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Time propagation and spectral filters in quantum dynamics: A Hermite polynomial perspective

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We present an investigation of Hermite polynomials as a basic paradigm for quantum dynamics, and make a thorough comparison with the well-known Chebyshev method. The motivation of the present study is to develop a compact and numerically efficient formulation of the spectral filter problem. In particular, we expand the time evolution operator in a Hermite series and obtain thereby an exponentially convergent propagation scheme. The basic features of the present formulation *vìs a vìs* Chebyshev scheme are as follows: (i) Contrary to the Chebyshev scheme Hamiltonian renormalization is not needed. However, an arbitrary time scaling may be necessary in order to avoid numerical hazards, and this time scaling also provides a leverage to accelerate the convergence of the Hermite series. We emphasize the final result is independent of the arbitrary scaling. (ii) As with the Chebyshev scheme the method is of high accuracy but not unitary by definition, and thus any deviation from unitarity may be used as a guideline for accuracy. The calculation of expansion coefficients in the present scheme is extremely simple. To contrast the convergence property of present method with that of the Chebyshev one for *finite time propagation*, we have introduced a *time–energy scaling* concept, and this has given rise to a unified picture of the overall convergence behavior. To test the efficacy of the present method, we have computed the transmission probability for a one-dimensional symmetric Eckart barrier, as a function of energy, and shown that the present method, by suitable *time–energy scaling*, can be very efficient for numerical simulation. *Time–energy scaling* analysis also suggests that it may be possible to achieve a faster convergence with the Hermite based method for finite time propagation, by a proper choice of scaling parameter. We have further extended the present formulation directed toward the spectral filter problem. In particular, we have utilized the Gaussian damping function for the purpose. The Hermite propagation scheme has allowed all the time integrals to be done fully analytically, a feature not completely shared by the Chebyshev based scheme. As a result, we have obtained a very compact and numerically efficient scheme for the spectral filters to compute the interior eigenspectra of a large rank eigensystem. The present formulation also allows us to obtain a closed form expression to estimate the error of the energies and spectral intensities. As a test, we have utilized the present spectral filter method to compute the highly excited vibrational states for the two-dimensional LiCN ($J=0$) system and compared with the exact diagonalization result. © *1999 American Institute of Physics.* [S0021-9606(99)00647-9]

I. INTRODUCTION

Quantum dynamics is the underlying theory for understanding molecular processes and hence establishing efficient numerical schemes to solve the quantum equations of motion that are very crucial for the simulation of various physical processes. In this context, the gradual evolution of pseudospectral and DVR methods has been very important and recent years have witnessed a tremendous upsurge of research in this sector of science.[1–3] A key ingredient of the pseudospectral method is an accurate representation of the time evolution operator ($e^{-i\hat{H}t/\hbar}$, where $\hat{H}$ is the Hamiltonian operator), and in this pursuit, several numerical schemes with varying degrees of success have been proposed.[3] In this paper we focus our attention on methods that involve recursive Hamiltonian operations in order to accomplish the desired time propagation. In this category, a formal decomposition of the time evolution operator into sum of products of a recursive Hamiltonian part and a time part is generally affected by the choice of a suitable polynomial expansion—the preferred choice is the classical orthogonal polynomial set, for this is the most well-studied set in mathematical physics.[4] An obvious advantage of polynomial based approximation of the evolution operator is that it is global in nature and hence the quantum propagation can be carried out for an arbitrary time step, provided a sufficient number of terms are included in the series—a philosophy consistent with the infinite limiting process in the theory of

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approximation.[5] In this context, the introduction of the Chebyshev polynomial expansion of the evolution operator by Tal-Ezer and Kosloff[6] has been an important contribution. Later, a Legendre polynomial based scheme was also suggested for the purpose.[7] The development of a global time propagation scheme based on Chebyshev polynomials (Legendre polynomials provides an almost identical analytical frame) is considered generally satisfactory for *finite* time propagation, and in this situation there does not seem any pressing need to develop an alternative procedure. However, in the event of *infinite* time propagation (this is equivalent to carrying out the time propagation fully analytically up to infinity—an exercise frequently encountered in the time domain theory of spectral filters[8]), several alternate propagation schemes need to be developed to suit the analytical problems at hand. From the *finite* time propagation perspective, also, the Chebyshev method provides only ''fixed'' convergence characteristics of the approximating series and this convergence is determined by the spectral range represented in the input Hamiltonian. It is therefore worth exploring alternate polynomial based schemes with the convergence objective in mind and to devise a propagation method that is still recursive but with an accelerated convergence feature, so that we can minimize the total numerical effort.

In this paper we present our investigation of the Hermite polynomials as a basis for quantum time evolution. The use of Hermite polynomials for time propagation has been explored earlier by other authors. In particular, Kouri and Hoffman *et al.* have expressed the so-called *distributed approximating functions* (DAF) in terms of Hermite functions, and derived thereby a continuous DAF class free particle propagator, which has been explored for real time quantum dynamics in a series of papers.[9] Much closer to the present study, Hu has very recently presented the use of a Hermite polynomial based propagation system (which is referred to as a ''Laguerre scheme''), and performed test calculations on one-dimensional harmonic and morse oscillator potentials.[10] Hu has amply discussed the error in the norm during *finite* time propagation, while ignoring the importance of phase error that is crucial for correct dynamics. The present elaboration is focused more on the practical issues, and pedagogically perhaps much more complete. Hermite polynomials have also been used to obtain semiclassical equations of motion.[11]

The motivation of the present investigation of Hermite polynomials has been to develop a compact and numerically efficient formulation of the spectral filter problem. Recent years have witnessed a tremendous upsurge of interest in the time domain theory of spectral filters, with the prime objective of devising efficient computational methods to extract an arbitrary window of eigenspectrum of a system involving a large rank Hamiltonian, for which a direct matrix diagonalization procedure may be extremely prohibitive.[8] The advent of the time domain theory of spectral filter is due to an important realization that—''an arbitrary initial state $\psi(x)$ (assumed not to be orthogonal to any eigenstate of the system), after evolving under the spell of the Hamiltonian for a relatively short time projects into the space spanned by the energies close to ϵ, and various such propagated wave packets at different energies within a window, could well serve as a basis for the conventional matrix diagonalization, resulting thereby the spectrum belonging to the chosen window.'' This appealing viewpoint, through the innovation of Neuhauser,[12] has come to be known as *filter diagonalization* (FD) methods in different guises. This is now a well-documented sector of research, and we note that various formulations of the original doctrine as promulgated by Neuhauser,[12] aside from the implementation strategy, fundamentally differentiate only in the choice of *damping function*. Of the damping functions, the *Gaussian* type has been frequently utilized, as this facilitates the evaluation of one of the double integrals analytically. A more elaborate choice of damping functions has also been made.[13,14] In this paper, we develop a compact and numerically efficient formulation of the spectral filter problem, using Hermite polynomials, which is based on the analytical settings originally proposed by Wall and Neuhauser,[15] who utilized Chebyshev polynomials along with the Gaussian damping function. Chebyshev polynomials as a basis for global time propagation has been very successful for general quantum dynamical problems. In the context of spectral filtering utilizing Gaussian damping, the major drawback of Chebyshev polynomials is that the crucial integral involving the time parameter cannot be done fully analytically and, as a result, the ensuing numerical scheme is computationally less efficient. In the present work, we follow the Gaussian damping based time domain theory of spectral filters,[15] with a difference that we utilize the Hermite method of time evolution in the numerical implementation. As a result, we have been able to carry out all the time integrals fully analytically and obtained thereby a very compact numerical scheme. With the present approach, we also outline a very clear picture of the mechanism of Gaussian filtering in actual numerical terms.

The organization of this paper is as follows. In Sec. II, we derive the fundamental Hermite propagation equation and continue the analysis from both a *finite* and *infinite* time propagation perspective, by invoking the *time–energy scaling* concept. We elaborate the time domain theory of spectral filters from Hermite polynomial perspective and derive different quantities of interests in Sec. III. We discuss the details of the model system studied here in Sec. IV, and in Sec. V we present the computational results. We conclude the presentation in Sec. VI.

II. THE HERMITE PROPAGATOR

We consider the time-dependent Schrödinger equation (TDSE),

$$i\hbar \frac{\partial \psi(x,t)}{\partial t} = \hat{H}\psi(x,t), \tag{1}$$

which is subject to an initial condition. For a stationary Hamiltonian, the formal solution is

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

where $e^{(-i/\hbar)\hat{H}t}$ is the time evolution operator in the Schrödinger representation. We now wish to expand $e^{(-i/\hbar)\hat{H}t}$ in the Hermite polynomials, $H_m(\hat{H})$, as follows:

$$e^{(-i/\hbar)\hat{H}t} = \sum_m a_m(t) H_m(\hat{H}). \tag{3}$$

Here t and $\hat{H}$ are assumed to be properly scaled (say, using unit factors) to render them dimensionless. This point will be clarified later. We further note there is no restriction in the range of the Hamiltonian. Following standard algebra, the expansion coefficients in Eq. (3) can be computed to obtain

$$a_m(t) = \frac{(-i)^m}{m!} \tilde{t}^m e^{-\tilde{t}^2}, \tag{4}$$

where $\tilde{t}$ is defined as $t/2\hbar$. Hence, the working equation for the solution of the TDSE is

$$\psi(x,t) = e^{-\tilde{t}^2} \sum_m \frac{(-i)^m}{m!} \tilde{t}^m H_m(\hat{H}) \psi(x,0). \tag{5}$$

Finally, the Hermite polynomial recurrence relation provides a recursive algorithm for the evolution operator. As to the convergence of the series (5), it is easy to verify by the simple ratio test that the series eventually converges because of the factorial factor in the denominator. The exponential convergence of Eq. (5) has also been noted by Hu.[10] As with the Chebyshev based scheme,[6] the present propagation method is not unitary by definition [cf. Eq. (3)], and thus any deviation from unitarity may be used as a guideline for accuracy.

There are two distinct situations wherein we seek to establish the efficacy of a given time propagation scheme in quantum mechanics. First, what we call *finite time* propagation, is concerned with the efficiency of the method to propagate the wave function for a given finite duration. Within the realm of polynomial based approximations, the question is how fast the ensuing series converges. In another situation, which we refer to as *infinite time* propagation, one carries out the entire time propagation analytically up to infinity (typical examples being the eigenvalue determination by time-dependent spectral filter methods) and here, aside from the usual convergence issue, one is also concerned with the analytical behavior of the approximating polynomial series that may affect the final numerical scheme. From the perspective of these issues, we will discuss the efficiency of the present scheme and also make a comparison with the similar Chebyshev based scheme.

A. Finite time propagation

In this situation, the propagation is carried out by recursively applying the elementary propagator for each time step. In this case, we here wish to discuss the convergence property of Eq. (5) for a given finite time step and also compare the dynamics with a Chebyshev based scheme. In the analysis of the convergence behavior, one is not unduly concerned for what eventually happens to the series, which, in most cases, converges. Rather, one is more interested in the nature of the error term of a finitely truncated series and the means to accelerate the convergence.

First we note that Eq. (5) states an approximation of an operator-valued function in terms of truncated Hermite series. From the theory of approximation we know an arbitrary function, subject to a few conditions (e.g., absolute integrability) can be expanded in any of the orthogonal polynomials;[16] however, the choice is often dictated by the error term associated with a finitely truncated series. In the realm of orthogonal polynomials the error behavior is essentially controlled by the nature of an associated weight function, and the reason for the Chebyshev based approximation scheme being popular, is that the error is uniformly distributed throughout the polynomial range.[16] This does not necessarily mean that all other orthogonal polynomials are not at all suitable for the approximation purposes. Here we argue that the hallmark for fast convergence of the polynomial series is our realization of *time–energy scaling*—one affecting the another for being the conjugate variables. This concept of scaling gives rise to an enhanced understanding of the mechanism of convergence. In order to elaborate this concept, we analyze the time evolved wave function expressed in the Chebyshev series, T_m, which is given as[6]

$$\psi(x,t) = \sum_m (2-\delta_{m0})(-i)^m e^{-2i\bar{\lambda}\tilde{t}} \times J_m(2\tilde{t}\,\Delta\lambda) T_m\left(\frac{\hat{H}-\bar{\lambda}}{\Delta\lambda}\right)\psi(x,0), \tag{6}$$

where $\Delta\lambda$ and $\bar{\lambda}$ are the scaling parameters to readjust the range of the Hamiltonian. Within the Chebyshev framework, the *time–energy scaling* concept is interwoven with the requirement of fixing the range of the Hamiltonian, as dictated by the property of Chebyshev polynomial, and here the time scaling [$\Delta\lambda$, in the argument of the Bessel function, J_m, in Eq. (6)] obviously determines the convergence characteristics by the property of the Bessel function. Here we have accomplished the scaling from the Hamiltonian side, and thereby we have obtained a ''constant'' scaling factor ($\Delta\lambda$) for the time variable. We therefore refer to this as ''fixed range'' time scaling. As a result, we obtain a natural (but fixed) convergence behavior of Eq. (6) through the fixed argument of the Bessel function, and by way of scaling there is no freedom to further accelerate the convergence of the Chebyshev series.

We now analyze the convergence behavior of the Hermite series [Eq. (5)] from the *time–energy scaling* perspective. First of all, we point out that there is no pressing need to embark upon any scaling for the Hermite based scheme, though it turns out to be a useful exercise. As there is no restriction in the range of Hermite functions, we are not constrained to affect the time scaling through the Hamiltonian renormalization, contrary to the situation with the Chebyshev based scheme. Instead, it turns out to be convenient to follow a more flexible line, and allow ourselves for a ''flexible range'' time scaling. By ''flexible range'' we simply mean to multiply the time variable with an arbitrary scale factor and accordingly readjust the Hamiltonian. This essentially amounts to an arbitrary shift in the energy axis, with absolutely no observable consequence. This means that the flex-

ible range time scaling in the Hermite context does not constrain the spectrum of the system in any way, which is contrary to the situation of fixed range time scaling in the Chebyshev method. In a practical situation, however, potential energy cutoff (*if any*) will be the common denominator affecting identically the behavior of both Hermite and Chebyshev based schemes. As will become clear later, the time scaling in the Hermite context is not a parameter affecting the system. It is just a convenient device to avoid numerical hazards (*if any*) and at the same time it possibly provides leverage to accelerate the convergence of the Hermite series. We note the truncated Hermite series has also been utilized in the area of signal and image processing, and it is well recognized that the rate of convergence of the series can be enhanced by choosing a good center and a good scale factor for the Hermite functions.[17] That an arbitrary scale factor may play an important role for the fast convergence of the Hermite series is not difficult to discern if we carefully examine Eq. (5). We first recognize that the coefficients a_m in Eq. (5) can be absorbed into the recurrence scheme for the Hermite polynomials to obtain the following expression:

$$\psi(x,t)=\sum_m S_m, \tag{7}$$

where S_m can be computed by the three-term recurrence relation:

$$S_m=\frac{2\tilde{t}}{m}(\tilde{t}S_{m-2}-i\hat{H}S_{m-1}), \tag{8}$$

with $S_0=\exp(-\tilde{t}^2)\psi(x,0)$ and $S_1=-2i\tilde{t}\hat{H}S_0$. The convergence of the Hermite series manifests here itself by the presence of factor m in the denominator of Eq. (8). As the factor $\exp(-\tilde{t}^2)$ in the expression for S_0 (which is the ramification of the weight factor associated with the Hermite polynomials) approaches zero rather quickly when $|\tilde{t}|$ is substantially larger than unity, the present scheme is ideally suited to approximate functions that either have a finite support or are very concentrated (in time or space). Lanczos has also argued[16]—if the weight factor is such that it is large in the immediate neighborhood of zero (center) and then drops to a small value, a finite sum of the corresponding orthogonal polynomials will approximate the given function with great accuracy around the origin, but the accuracy in the rest of the interval will be less. This behavior is expected to manifest here also and therefore a time scaling of Eq. (5) may be necessitated to ensure fast convergence of the series by adjusting the $\exp(-\tilde{t}^2)$ term. There could be different procedures for time scaling, and the ''Chebyshev style'' scaling (that is, to force the range of the Hamiltonian to fall between -1 and $+1$) leads to the following expression:

$$\psi(x,t)=\sum_m \frac{(-i)^m}{m!}e^{-2i\bar{\lambda}\tilde{t}}(\tilde{t}\,\Delta\lambda)^m \times e^{-(\tilde{t}\Delta\lambda)^2}H_m\left(\frac{\hat{H}-\bar{\lambda}}{\Delta\lambda}\right)\psi(x,0). \tag{9}$$

Here $\Delta\lambda$ and $\bar{\lambda}$ are defined as in the Chebyshev based scheme. On the other hand, if we follow the ''flexible range'' time scaling, we obtain the following expression:

$$\psi(x,t)=\sum_m \frac{(-i)^m}{m!}(\lambda\tilde{t})^m e^{-(\lambda\tilde{t})^2}H_m\left(\frac{\hat{H}}{\lambda}\right)\psi(x,0), \tag{10}$$

where λ is some arbitrary scale factor, and Eq. (8) becomes

$$S_m=\frac{2}{m}[(\lambda\tilde{t})^2S_{m-2}-\tilde{t}\hat{H}S_{m-1}], \tag{11}$$

with $S_0=\exp[-(\lambda\tilde{t})^2]\psi(x,0)$ and $S_1=-2i\tilde{t}\hat{H}S_0$.

Though time scaling is recommended here for accelerating the convergence of the Hermite series, it is not a mandatory step for a successful application of the present method. However, another reason has to do with the practical issue of which units one is using in actual numerical computations. We notice that the time factor appears as the argument of the Gaussian in the expression for S_0, and it also appears as a multiplicative factor [see Eq. (8)]; there is a real danger of multiplication of a very small number with a large number if one is using atomic units in the calculation and a judicious choice of scale factor will help to avoid the numerical problem (*if any*). We emphasize that there is no natural instability associated with the present method of time propagation. To forestall this problem, we prefer to use the so-called ''molecular unit'' in the numerical implementation.[18]

B. Infinite time propagation

An important feature of orthogonal polynomial based approximation of the evolution operator is a clear separation of the operator into a recursive Hamiltonian part and a time part, and the latter usually appears as a mixture of elementary transcendental functions and some special functions. This feature allows us to carry out the integrals involving the time parameter analytically, which, in practice, amounts essentially to *infinite time* propagation. The convergence of the resulting series then follows the arguments of an infinite limiting processes of applied analysis (characterized by recursive Hamiltonian operation on a wave function), and could be used as such for different purposes. As a general example, we consider the following equation:

$$\phi(x,\epsilon_l)=\frac{1}{2\pi}\int dt\, e^{i\epsilon_l t}\psi(x,t)g(t), \tag{12}$$

where $\psi(x,t)$ is the time-evolved wave function and $g(t)$ is the damping function that may be required to make the integral converge faster. In general, the range of the integral goes from 0 to ∞; however, in the presence of time reversal symmetry the integral would be evaluated from $-\infty$ to $+\infty$. From the eigenvalue perspective, Eq. (12) is the Fourier transformation[19] of the wave function from the time domain to the energy domain. In the parlance of *filter diagonalization*,[15] $\phi(x,\epsilon_l)$ in Eq. (12) is a function (not necessarily an eigenfunction) ''filtered'' at a given energy ϵ_l from the time-evolved wave function, $\psi(x,t)$. Here we ex-

amine the cases when $g(t)$ is either unity or a Gaussian damping function, and carry out the integration from $-\infty$ to $+\infty$. These two choices for the damping function are very popular in spectral filter problems.[14,15,20]

(i) $g(t)$ *is unity*: This situation is usually referred to as the *delta filter* or *box filter*.[14,20] Within the Chebyshev based scheme, the integral (12) can be evaluated to obtain

$$\phi(x,\epsilon_l)=\frac{2}{\Delta\lambda}(1-\bar{\epsilon}_l)^{-1/2}\sum_{m=0}^{\infty}(2-\delta_{m0})T_m(\bar{\epsilon}_l)\times T_m(\bar{H})\psi(x,0), \tag{13}$$

where $\bar{\epsilon}_l$ and $\bar{H}$ are the normalized energy and Hamiltonian, respectively, and $\Delta\lambda$ is the scaling parameter. On the other hand, Eq. (12) within the Hermite based scheme takes the form

$$\phi(x,\epsilon_l)=\sum_{m=0}^{\infty}\frac{e^{-\epsilon_l^2/2}H_m(\epsilon_l)}{\sqrt{2^m\sqrt{\pi}m!}}\frac{e^{-\epsilon_l^2/2}H_m(\hat{H})}{\sqrt{2^m\sqrt{\pi}m!}}\psi(x,0). \tag{14}$$

We note that Eqs. (13) and (14) are essentially the statement of the resolution of identity in a complete set of states. Here, the analytical properties of Eqs. (13) and (14), in practical applications, take precedence over the convergence issue, though there is no doubt that both series will eventually converge. In the problem of filter diagonalization, Eq. (13) is somewhat easier to further manipulate because of the special property of the product of two Chebychev functions, and this has been very nicely exploited for practical purposes.[14]

(ii) $g(t)$ *is a Gaussian function*, $e^{-t^2/4T^2}$: This is usually referred to as *the Gaussian filter*.[15] Within the Chebyshev based scheme, Eq. (12) cannot be integrated fully analytically because of the presence of the Bessel function in Eq. (6). In the filter diagonalization applications, one has to resort to numerical integration at some stage.[15] In addition, the physical picture associated with Gaussian damping also remains fully masked in the equation, and we do not understand the mechanism of Gaussian filtering in actual numerical terms. On the contrary, the Hermite based propagation scheme permits the evaluation of Eq. (12) fully analytically to obtain a closed form expression,

$$\phi(x,\epsilon_l)=\sum_{m=0}^{\infty}\eta^{m+1}\frac{e^{-(\epsilon_l\eta)^2/2}H_m(\epsilon_l\eta)}{\sqrt{2^m\sqrt{\pi}m!}}\times\frac{e^{-(\epsilon_l\eta)^2/2}H_m(\hat{H})}{\sqrt{2^m\sqrt{\pi}m!}}\psi(x,0). \tag{15}$$

where $\eta=T/\sqrt{1+T^2}$, is always less than unity. Thus, the physical effect of Gaussian damping in the Hermite case translates into a continuous geometrical trimming of the series through the η parameter, and this provides an enhanced convergence of the integral (12) at the cost of the Gaussian width as an extra parameter to be adjusted. This geometrical trimming of the series is very much reminiscent of the *Abel summation* technique, which has frequently been employed in studies of divergent series.[21] According to this interpretation, the parameter η defines the radius of the sphere within which the series is absolutely convergent (in fact, the series is absolutely and unconditionally convergent anywhere within the sphere of unit radius). In the limit of an infinite width Gaussian, η tends to unity, and this essentially has the effect of removing the impact of Gaussian damping, which is anyway an arbitrarily free parameter. This is very convenient if we would like to *switch on* damping only after some time has elapsed—a proposition put forth in a recent application[22]—in which case, both Eqs. (14) and (15) would be involved in the filtering process. Thus, we see that the Hermite polynomials have the edge over the corresponding Chebyshev polynomials in approximating the evolution operator for the applications of Gaussian damping based filter diagonalization.

We conclude this section by highlighting the important observation—while the issue of convergence takes a prominent stage for orthogonal polynomial based *finite time* quantum propagation, the analytical properties of the approximating series may be important for an improved numerical implementation, in the event of *infinite time* propagation.

III. SPECTRAL FILTERS

In the following we will develop the Hermite polynomial based spectral filter procedure along the analytical settings originally put forth by Wall and Neuhauser.[15] As the filter procedure has been elaborated in detail earlier, we present here only a brief outline and discuss the theory only from the Hermite polynomial perspective.

A. Basic principles and construction of Hamiltonian matrix

We consider the time-independent Schrödinger equation (TISE) as a formal statement of the eigenvalue problem, $\hat{\mathcal{H}}\Psi(x,E_l)=E_l\Psi(x,E_l)$. If we express the eigenfunction, $\Psi(x,E_l)$ in a nonorthogonal basis,

$$\Psi(x,E_l)=\sum_{m=1}^{L}B_{lm}\phi(x,\epsilon_m), \tag{16}$$

we obtain the eigenvalue problem in the matrix form as $\mathcal{H}B=SB\epsilon$. Here ϵ is a diagonal matrix containing the eigenvalues, and the Hamiltonian and overlap matrices are defined, respectively, as follows:

$$S_{m,m'}=\int_{-\infty}^{\infty}dx\ \phi^*(x,\epsilon_m)\phi(x,\epsilon'_m), \tag{17}$$

$$\mathcal{H}_{m,m'}=\int_{-\infty}^{\infty}dx\ \phi^*(x,\epsilon_m)\hat{\mathcal{H}}\phi(x,\epsilon'_m). \tag{18}$$

Here the notation ϵ_m refers to an arbitrary energy and it has meaning in the context of time–energy Fourier analysis, as will be clear later. At this point, any set of basis functions

could serve the purpose, and if we are interested in the eigenvalues from the highly excited region of a large rank Hamiltonian, the procedure is going to be extremely expensive.

Within the FD premise the basis $\phi(x,\epsilon_m)$ is extracted from the time evolving wave function by utilizing the Fourier integral theorem,

$$\phi(x,\epsilon_m)=\frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty} dt\, e^{i\epsilon_m t}\psi(x,t)e^{-t^2/2T^2}, \tag{19}$$

where the Gaussian damping term, $e^{-t^2/2T^2}$, has been inserted to make the integral converge faster, and $\{\epsilon_m : m=1,L\}$ constitutes a set of discrete energies within a given energy window. This is the filter step of the FD method. The Fourier integral theorem[19] asserts that a time evolving function (provided it did not start orthogonal to any of the eigenstates of the Hamiltonian) represents all the energy components due to an *infinite* time baseline [In theoretical terms, the time parameter does go to infinity. However, in the situation when ϵ_m is one of the eigenvalues of the Hamiltonian, the concept *infinity* refers to a *limiting process* and it is the minimum time that the wave function, $\psi(x,t)$, has to be propagated in order to resolve the eigenfunction corresponding to the eigenvalue ϵ_m correctly]. We point out that the range of integration in Eq. (19) (i.e., from $-\infty$ to ∞) indicates the validity of time reversal symmetry, which is fully justified for the eigenvalue problems in quantum mechanics. In fact, the imposition of time reversal symmetry in quantum mechanics essentially amounts to a definite choice of the ''phase factor,'' which, however, has no consequence from the measurement perspective.[23] The crux of the FD method lies in an important observation from Eq. (19). The integrand in Eq. (19) is highly oscillatory (this is the reason a damping function, in the form of Gaussian has been inserted), and therefore reflects the possibility of strong cancellation for a moderately large value of t. As time goes on, we expect smaller contributions from the energy components away from ϵ_m. This phenomenon is known as the *loss of phase coherence*, the result of which leads to the crucial conviction that—''*after a relatively short time the filtered function*, $\phi(x,\epsilon_m)$ *will span the space of quantum states with energies close to* ϵ_m,'' and several such filtered functions at a discrete set of energies within a given window could well serve as a set to obtain the eigenvalues within the window, by conventional matrix diagonalization.[12] In this sense, the time propagation step in the FD method acts as a *preconditioner* of the basis for eventual disentanglement of eigenstates by the diagonalization process. The filtered functions $\phi(x,\epsilon_m)$ are not expected to be orthogonal and, in practical applications, we need to make sure that the set is overcomplete, that is, the size of the matrix (L) we diagonalize is larger than the number of eigenvalues within the given window.

The above discussion essentially completes the basic ideas involved in the FD. Here, Eqs. (16)–(19) form the basic structure of the FD method, and the obvious question that remains is as how efficiently can we cast the working equations for the matrix elements [Eqs. (17) and (18)]. Along this goal, we have followed the algebra originally elaborated for the purpose by Wall and Neuhauser.[15] In Eq. (19), $\psi(x,t)$ is the time evolved wave function as given in Eq. (2). To this end, we could use any *short time* propagator to generate $\psi(x,t)$ at different times in an interval and carry out the integral (19) numerically. However, the numerical integration procedure is fraught with difficulties as one has to take cognizance of the sampling theorem[24] (even though the sampling issue will manifest in the present FD context only indirectly), apart from the length one has to carry out the time propagation. As Eq. (19) involves an integration over time, it would be very convenient to utilize a propagation method that splits the evolution operator into a Hamiltonian part and a time part, so that one can attempt to carry out the time integral analytically. In this context, orthogonal polynomial based recursive propagation method is an ideal choice (e.g., Chebyshev propagation). As it has been noted by Wall and Neuhauser,[15] the time integration with the Chebyshev method could not be accomplished fully analytically, rendering the resulting computational recipe somewhat less efficient and transparent. It is at this stage that the Hermite polynomial based propagation method holds an edge over the Chebyshev method.

In what follows, we present a derivation for the overlap and Hamiltonian matrices. With Eq. (19), the expression for overlap and Hamiltonian matrices takes the form as follows:

$$S_{m,m'}=\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} dt\, dt'\, e^{-(t^2+t'^2)/2T}e^{i(\epsilon_m t+\epsilon_{m'}t')} \times\int_{-\infty}^{\infty} dx\, \psi^*(x,t)\psi(x,t), \tag{20}$$

$$\mathcal{H}_{m,m'}=\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} dt\, dt'\, e^{-(t^2+t'^2)/2T}e^{i(\epsilon_m t+\epsilon_{m'}t')} \times\int_{-\infty}^{\infty} dx\, \psi^*(x,t)\hat{\mathcal{H}}\psi(x,t). \tag{21}$$

The time reversal symmetry allows one to choose $\Psi(x,E_l)$ and hence $\phi(x,\epsilon_m)$ as a real function, and therefore we can consider $\psi^*(x,t)$ as the wave function evolved for negative time, $\psi(x,-t)$, along with some arbitrary phase factor that may conveniently be taken as unity. This consideration essentially follows from the Fourier analysis, which also suggests that the initial wave function, $\psi(x,0)$, be real valued. Thus, the space part of the integral in Eq. (20) takes the form of a correlation amplitude, $C(t)$:

$$\begin{aligned}\int_{-\infty}^{\infty} dx\, \psi^*(x,t)\psi(x,t)&=\int_{-\infty}^{\infty} dx\, \psi(x,-t)\psi(x,t)\\&=\int_{-\infty}^{\infty} dx\, \psi(x,0)\psi(x,t+t')\\&=C^s(t+t').\end{aligned} \tag{22}$$

Here we have utilized the fact that the correlation amplitude belongs to the class of *stationary random function*, and is thus invariant under a change of the origin of times as the

choice of time origin is entirely arbitrary.[25] Along the same argument we have the space part of the integral (21) to be written as follows:

$$\begin{aligned}\int_{-\infty}^{\infty} dx\ \psi^*(x,t)\hat{\mathcal{H}}\psi(x,t) &= \int_{-\infty}^{\infty} dx\ \psi(x,-t)\chi(x,t)\\ &= \int_{-\infty}^{\infty} dx\ \psi(x,0)\chi(x,t+t')\\ &= C^h(t+t')\\ &= \int_{-\infty}^{\infty} dx\ \psi(x,0)\hat{\mathcal{H}}\psi(x,t+t').\end{aligned} \tag{23}$$

On making a change of variables as $t=\alpha/2+\beta$ and $t'=\alpha/2-\beta$ in Eqs. (20) and (21), and integrating out the β variable analytically, we obtain

$$S_{m,m'} = \frac{T}{2\sqrt{\pi}} e^{-(\epsilon_m-\epsilon_{m'})^2T^2/4} \times \int_{-\infty}^{\infty} dt\, e^{i(\epsilon_m-\epsilon_{m'})t/2} e^{-t^2/4T^2} C^s(t), \tag{24}$$

$$\mathcal{H}_{m,m'} = \frac{T}{2\sqrt{\pi}} e^{-(\epsilon_m-\epsilon_{m'})^2T^2/4} \times \int_{-\infty}^{\infty} dt\, e^{i(\epsilon_m-\epsilon_{m'})t/2} e^{-t^2/4T^2} C^h(t), \tag{25}$$

where $C^s(t)$ and $C^h(t)$ are the integrals involving the space part, as defined in Eqs. (22) and (23). Now, if we accept the Hermite polynomials, $H_k(\hat{\mathcal{H}})$ as the basis for time propagation [Eq. (5)] we can write the correlation amplitude [cf. Eqs. (22) and (23)] as

$$C^s(t) = \sum_{k=0}^{\infty} a_k(t) \int_{-\infty}^{\infty} dx\ \psi(x,0) H_k(\hat{\mathcal{H}})\psi(x,0), \tag{26}$$

$$C^h(t) = \sum_{k=0}^{\infty} a_k(t) \int_{-\infty}^{\infty} dx\ \psi(x,0) \times [\tfrac{1}{2}H_{k+1}(\hat{\mathcal{H}}) + kH_{k-1}(\hat{\mathcal{H}})]\psi(x,0), \tag{27}$$

where we have utilized the property of Hermite polynomials to arrive at Eq. (27). We now substitute $C^s(t)$ and $C^h(t)$ from Eqs. (26) and (27) into Eqs. (24) and (25), respectively, and evaluate the integral involving time analytically to finally obtain the following expressions for the overlap and Hamiltonian matrices:

$$S_{m,m'} = T\sqrt{\pi} e^{-(\epsilon_m-\epsilon_{m'})^2T^2/4} \sum_{k=0}^{\infty} \eta^{k+1} \frac{e^{-\tau^2/2}H_k(\tau)}{\sqrt{2^k\sqrt{\pi}k!}} X_k, \tag{28}$$

$$\mathcal{H}_{m,m'} = T\sqrt{\pi} e^{-(\epsilon_m-\epsilon_{m'})^2T^2/4} \times \sum_{k=0}^{\infty} \eta^{k+1} \frac{e^{-\tau^2/2}H_k(\tau)}{\sqrt{2^k\sqrt{\pi}k!}} \times \left[\sqrt{\frac{k+1}{2}} X_{k+1} + \sqrt{\frac{k}{2}} X_{k-1} \right], \tag{29}$$

where $\eta = T/\sqrt{1+T^2}$ and $\tau = \eta(\epsilon_m+\epsilon_{m'})/2$. X_k is formally given as follows:

$$X_k = \int_{-\infty}^{\infty} dx\ \psi(x,0) \frac{e^{-\tau^2/2}H_k(\hat{\mathcal{H}})}{\sqrt{2^k\sqrt{\pi}k!}} \psi(x,0). \tag{30}$$

Denoting $H_k(\hat{\mathcal{H}})/\sqrt{2^k\sqrt{\pi}k!}\,\psi(x,0)$ as vector f_k, we can use the following three-term recursion relation as derived from the property of Hermite polynomials, to compute X_k very efficiently,

$$f_k = \sqrt{\frac{2}{k}}\hat{\mathcal{H}} f_{k-1} - \sqrt{\frac{k-1}{k}} f_{k-2}. \tag{31}$$

Equations (28) and (29) are the main results that can be utilized to solve the generalized eigenvalue problem to obtain the eigenspectrum belonging to the given window.

Few remarks concerning the final expression for overlap and Hamiltonian matrices are in order. First, the parameter η is always less than unity and its physical significance has been pointed out earlier (*vide supra*). As the Hermite functions, $H_k(\hat{\mathcal{H}})$ increases without bound, this will eventually lead to a numerical hazard. To avoid this, we have distributed the factor that is obtained after time integration symmetrically so that in practical calculations we deal only with the normalized terms as clear from Eqs. (28)–(30). Such a distribution of the time integrated factor is not required in the Chebyshev based spectral filter algorithm. We now examine the asymptotic behavior of other terms in Eqs. (28) and (29). For large values of k, the Hermite function may be approximated as follows:[26]

$$\frac{e^{-\tau^2/2}H_k(\tau)}{\sqrt{2^k\sqrt{\pi}k!}} \equiv \sqrt{\frac{2}{\pi}} (2k-\tau^2)^{-1/4} \times \cos\left[(2k+1/2)\frac{\tau}{\sqrt{2k}} - k\frac{\pi}{2} \right]. \tag{32}$$

We thus see that the individual terms in Eqs. (28) and (29) are highly oscillatory for large k, and thus the average value over many periods would be zero. This observation signifies the asymptotic nature of the convergence of the Hermite series in the present context. As the filtered wave functions in a given window are not expected to form an orthogonal set, we are essentially led to an overcomplete eigensystem. As a result, the overlap matrix S is generally *near singular*. This fact has also been noted by other authors. To this end, we have employed the singular value decomposition (SVD) technique, which is well discussed in the literature.[27]

B. Computation of spectral intensities

The spectral intensity is formally defined in terms of eigenstates, as given below:

$$I_l = |d_l|^2 = \left| \int_{-\infty}^{\infty} dx\ \psi(x,0)\Psi(x,E_l) \right|^2. \tag{33}$$

The present formulation permits the computation of spectral intensities with great ease, as we explain here. Using Eqs. (16), (19), and (22), we can express d_l as follows:

$$d_l = \sum_{m=0}^{M} B_{lm} \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} dt\, e^{-t^2/2T^2} e^{i\epsilon_m t} C^s(t). \tag{34}$$

Now we substitute the expression for $C^s(t)$ from Eq. (26) and carry out the time integral explicitly to obtain

$$d_l = \sqrt{2\pi} \sum_{m=0}^{M} B_{lm} \sum_{k=0}^{\infty} \zeta^{k+1} \frac{e^{-\epsilon_m^2\beta^2/2} H_k(\epsilon_m \beta)}{\sqrt{2^k \sqrt{\pi} k!}} X_k, \tag{35}$$

where X_k is defined in Eq. (30) and ζ is $T/\sqrt{2+T^2}$.

C. Error estimates

Eigenvalues obtained by the present method are not all true eigenvalues of the system, and therefore it is mandatory that an independent check is carried out in order to differentiate spurious eigenvalues from the genuine ones. As it has been noted by Wall and Neuhauser,[15] the occurrence of spurious eigenvalues are either an artifact of the singularity of the overlap matrix, S, or due to ''incomplete coverage'' of the frequencies. For this purpose, one can compare the results as obtained from the adjacent overlapping energy windows. The magnitude of the vector, $(\hat{\mathcal{H}} - E_m)\Psi(x,E_m)$, can also serve as a parameter to serve the accuracy of computed results. To be specific, we can compute the error norm ΔE_m defined as follows:

$$\begin{aligned} \Delta E_m^2 &= \left| \int_{-\infty}^{\infty} dx\, \Psi(x,E_m)(\hat{\mathcal{H}} - E_m)^2 \Psi(x,E_m) \right| \\ &= |(B^t H_2 B)_{mm} - E_m^2 (B^t S B)_{mm}|. \end{aligned} \tag{36}$$

Here, the H_2 matrix is defined as follows:

$$(H_2)_{mm'} = \int_{-\infty}^{\infty} dx\, \Psi(x,E_m) \hat{\mathcal{H}}^2 \Psi(x,E_{m'}). \tag{37}$$

As we have explained earlier, Eq. (37) can be computed to obtain

$$\begin{aligned} (H_2)_{mm'} = T\sqrt{\pi} e^{-(\epsilon_m - \epsilon_{m'})^2 T^2/4} & \\ \times \sum_{k=0}^{\infty} \eta^{k+1} \frac{e^{-\tau^2/2} H_k(\tau)}{\sqrt{2^k \sqrt{\pi} k!}} & \\ \times \left[\frac{\sqrt{(k+1)(k+2)}}{2} X_{k+2} \right. & \\ \left. + \left(k + \frac{1}{2} \right) X_k + \frac{\sqrt{k(k-1)}}{2} X_{k-2} \right]. & \end{aligned} \tag{38}$$

It has been shown that ΔE_m^2 represents the upper bound on the true error of the eigenvalues.[28] For the purpose of error estimation, one may also use different variational principles, as suggested by Beck and Meyer,[13] and the extension of the present formulation would be straightforward.

IV. MODELS

A. One-dimensional tunneling

In order to analyze the *finite time* propagation behavior, we have applied the present method to a model one-dimensional scattering problem for which we have the analytical results to compare. One such system is transmission through a symmetric Eckart barrier,

$$V(x) = \frac{V_0}{\cosh^2(\alpha x)}. \tag{39}$$

The transmission factor, i.e., the probability for a particle to pass the barrier has been shown to be[29]

$$P(k) = \frac{\cosh\left(\frac{2\pi k}{\alpha}\right) - 1}{\cosh\left(\frac{2\pi k}{\alpha}\right) + \cosh\left(\pi \sqrt{\frac{8\mu V_0}{\alpha^2 \hbar^2} - 1}\right)}, \tag{40}$$

where k is the wave number related to the energy, $E = \hbar^2 k^2/2\mu$, V_0 and α are the height and width of the barrier, respectively. The parameters chosen for the test are $V_0 = 1\,\hat{\epsilon}$, $\mu = 1$ amu, and $\alpha = 2$ Å. To solve this tunneling problem we have followed the standard pseudospectral grid method.[2] In particular, the system is started by initializing the wave function,

$$\psi(x, t=0) = N \exp[-ik_0 x - a(x - x_0)^2], \tag{41}$$

where $a = 1/(4\sigma^2 - ig)$, $g = (2/k_0)(x_0 - x_f)$, $N = (A/\pi)^{1/4}$, and $A = 8\sigma^2/(16\sigma^4 + g^2)$. The wave packet is centered at x_0 in the position space and at k_0 in the momentum space, with an additional feature that it has its minimum width at the focus point x_f, which may be different from the initial starting point, x_0. We focus the wave packet to have minimum uncertainty just before the potential region, to avoid any interference from the grid boundary due to its fast spreading. The operation of the Hamiltonian on the wave function is obtained by the standard grid method wherein the kinetic energy operator is evaluated by the application of FFT and the potential energy is diagonal on the grid. We discretized the one-dimensional grid into 512 points, ranging from -20 to 20 Å. In order to extract the transmission probability as a function of energy, we numerically evaluate the flux $F(k)$ across the dividing line placed well after the potential. By this technique we can compute the transmission probability as a function of energy by a single wave packet propagation. The transmission probability $P(k)$ across the barrier is then obtained as the ratio between the outgoing and the incoming flux, $P(k) = F_{\text{out}}(k)/F_{\text{in}}(k)$. The incoming flux is computed as

$$F_{in}(k) = \frac{k}{\mu} |\psi_k^-|^2, \tag{42}$$

TABLE I. Numerical parameters used in the LiCN calculations.

Parameter	Value	Description
N_R, N_θ	64, 64	Number of grid points
$R_{\min}$, $R_{\max}$	2.2 a.u., 5.7 a.u.	Spatial range for R coordinate
$\theta_{\min}$, $\theta_{\max}$	0, π	Spatial range for θ coordinate
r_0	2.186 a.u.	Frozen C–N bond length
μ_R, μ_r	10 071 a.u., 11 779 a.u.	Reduced mass for Li–CN, C–N
V_{cut}	12 000 cm^{-1}	Potential energy cutoff
T	0.27 ps	Width of the Gaussian filter
L	100	Number of equispaced energies in each window

where

$$\psi_k^- = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} dx\, e^{ikx} \psi(x, t=0); \tag{43}$$

Eq. (43) can be evaluated analytically. To obtain the outgoing flux $F_{\text{out}}(k)$ we use the time–energy transform instead of space–momentum transform, as the latter requires all the wave functions at a later time on the grid. Thus the outgoing flux is given as

$$F_{\text{out}}(k) = \frac{\hbar^2 k^2}{\mu^2} \frac{k}{\mu} |\psi_E^+|^2, \tag{44}$$

where

$$\psi_E^+ = \frac{1}{\sqrt{2\pi}} \int_0^{\infty} dt\, e^{iEt/\hbar} \psi(x^*, t), \tag{45}$$

where x^* is the projection point. In the present application, the outgoing flux has been evaluated by numerical integration with a time step of 1 fs and the total propagation time was 0.2 ps.

B. Eigenspectrum of LiCN

We utilize the Hermite formulation of the spectral filter problem to study the eigenspectrum of a two-dimensional model of LiCN. In this model, the LiCN Hamiltonian is given by[30]

$$\hat{\mathcal{H}} = -\frac{\hbar^2}{2\mu_R} \frac{\partial^2}{\partial R^2} - \left(\frac{\hbar^2}{2\mu_R R^2} + \frac{\hbar^2}{2\mu_r r_0^2} \right) \times \frac{1}{\sin\theta} \frac{\partial}{\partial \theta} \sin\theta \frac{\partial}{\partial \theta} + V(R, \theta), \tag{46}$$

where the Jacobi coordinates R and θ denote, respectively, the distance between Li and the center of mass of CN moiety, and the angle between R and the CN axis, whereas r_0 specifies the frozen CN distance. The reduced mass parameters are given as, $\mu_R = m_{\text{Li}}(m_{\text{C}} + m_{\text{N}})/(m_{\text{Li}} + m_{\text{C}} + m_{\text{N}})$, and $\mu_r = m_{\text{C}} m_{\text{N}}/(m_{\text{C}} + m_{\text{N}})$. The potential was taken from Ref. 31, which has the form $V(R, \theta) = \Sigma_m^9 C_m(R) \mathcal{P}_m(\cos\theta)$, where $\mathcal{P}_m(\cos\theta)$ is the Legendre polynomial. In order to accomplish the Hamiltonian operation on the wave function, we have utilized a spectral method for the θ derivative and a Fast Fourier Transformation algorithm for the R derivative. In particular, we take the Legendre polynomial basis for the θ variable to obtain the Hamiltonian in the following form:

$$\mathcal{H}_{pp'} = \delta_{pp'} \left[-\frac{\hbar^2}{2\mu_R} \frac{\partial^2}{\partial R^2} + p(p+1) \left(\frac{\hbar^2}{2\mu_R R^2} + \frac{\hbar^2}{2\mu_r r_0^2} \right) \right] + \frac{\sqrt{(2p+1)(2p'+1)}}{2} \times \langle \mathcal{P}_{p'}(\cos\theta) | V(R, \theta) | \mathcal{P}_p(\cos\theta) \rangle. \tag{47}$$

We have also imposed a cutoff, V_{cut} on the potential, and evaluate the integral involving potential using a Gauss–Legendre quadrature method.[32] We note that the cutoff in the potential implicitly determines the number of terms in the polynomial series to achieve the convergence. We have taken random numbers for the initial wave function. We list the numerical parameters used in the present calculation in Table I.

In order to make a comparison, we have also obtained the eigenspectrum of LiCN by direct diagonalization of the full Hamiltonian matrix (4096×4096). In order to construct the Hamiltonian matrix, we define the R grid using the functions $f(R_j) = \delta(R_i - R_j) = 1/\pi\, \text{sinc}[2\pi(R_i - R_j)/\Delta R]$, ($\text{sinc}(z) = \sin(z)/z$). This basis function is zero on all other grid points except j, where its value is 1. The potential energy matrix is diagonal on this grid. To obtain the kinetic energy matrix elements, a discrete Fourier transform is applied to the expansion function f_j, then multiplied by $\hbar^2 k^2/2\mu$ and back transformed.

V. RESULTS AND DISCUSSION

Even though we have based a significant part of our analysis on the eigenvalues perspective, we test the efficacy

TABLE II. A comparison of exact and numerical tunneling probabilities by Hermite and Chebyshev propagation.

Energy[a]	Exact	Hermite	Chebyshev
0.453 740	0.129 987E−09	0.135 679E−09	0.135 679E−09
0.516 255	0.300 798E−08	0.294 798E−08	0.294 798E−08
0.582 804	0.696 068E−07	0.691 266E−07	0.691 266E−07
0.653 385	0.161 075E−05	0.160 949E−05	0.160 949E−05
0.728 000	0.372 725E−04	0.372 865E−04	0.372 865E−04
0.806 648	0.861 800E−03	0.861 713E−03	0.861 713E−03
0.889 330	0.195 692E−01	0.195 694E−01	0.195 694E−01
0.976 045	0.315 952E+00	0.315 957E+00	0.315 957E+00
1.066 793	0.914 445W+00	0.914 454E+00	0.914 454E+00
1.161 574	0.995 973E+00	0.995 980E+00	0.995 980E+00

[a]Energy in $\hat{\epsilon}(1\ \hat{\epsilon} = 100$ kJ).

of the present method on a one-dimensional scattering problem for the following reason. In an approximate quantum propagation method there are two sources of errors—one is the stability of the norm and the other error creeps into the phase. While the error in the norm reflects the instability in the propagation scheme due to ''numerical dissipation,'' the error in the phase gives rise to incorrect dynamics of the system being studied. With the present test problem on tunneling, the error in the phase is clearly monitored for the very simple reason that the computed transmission probability will not be accurate because of the phase error, even though the norm remains conserved throughout the propagation. In Table II, we compare the exact transmission probabilities as a function of energy with those obtained by the Hermite propagation method. The excellent agreement of the computed result with the exact one, as seen in Table II, clearly indicates that the error in phase is fully controlled. Throughout the time propagation, the norm of the wave function was preserved to the 16 decimal accuracy. In order to make a comparison of the dynamics generated by the present method, we have also utilized the Chebyshev propagation method and listed the result in Table II. We note the transmission probabilities as obtained by the Hermite and the Chebyshev methods are exactly the same. We also present

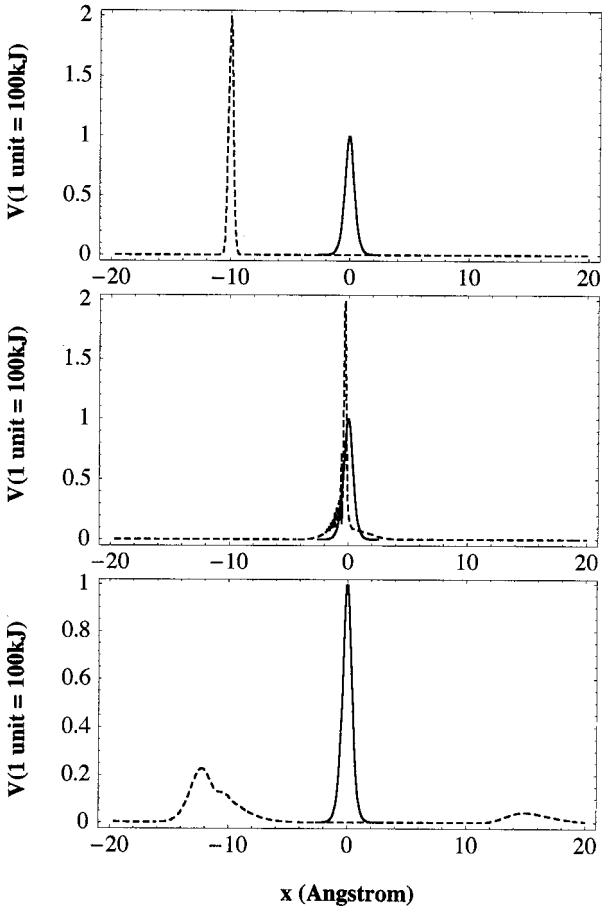

FIG. 1. Snapshots of the amplitude of the wave function at different times. The top panel refers to $t=0$, the central panel to $t=0.084$ ps, and the bottom panel to $t=0.2$ ps. A solid line denotes the potential barrier and the broken line denotes the wave function.

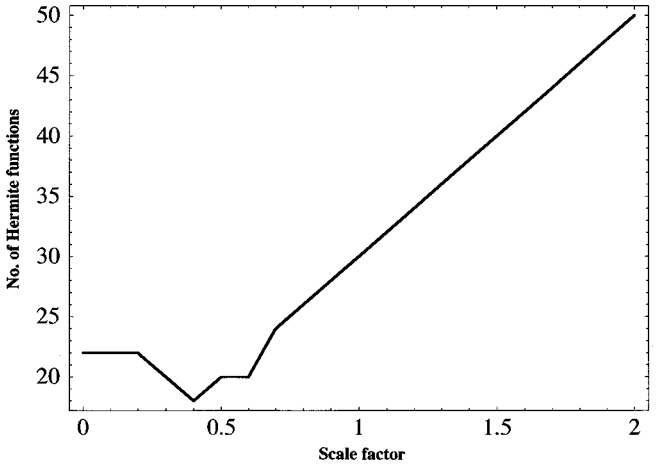

FIG. 2. The number of Hermite functions required for a fixed accuracy in norm (10^{-12}) as a function of the scale factor. For each scale factor, the Hermite propagator was iterated 2000 times with a time step of 1 fs.

snapshots of the amplitude of the moving wave function in Fig. 1. At every instant of time, the Hermite propagated wave function exactly matches the one obtained using the Chebyshev method. This clearly indicates that the dynamics generated by the present method is in complete harmony with the Chebyshev propagation method.

We now make a comparison of the numerical effort involved in both methods to achieve a fixed accuracy (10^{-12}) in the norm. For the present model system, the Chebyshev method utilizes a fixed 22-term expansion of the series [Eq. (6)] for 1 fs time step, which implies a total 22 normalized Hamiltonian operations on a vector, along with some numerical overhead to compute the Bessel function. On the other hand, there is no extra numerical overhead, apart from the Hamiltonian operations, with the present method [cf. Eqs. (8) and (11)]. However, the performance of the present scheme is dependent on the choice of scale factor. For a fixed accuracy in the norm (10^{-12}), we plot in Fig. 2 the number of Hermite polynomials required for the convergence as a function of scale factor. The plot in Fig. 2 is quite revealing and it clearly demonstrates that by choosing a suitable scale factor one can achieve an enhanced performance by the present method. In particular, in the present calculation a 18 terms Hermite expansion gives identical accuracy in contrast with 22 terms Chebyshev expansion. This suggests that the Hermite propagation method is comparable to the Chebyshev based method and by a proper choice of scaling parameter it may be possible to achieve a faster convergence with the Hermite based method for finite time propagation. We point out that the optimization of the scale factor has to be carried out only once in the beginning of the propagation, and a ceiling on the number of terms in the expansion (5) can be imposed at the beginning of the calculation.

Now we turn to the Hermite polynomial based spectral filter method to compute the interior eigenspectrum of LiCN. For this purpose we start with random numbers for the initial wave function and compute the vector X_k [Eq. (30)]. In order to understand the numerical convergence of the overlap and Hamiltonian matrix elements, we note Eqs. (28) and (29) involve the sum of a product of two terms. The first term is

the normalized Hermite function of filter energy argument, which fluctuates symmetrically around the origin with ever diminishing amplitude. To get further insight, we have plotted the second term, X_k, in Fig. 3, which clearly shows the asymptotic nature of the convergence of Eqs. (28) and (29). We note from Fig. 3 that the quantity X_k falls off sharply with increasing k, with a minimum at around $k=4000$ and then it fluctuates with ever diminishing amplitude. This minimum point was found to be sufficient to yield good result. We have therefore employed 4000 terms in the Hermite expansion. We have not enforced any time–energy scaling in the present test. To compute the eigenvalues we select a window of size 1000 cm^{-1} and discretize it into 100 equispaced parts. Next, we shift the window's starting point in steps of 250 cm^{-1}. For each window, we calculate the overlap and Hamiltonian matrices and solve the generalized eigenvalue problem. We retain only those eigenvalues in each window that lies at the internal region covering only half of the size and compute the average of the predictions from the adjacent windows. In Table III, we compare the eigenvalues obtained by the present spectral filter method with those obtained by exact diagonalization. Also included in Table III are the error estimates using Eq. (36). It is clear from Table III that the computed results are within a few cm^{-1} from the exact one. Much of the differences are due to inadequate optimization of the Gaussian damping cutoff parameter and the eventual convergence of the series. In the present study, our motivation has been to test the functioning of the method and therefore we have not tried to optimize the Gaussian width parameter. We also note the recent study of Beck and Meyer,[13] which shows that the filter diagonalization procedure, in their implementation, does not produce very good results with a Gaussian damping function, and they have instead suggested the use of a cosine type damping function, which could be explored in future studies.

We now make a comparison of the numerical effort involved in the Hermite method with the Chebyshev method for the spectral filter problem. Within the Chebyshev polynomial framework, the expression for the overlap and Hamiltonian matrix elements is given as[15]

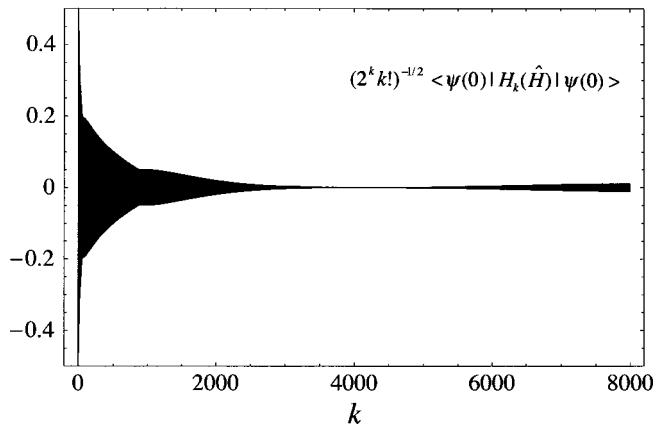

FIG. 3. The behavior of X_k [Eq. (30)] as a function of recursion.

TABLE III. A comparison of eigenvalues (cm^{-1}) for the two-dimensional model of LiCN. All eigenvalues are given relaitve to the numerically exact ground state. The calculated values are the average between the adjacent windows.

n	E_n(exact)	E_n(calc.)	ΔE_n [Eq. (36)]
36	2530.3	2528.5	0.1267
37	2581.3	2579.4	0.1263
38	2593.2	2590.7	0.1263
39	2609.8	2607.6	0.1263
40	2667.6	2664.1	0.1257
41	2693.2	2692.3	0.1256
42	2742.9	2743.1	0.1252
43	2760.9	2764.3	0.1275
44	2823.7	2820.9	0.1259
45	2852.5	2849.2	0.1253
46	2896.9	2894.4	0.1249
47	2916.7	2917.0	0.1249
48	2917.4		
49	2927.9	2928.3	0.1248
50	2952.3	2950.9	0.1243
51	2975.3	2973.5	0.1237
52	2993.8	2996.1	0.1232
83	3751.1	3749.6	0.1158
84	3760.4	3761.0	0.1151
85	3769.4	3772.3	0.1144
86	3818.1	3817.7	0.1128
87	3836.7	3840.3	0.1126
88	3852.8	3851.7	0.1125
89	3872.4	3874.4	0.1123
90	3895.5	3897.1	0.1119
91	3911.3	3908.5	0.1116
92	3919.4	3919.8	0.1114
93	3967.0	3965.2	0.1110
94	3978.3	3976.5	0.1111
95	3985.6	3987.8	0.1113
96	4015.0	4015.1	0.1092
97	4032.4	4032.1	0.1088
98	4061.1	4060.5	0.1087
99	4080.6	4083.3	0.1087
100	4096.6	4094.6	0.1086
101	4114.9	4111.6	0.1082
102	4122.7	4123.0	0.1080
103	4146.0	4145.7	0.1074
104	4177.8	4074.1	0.1071
105	4206.8	4208.2	0.1067
106	4215.7	4213.9	0.1066
107	4224.7	4225.3	0.1064

$$(H)S_{m,m'} = T\sqrt{\pi}e^{-(\epsilon_m-\epsilon_{m'})^2T^{2/4}} \times \sum_{k=0}^{\infty} f_k b_k[(\epsilon_m+\epsilon_{m'})/2,T], \tag{48}$$

with $f_k=g_k$ and $[\Delta\lambda/2(g_{k+1}+g_{k-1})+\bar{\lambda}g_k$ for the overlap and Hamiltonian matrix elements, respectively, and g_k is $\langle\psi(x,0)|T_k(\mathcal{H}_{\text{norm}})|\psi(x,0)\rangle$. Here $b_k(\epsilon,x)$ is given as $(2-\delta_{k0})(2x/\sqrt{\pi})(-1)^k\int_{-1-\cos\theta^*}^{1-\cos\theta^*}du[T_k(u+\cos\theta^*)/\sqrt{1-(u+\cos\theta^*)^2}]\exp[-(x\Delta\lambda)^2u^2]$, with $\cos\theta^*=(\bar{\lambda}-\epsilon)/\Delta\lambda$ and T_k is the Chebyshev polynomial. Now X_k in Eqs. (28) and (29) and f_k in Eq. (48) involve a similar three-term recursion scheme, with equivalent numerical scaling. However, b_k's in Eq. (48) have to be evaluated by numerical integration and we can immediately see that the corresponding quantity in Eqs. (28) and (29) are much easier to evaluate

by the well-known Hermite recursion scheme. In fact, the evaluation of b_k's in Eq. (48) becomes the numerical bottleneck if the energy window is large and densely discretized. This clearly displays the feasibility of the present method with much less numerical effort in comparison to the Chebyshev polynomial formulation.

VI. CONCLUSION

We have demonstrated in this paper the feasibility of the Hermite polynomial based propagation method to study quantum dynamical problems, and carried out a detailed comparison with the well-known Chebyshev based scheme. In order to understand the convergence behavior of the approximating series for a *finite* time propagation, we have introduced the *time–energy scaling* concept, and this has clearly demonstrated that the Hermite propagation method, by suitable time–energy scaling, offers a competitive numerical tool for the purpose. In the *infinite* propagation scenario, the present approach can provide a compact and numerically efficient paradigm for certain problems, due to a more ''friendly'' analytical behavior of the ensuing series, compared to the Chebyshev propagation method. In particular, we have applied the Hermite propagation method to the time domain theory of spectral filters with Gaussian damping and thereby obtained a very compact and numerically efficient scheme for the purpose. We have thus presented a new and complementary propagation method to study quantum dynamics. In the present study we have not explored the use of other types of damping functions (e.g., the cosine type, as suggested by Beck and Meyer[13]) and left it for future investigation. Time–energy scaling could also provide additional leverage for accelerating the convergence of the series in the spectral filter context, and this issue will be studied in the future.

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