Using $\nu=1/2$ and $C_m^{(1/2)}(\hat{H}_{sc})=P_m(\hat{H}_{sc})$ in Eq. (23), we recover the Legendre polynomial expression,

$$\delta(E-\hat{H})=\frac{1}{2\Delta\lambda}\sum_{m=0}^{\infty}(2m+1)P_m(E_{sc})P_m(\hat{H}_{sc}). \quad (25)$$

Case 3: For $\nu=1$ and $C_m^{(1)}(\hat{H}_{sc})=U_m(\hat{H}_{sc})$ in Eq. (23), the spectral density operator is expressed in terms of the Chebyshev polynomials of second kind,

$$\delta(E-\hat{H}) = \frac{2}{\pi\Delta\lambda}\sum_{m=0}^{\infty}\sin[\arccos(E_{sc})]\ \ U_m(E_{sc})\ \ U_m(\hat{H}_{sc}). \quad (26)$$

We note that Eqs. (24) and (25) were used by Kouri and co-workers[24] for computing bound states as well as resonances. Equation (24) has also been used as the building block for certain implementations of spectral filter algorithms.[39–41,43,44]

IV. THE GREEN'S FUNCTION

In the following, we derive a series expansion for the general quantum mechanical Green's function using the framework developed in this paper. We first start with the following representation of the causal Green's function:

$$G(E^+)=\lim_{\epsilon\to 0}\frac{i}{2\pi}\frac{1}{(E+i\epsilon-\hat{H})} = \lim_{\epsilon\to 0}\frac{1}{2\pi\hbar}\int_0^{\infty}dt e^{iEt/\hbar}e^{-i\hat{H}t/\hbar}e^{-\epsilon t/\hbar}. \quad (27)$$

We substitute Eq. (14) for the propagator, $e^{-i\hat{H}t/\hbar}$, interchange the integration and the summation operations, and carry out the integral over the time t analytically, to obtain

$$G(E^+)=\frac{i}{\pi\Delta\lambda}\sum_{m=0}^{\infty}\frac{(m+\nu)}{[2(E_{sc}+i\epsilon_{sc})]^{m+1}}B(\nu,m+1) \times F\left(\frac{m+1}{2},\frac{m+2}{2};m+\nu+1;\frac{1}{(E_{sc}+i\epsilon_{sc})^2}\right) \times C_m^{(\nu)}(\hat{H}_{sc}), \quad (28)$$

where $\epsilon_{sc}=\epsilon/\Delta\lambda$ and $E_{sc}=(E-\bar{\lambda})/\Delta\lambda$. Here $B(x,y)$ and F are the beta function[49] and the hypergeometric function,[49] respectively. The interchange of the integration and the summation operations is justified here, since Eq. (14) is a convergent series and the integral in Eq. (27) is convergent. To pass from Eq. (27) to Eq. (28), we have used,[49] $\int_0^{\infty}dx \exp(-\alpha x)J_\nu(\beta x)x^{\mu-1}=(\beta/2)^{\nu}\alpha^{-(\mu+\nu)}[\Gamma(\mu+\nu)/\Gamma(\nu+1)]F((\mu+\nu)/2,(\mu+\nu+1)/2;\nu+1;-(\beta^2/\alpha^2))$, which is valid for $\mathrm{Re}(\mu+\nu)>0$ and $\mathrm{Re}(\alpha\pm i\beta)>0$. The expression for the anticausal Green's function can be obtained by replacing i with $-i$ in Eq. (28). Thus, Eq. (28) provides a general recursive expression for the Green's function. Several special representations can be obtained by taking specific values of the free parameter, ν. For example,

Case 1: With $\nu=0$, the hypergeometric series in Eq. (28) simplifies to

$$G(E^+)=\left(\frac{1}{2\pi\Delta\lambda}\right)\sum_{m=0}^{\infty}(2-\delta_{m0}) \times\frac{[(E_{sc}+i\epsilon_{sc})-i\sqrt{1-(E_{sc}+i\epsilon_{sc})^2}]^m}{\sqrt{1-(E_{sc}+i\epsilon_{sc})^2}}T_m(\hat{H}_{sc}), \quad (29)$$

where we have used the relation,[52,54] $F(b,b+1/2;2b;z)=[(1+\sqrt{1-z})/2]^{1-2b}/\sqrt{1-z}$, and the limiting relation involving the ultraspherical and the Chebyshev polynomials, $\lim_{\nu\to 0}(1/\nu)C_m^{(\nu)}(\hat{H}_{sc})=(2/m)T_m(\hat{H}_{sc})$.

Case 2: With $\nu=1/2$ we obtain the Green's function expressed in terms of Legendre polynomials. Using the well known relation $(2z)^{m+1}\Gamma(m+3/2)Q_m(z)=\Gamma(m+1)\Gamma(1/2)F((m+1)/2,(m+2)/2;(2m+3)/2;z^{-2})$, where $Q_m(z)$ is the Legendre function of the second kind,[49] Eq. (28) is simplified as follows:

$$G(E^+)=\left(\frac{i}{2\pi\Delta\lambda}\right)\sum_{m=0}^{\infty}(2m+1) \times Q_m(E_{sc}+i\epsilon_{sc})P_m(\hat{H}_{sc}). \quad (30)$$

Case 3: With $\nu=1$, there is an interesting closed form expression for the hypergeometric series which gives rise to the Chebyshev polynomials of the second kind,

$$G(E^+)=\left(\frac{1}{\pi\Delta\lambda}\right)\sum_{m=0}^{\infty}(-i)^m[\sqrt{1+(\epsilon_{sc}-iE_{sc})^2} -(\epsilon_{sc}-iE_{sc})]^{m+1}U_m(\hat{H}_{sc}), \quad (31)$$

where we have used the relation,[52,54] $F(b-1/2,b;2b;z)=[(1+\sqrt{1-z})/2]^{1-2b}$.

A comment regarding the explicit limit, $\epsilon\to 0$ in Eqs. (28)–(31) and the numerical implementation is in order. In fact, with the limit $\epsilon_{sc}\to 0$ in Eq. (28), we will have $1\leqslant E_{sc}^{-2}\leqslant\infty$, because $-1\leqslant E_{sc}\leqslant +1$. We note that the complex hypergeometric function in Eq. (28) is an analytical continuation of the well known hypergeometric series. Now the hypergeometric series, $F(a,b;c;z)$, converges only within the unit circle, $|z|<1$, and therefore $F(a,b;c;z)$ for an arbitrary z is typically evaluated by direct line integration in the complex plane.[57] The series expansion of the hypergeometric function for the real value of E_{sc} in the present situation is thus divergent. Also, the hypergeometric series remains singular at $z=1$. These observations, therefore, suggest the use of $i\epsilon_{sc}$ in actual numerical implementation, instead of taking the explicit limit beforehand.

V. THE COMPLEX TIME PROPAGATOR

The quantum propagator in complex time is one of the key ingredients in the implementation of flux–flux autocorrelation function based quantum canonical rate theory, where the imaginary part is related to the temperature.[58–63] In principle, the evolution operator, as developed in Sec. II, can directly be used for this purpose, with the understanding that the Bessel function now acquires an imaginary argument. If the complex argument of the Bessel function has an arbitrary phase, it may not be possible to utilize any simple analytic continuation for its evaluation. It is possible, however, to separate a complex argument in a Bessel function into real and imaginary parts, which is useful for practical calculations. As a specific example we here work with the Chebyshev expansion of the time evolution operator, Eq. (18), and this, for complex time, is

$$e^{i\hat{H}t_c^*/\hbar}=\exp\left(\frac{i\bar{\lambda}t}{h}-\frac{\bar{\lambda}\beta}{2}\right)\sum_{m=0}^{\infty}(2-\delta_{m0})\times i^m J_m\left(\frac{t\Delta\lambda}{\hbar}+i\frac{\beta\Delta\lambda}{2}\right)T_m(\hat{H}_{sc}). \tag{32}$$

Here t_c^* is the complex conjugate of $t_c=t-i\hbar\beta/2$ and $\beta=1/(k_BT)$, with k_B the Boltzmann constant and T the temperature. Now, we can use the relation $J_m(x+iy)=\Sigma_{-\infty}^{\infty}i^{m-s}J_s(x)I_{m-s}(y)$, where $J_m(x)$ and $I_m(y)$ are the Bessel and the modified Bessel functions respectively,[50] in Eq. (29) to obtain,

$$e^{i\hat{H}t_c^*/\hbar}=\exp\left(\frac{i\bar{\lambda}t}{\hbar}-\frac{\bar{\lambda}\beta}{2}\right)\sum_{m=0}^{\infty}(2-\delta_{m0})i^m T_m(\hat{H}_{sc})\times\left\{\sum_{s=0}^{\infty}\left(1-\frac{\delta_{s0}}{2}\right)i^{m-s}J_s\left(\frac{t\Delta\lambda}{\hbar}\right)\left[I_{|m-s|}\left(\frac{\beta\Delta\lambda}{2}\right)+I_{m+s}\left(\frac{\beta\Delta\lambda}{2}\right)\right]\right\}. \tag{33}$$

A similar expression for $e^{-i\hat{H}t_c/\hbar}$ can also be obtained.

The theory developed above is general and may be useful for many problems in quantum dynamics. The algorithm involves a three-term recursion for the Hamiltonian matrix operation on a vector and is suitable for large scale parallel computations using standard spectral and pseudospectral methods.

VI. RESULTS AND DISCUSSION

In order to determine the preformance of the time propagator given by Eq. (14), we have studied the evolution of a Gaussian wave packet in a Morse potential well. We have also utilized the spectral density operator [Eq. (23)] to compute the bound state spectrum of the Morse oscillator. As a further test we calculate the transmission coefficient for tunneling through an Eckart barrier. We have chosen these systems because we know the exact results. We have performed all the calculations using fast Fourier transforms to evaluate the powers of the Hamiltonian operator acting on the initial wave packet.

The parameters describing the Morse potential are given in Table I. The system supports 224 bound states.

To determine the optimum spatial grid for the calculations we calculated the matrix of the Hamiltonian in coordinate representation and diagonalized it. The matrix element of the kinetic energy operator was obtained by using discrete Fourier transforms. We increase the number of grid points until all eigenvalues converge within $10^{-7}\%$ in absolute error. We thus find that 2048 grid points to be sufficient to obtain all bound states of this system.

TABLE I. Numerical parameters used for Morse oscillator, $V(R)=D_e[e^{-2a(R-R_e)}-2e^{-a(R-R_e)}]$.

Parameter	Value[a]	Description
a	1.423 4	Morse parameter
R_e	2.074 38	Morse equilibrium
D_e	4.0	Morse dissociation energy
$R_{\min}, R_{\max}$	0.0, 16.0	Spatial range for the R coordinate
M	12 766.362 5	Mass
$V_{\max}$	5.0	Potential energy cutoff
N grid	2 048	Number of grid points
$\Delta\lambda$	7.633 318 795	Hamiltonian scaling parameter
$\bar{\lambda}$	3.651 114 885	Hamiltonian scaling parameter

[a]All values are given in atomic units.

We first discuss the preformance of the time propagator. We have already seen that the series expansion of the time evolution operator [Eq. (15)] in terms of Jacobi polynomials contains a parameter, α, which is constrained to be greater than -1, but is otherwise arbitrary. The value of this parameter affects the rate of convergence of this series. We would like to know the range of α, for which the series converges with the smallest number of terms. We first choose $\alpha=-0.5$, which is the Chebyshev expansion, as a reference point and find out the total number, N, of terms in the series (15) (which has to be greater than $t\Delta\lambda/\hbar$), required for a fixed accuracy (error less than 10^{-12}) in the norm of $|\psi(x,t)\rangle$. The initial wave function is a complex Gaussian. In the present study, the value of N was found to be 280, 1200, and 2760 for 1 femtosecond (fs), 5 fs, and 12 fs propagation of the wave packet, respectively. Next, we fix these values of N and compute $\langle\psi(R,t)|\psi(R,t)\rangle$, for various choices of α. The results are shown in Fig. 1. It is clear from Fig. 1 that the error in the norm of the wave packet increases

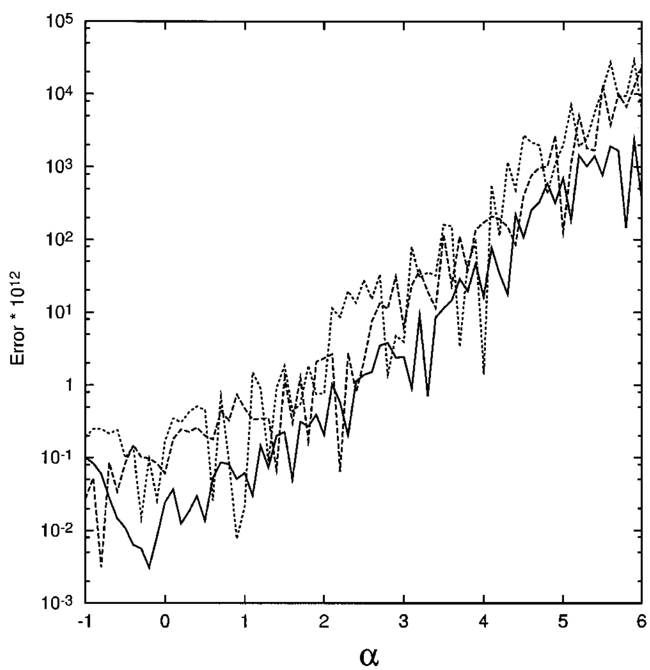

FIG. 1. Error in the norm of the propagated wave packet as a function of α. Full, broken, and dotted lines correspond to 1, 5, and 12 fs propagation, with 280, 1200, and 2760 terms in Eq. (10), respectively.

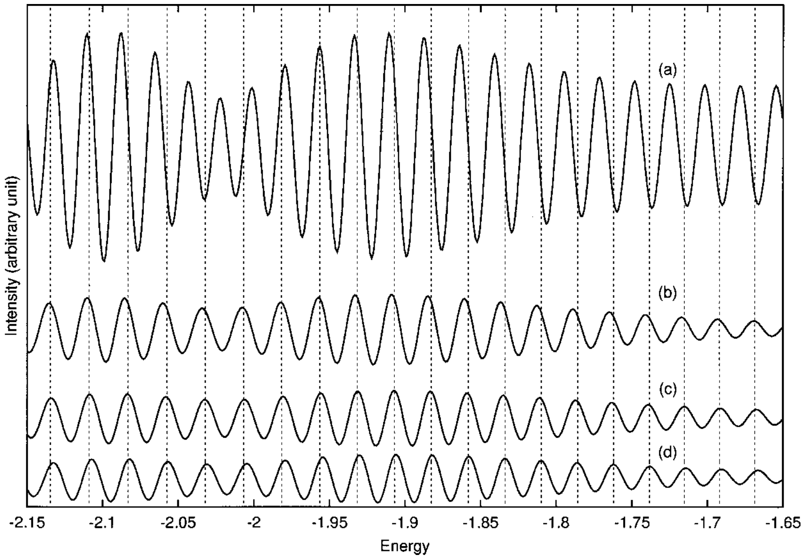

FIG. 2. The spectral intensity as a function of the parameter, ν. Curves (a), (b), (c), and (d) correspond to $\nu=-0.4$, 0.0, 0.5, and 1.0 for 1450 terms in Eq. (32), respectively. The energy is given in atomic units and the intensity is plotted in arbitrary units. Dotted lines show the exact location of the eigenvalues.

with α almost monotonically, even though there are some "local fluctuations." We have also examined the stability of Eq. (15) for a long time propagation, with different choices of α. For this purpose, we have propagated the initial Gaussian wave packet for 200 fs, by recursively applying the propagator 200 times with a time step of 1 fs, with the fixed number of terms ($N=280$) in Eq. (15) for each time step. We find that the error in the norm grows linearly with time, for different choices of α. In fact, the error growth with time can be represented as At and we find A to be 10.0, 1.0, 2.3, 1.4, and 6.0 in units of 10^{-14} for α equal to -1, -0.5, 0.0, 0.5, 1.0, respectively. This shows Eq. (15) to be stable for a long time propagation, for different choices of α. From the numerous tests carried out in the present study we find that $-1<\alpha<+1$ leads to the best performance. We also note that the three-term recursion with the Jacobi polynomial remains stable even for very large N.

We next examine the performance of the series expansion of the density of states operator as a function of $\nu=\alpha+1/2$. For this, we have computed the bound state spectrum of the Morse oscillator, using Eq. (23), as follows. In fact, an arbitrary state, $|\psi(x,0)\rangle$ can be written in terms of the energy eigenstates, $|\chi(x,\epsilon_m)\rangle$, as $\Sigma_m \rho(\epsilon_m)|\chi(x,\epsilon_m)\rangle$, where $\rho(\epsilon_m)$ is an expansion coefficient independent of x or time. We can compute $|\rho(\epsilon_m)|^2$ from

$$|\rho(\epsilon_m)|^2=\frac{1}{2\pi}\int_{\infty}^{-\infty} dt e^{i\epsilon_m t}\langle\psi(x,0)|\psi(x,t)\rangle$$

$$=\langle\psi(x,0)|\delta(\epsilon_m-\hat{H})|\psi(x,0)\rangle. \tag{34}$$

Using Eq. (23), Eq. (34) can easily be written as follows:

$$|\rho(\epsilon_m)|^2=\frac{1}{\pi\Delta\lambda}(1-E_{sc}^2)^{\nu-1/2}\sum_{m=0}^{\infty} Y_m^{\nu}(E_{sc})$$

$$\times\langle\psi(x,0)|Y_m^{\nu}(\hat{H})|\psi(x,0)\rangle, \tag{35}$$

where $E_{sc}=\epsilon_m/\Delta\lambda$, and $Y_m^{\nu}(x)$ satisfies the following three-term recursion relation:

$$Y_m^{\nu}(x)=\left(\frac{m+\nu}{m+2\nu-1}\right)^{1/2}\left[2\left(\frac{m+\nu-1}{m}\right)^{1/2} xY_{m-1}^{\nu}(x)\right.$$

$$\left.-\left(\frac{(m-1)(m+2\nu-2)}{m(m+\nu-2)}\right)^{1/2} Y_{m-2}^{\nu}(x)\right], \tag{36}$$

where $Y_m^{\nu}(x)=[\sqrt{\pi}\Gamma(\nu+1)/\Gamma(\nu+1/2)]^{1/2}$, $\sqrt{2(\nu+1)}xY_0^{\nu}(x)$, and $\sqrt{(\nu+2)/(2\nu+1)}[\sqrt{2(\nu+1)}xY_1^{\nu}(x)-Y_0^{\nu}(x)]$, for $m=0$, 1, and 2, respectively. A finite summation in Eq. (35) would give a sequence of sinclike functions, with an eigenvalue at the maximum of each sinc function.

Using Eq. (35) we have computed the spectral intensity for various energy windows of the Morse Hamiltonian. For the present test, we have constructed the initial state, $|\psi(x,0)\rangle$, by explicitly using the eigenvectors of the Hamiltonian matrix, to ensure that it has finite overlap with all eigenstates. We note that the initial state can, in fact, be chosen arbitrarily. We show results for -2.15 a.u. to -1.65 a.u. energy window in Fig. 2. We first choose $\nu=0$, which is the Chebyshev expansion, as a reference point, and then find out the total number of terms, N, required in Eq. (35) to faithfully recover the spectrum. For the energy window selected here, N is found to be 1450. We now fix $N=1450$ and compute the spectrum using Eq. (35) for various choices of ν. It is clear from Fig. 2 that the spectrum gets distorted as we increase the parameter ν, while keeping the number of terms, N, in Eq. (35) fixed. From the numerical tests carried out in the present study, we find a prefered choice of ν to be in the range of -0.5 and 0.5.

We now examine the performance of the series expansion of the propagator to study the transmission of a quantum particle through Eckart's barrier. We list the numerical parameters in Table II. The transmission probability is

$$P(k_{in})=\frac{|A^+|^2}{|A^-|^2}. \tag{37}$$

A^+ is the amplitude of the transmitted wave and A^- is that of the incident one. A^- can easily be obtained from

TABLE II. Numerical parameters used for Eckart's barrier, $V(x) = V_0/\cosh^2(ax)$.

Parameter	Value	Description
a	2.0 Å	Barrier width
V_0	1.036 44 eV	Barrier height
M	1 amu	Mass
$R_{\min}, R_{\max}$	20.0 Å, −20.0 Å	Spatial range for the x coordinate
N grid	512	Number of grid points

$$A^- = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} dx e^{ikx} \psi(x,t=0), \tag{38}$$

where $\psi(x,t=0)$ is the initial incoming wave packet, which was chosen to be a complex Gaussian function. The integral in Eq. (38) can be done analytically. In principle, A^+ can be obtained at the end of the time propagation, by the space-momentum Fourier transform of the transmitted part of the wavepacket. As explained in Appendix A, A^+ can also be obtained by the time-energy Fourier transform of the propagated wave packet as follows:

$$A^+ = \frac{1}{2\pi} \sqrt{\frac{2E}{\mu}} e^{(-i/\hbar)\sqrt{2\mu E} x_p} \int_{-\infty}^{\infty} dt e^{i(E-\hat{H})t/\hbar} \times \psi(x,t=0)\big|_{x=x_p}, \tag{39}$$

where $E = \hbar^2 k^2/2\mu$, μ is the mass of the particle, and $x = x_p$, is the projection point situated at the right-hand side of the barrier. Using the series representation of the time propagator, the time integral in Eq. (39) can also be done analytically as we have discussed earlier. We have computed the transmission probabilities for a range of energies, by varying the number of terms N in the series expansion of the propagator and the parameter α. In Table III, we present the results for a specific energy at 0.806 648 eV. It is clear from Table III that the total number of terms in the series for time propagator is larger for large value of α and a prefered choice of α is in the range −1.0 and 1.0. The results at other energies also show a similar behavior.

VII. CONCLUDING REMARKS

In this work, we have obtained a general orthogonal polynomial based scheme to evaluate the evolution operator, the Boltzmann operator, the spectral density operator and the Green's function, which has the convergence property of the Bessel function. The general expression derived here carries a parameter, α, and the special choices of this parameter allow us to recover previously known schemes based on Chebyshev and Legendre polynomials. Numerical tests on Morse oscillator for the time evolution operator and the spectral density operator, suggest an optimal choice of α to be in the range of −1.0 and 1.0, and this range includes the expansion in terms of Chebyshev ($\alpha = -0.5$) and Legendre ($\alpha = 0.0$) polynomials. In this study we have not examined the convergence property of the Green's function and left it for future investigation.

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APPENDIX: DERIVATION OF EQUATION (39)

We first note that the transmitted part of the wave packet, which is used to compute the outgoing flux, represents a free particle and can be represented as follows:

$$\psi(x,t) = \sum_k A_k^+ e^{ikx} e^{-i(\hbar^2 k^2/2\mu)t/\hbar}. \tag{A1}$$

In order to compute $A_{k_0}^+$, we multiply on both sides of Eq. (A1) with $\exp(iEt/\hbar)$ $(E = \hbar^2 k_0^2/2\mu)$ and integrate with respect to time from $-\infty$ to ∞. We thus obtain,

$$\begin{aligned}\frac{1}{2\pi} \int_{-\infty}^{\infty} dt e^{iEt/\hbar} \psi(x,t) &= \sum_k A_k^+ e^{ikx} \delta(E - \hbar^2 k^2/2\mu) \\ &= \sqrt{\frac{\mu}{2E}} \sum_k A_k^+ e^{ikx} [\delta(k-k_0) \\ &\quad + \delta(k+k_0)].\end{aligned} \tag{A2}$$

TABLE III. Transmission probability ($\times 10^3$)[a] for Eckart's barrier at 0.806 648 eV, as a function of the parameter α and number of terms (N) in the series expansion of the propagator.

	α						
N	−1.0	−0.5	0.0	0.5	1.0	2.0	5.0
500	1.840	1.457	0.961	0.529	0.308	0.648	0.961
525	0.994	1.289	1.444	1.392	1.150	0.528	1.606
550	0.865	0.996	1.089	1.094	0.994	0.659	1.370
575	0.903	0.917	0.901	0.857	0.804	0.799	0.781
600	0.862	0.855	0.850	0.853	0.865	0.891	0.880
625	0.862	0.863	0.863	0.862	0.859	0.854	0.837
650	0.862	0.862	0.862	0.862	0.862	0.862	0.884
675	0.861	0.861	0.861	0.861	0.861	0.862	0.855
700	0.862	0.862	0.862	0.862	0.862	0.862	0.862

[a]The exact value is 0.862×10^{-3}.

The two delta functions in Eq. (A2) pick up outgoing and incoming waves, respectively. As the transmitted wave packet carries only outgoing wave (that is, positive k-component), we obtain,

$$\frac{1}{2\pi}\int_{-\infty}^{\infty} dt e^{iEt/\hbar}\psi(x,t)=\sqrt{\frac{\mu}{2E}}A_{k_0}^{+}e^{ik_0x} \tag{A3}$$

which is the same as Eq. (39). The position variable x in Eq. (A3), which is an arbitrary projection point, is chosen to be on the right-hand side of the barrier to make sure that we account only for outgoing waves in actual calculations. To reduce the computational efforts, the variable x should be chosen just outside the potential barrier as the dynamical process is complete after the transmitted part of the wave packet has crossed the point x.

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