Laguerre scheme: Another member for propagating the time-dependent Schrödinger equation

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A global propagation scheme for the time-dependent Schrödinger equation is proposed on the basis of the generating function of the Hermite polynomial for expansion of the evolution operator $e^{-i\hat{H}t}$. Theoretical analysis and numerical tests have shown that the present scheme is an equivalent to the Chebyshev scheme with two extra advantages. [S1063-651X(99)02202-3]

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A time-dependent computational method for solving the Schödinger equation has already become a powerful tool for both the scattering and eigenvalue problems. Many excellent review articles are available for evaluating different time propagation schemes and their applications [1]. In this paper we present a time propagation approach which can be classified as equivalent to the Chebyshev scheme proposed by Tal-Ezer and Kosloff [2]. The main idea is extremely simple, and uses just the generating function of the Hermite polynomial for the expansion of the exponential operator $e^{-i\hat{H}t}$, where the Hamiltonian $\hat{H}$ of the system under study is assumed to be time independent: the same condition as that of the Chebyshev scheme. Using Gray's procedure [3], the Hermite polynomial in the expansion is replaced by the Laguerre polynomial.

The time-dependent Schödinger equation with the above $\hat{H}$ and its formal solution are given by

$$i\frac{\partial\psi(t)}{\partial t}=\hat{H}\psi(t),\quad \psi(t)=e^{-i\hat{H}t}\psi(0), \tag{1}$$

where $\psi(0)$ is an arbitrary initial wave function. Throughout the paper the atomic unit is used. Recall that the Hermite polynomial is related to its generating function by [4]

$$e^{-s^2+2sx}=\sum_{n=0}^{\infty}\frac{s^n}{n!}H_n(x), \tag{2}$$

where $H_n(x)$ denotes the Hermite polynomial of order n. Next, rearrange the exponential operator $e^{-i\hat{H}t}$ into the form

$$e^{-i\hat{H}t}=e^{-(t/2\lambda)^2}e^{-(-it/2\lambda)^2+2\lambda\hat{H}(-(it/2\lambda))}; \tag{3}$$

here an arbitrary parameter λ was introduced for convenience of later use. By comparing Eq. (3) with Eq. (2) by setting $s=-it/2\lambda$ and $x=\lambda\hat{H}$, we immediately obtain the Hermite expansion for $e^{-i\hat{H}t}$,

$$e^{-i\hat{H}t}=e^{-(t/2\lambda)^2}\sum_{n=0}^{\infty}\frac{(-i)^n}{n!}\left(\frac{t}{2\lambda}\right)^n H_n(\lambda\hat{H}), \tag{4}$$

and thus the formal solution of Eq. (1) can be formulated as

$$\psi(t)=e^{-(t/2\lambda)^2}\sum_{n=0}^{\infty}\frac{(-i)^n}{n!}\left(\frac{t}{2\lambda}\right)^n\phi_n, \tag{5}$$

where $\phi_n=H_n(\lambda\hat{H})\psi(0)$. It is easily shown that when $n>(et/2\lambda)-1$, the term $(1/n!)(t/2\lambda)^n$ will behave like $e^{-n\ln[(n+1)/e(2\lambda/t)]}$, which means that the expansion (4) converges exponentially. Likewise, the recurrence relation for the Hermite polynomial [4] can produce an recursive algorithm for expansion (5), i.e.,

$$\begin{aligned}&\phi_{n+1}=2(\lambda\hat{H})\phi_n-2n\phi_{n-1},\\ &\phi_0=\psi(0),\quad \phi_1=2\lambda\hat{H}\psi(0).\end{aligned} \tag{6}$$

Moreover, if imaginary time propagation is needed, the same procedure as the above can be used to obtain the corresponding expansion. The result is

$$\begin{aligned}\Psi(t)&=e^{-\hat{H}t}\psi(0)\\ &=e^{-(t/2\lambda)^2}e^{-(-it/2\lambda)^2+2(-i\lambda\hat{H})(-(it/2\lambda))}\psi(0)\\ &=e^{-(t/2\lambda)^2}\sum_{n=0}^{\infty}\frac{(-i)^n}{n!}\left(\frac{t}{2\lambda}\right)^n\Phi_n,\end{aligned} \tag{7}$$

where $\Phi_n=H_n(-i\lambda\hat{H})\psi(0)$, and the recursive algorithm for Φ_n, still in terms of the recurrence relation for the Hermite polynomial, now becomes

$$\begin{aligned}&\Phi_{n+1}=2(-i\lambda\hat{H})\Phi_n-2n\Phi_{n-1},\\ &\Phi_0=\psi(0),\quad \Phi_1=2(-i\lambda\hat{H})\psi(0).\end{aligned} \tag{8}$$

It is obvious that expansion (7) for the imaginary time propagation has the same rate of convergence as the real time propagation [Eq. (5)] because the corresponding coefficients and norm of the Hermite polynomial of the operator occurring in Eqs. (5) and (7) are the same.

A few remarks can be drawn from a comparison of the present expansion with the Chebyshev scheme: First, the present scheme is a global propagator which allows for large time steps while propagating the wave function. Next, there is no need to scale the Hamiltonian into a special norm, and hence no risk of numerical instability due to the inappropriate estimate for $\Delta E=E_{\max}-E_{\min}$, where $E_{\max}$ and $E_{\min}$ are the estimated maximal and minimal energies on the grids, respectively. Finally, the expansion coefficients relevant to time t are extremely simple monomials, multiplied by a common Gaussian function of time t, which are easy to operate both analytically and numerically. For example, in many applications we need to calculate the one-time correlation function $C(t)=\langle\psi(0)|\psi(t)\rangle$ and its windowed Fourier transform $\int w(t)C(t)e^{-iEt}dt$ for bound-state problems, and the two-time correlation function $I(t,\mathbf{x})=\int_0^t\phi(t-\tau,\mathbf{x})^*\psi(\tau,\mathbf{x})d\tau$ for scattering problems. These two integrals can be readily computed through the present propagation scheme. The following formula is given for the two-time correlation function:

$$I(t,\mathbf{x})=\sum_{n=0}^{\infty}\sum_{m=0}^{\infty}\frac{(-1)^m i^{n+m}}{n!m!}A_{n,m}(t)f_n^{\phi}(\mathbf{x})^*f_m^{\psi}(\mathbf{x}) \tag{9}$$

where

$$A_{n,m}(t)=2\lambda\left(\frac{t}{4\lambda}\right)^{n+m+1}e^{-2(t/4\lambda)^2}\times\int_{-1}^{+1}e^{-2(t/4\lambda)^2s^2}(1+s)^n(1-s)^m ds,$$
$$f_n^{\phi}(\mathbf{x})=H_n(\lambda\hat{H})\phi(0,\mathbf{x}),\quad f_m^{\psi}(\mathbf{x})=H_m(\lambda\hat{H})\psi(0,\mathbf{x}), \tag{10}$$

in which the integral in $A_{n,m}(t)$ can be easily calculated by the Legendre or Chebyshev quadrature. Similarly, the expression for the one-time correlation function can be obtained with less effort than the above. In the Chebyshev scheme, $A_{n,m}(t)$ involves an infinite series of the Bessel functions of integer order.

In actual implementation expansions (5) or (7) are truncated in terms of a given accuracy which may be the accuracy limit of the computer. In general, the total number of expansion terms will be slightly larger than the convergence criterion $(et/2\lambda)-1$. It is because of the truncation that the present scheme also becomes nonunitary, similar to the Chebyshev scheme; thus the deviation from unitarity can be used as an accuracy check for numerical calculations. In the following numerical test for the present scheme, Gray's procedure [3] has been adopted to replace the exponential operator $e^{-i\hat{H}t}$ with $\cos(\hat{H}t)$ and $\sin(\hat{H}t)$. This method allows a separation of the propagation into real and imaginary parts of the wave function $\psi(t)$, i.e.,

$$\psi_r(t+\tau)=-\psi_r(t-\tau)+2\cos(\tau\hat{H})\psi_r(\tau),$$
$$\psi_i(t+\tau)=+\psi_i(t-\tau)-2\sin(\tau\hat{H})\psi_r(\tau), \tag{11}$$

with the initial steps

$$\psi_r(\tau)=\cos(\tau\hat{H})\psi_r(0)+\sin(\tau\hat{H})\psi_i(0),$$
$$\psi_i(r)=\cos(\tau\hat{H})\psi_i(0)-\sin(\tau\hat{H})\psi_r(0), \tag{12}$$

where τ is a time propagation step. ψ_r and ψ_i represent the real and imaginary parts of the wave function ψ, respectively. The advantage of Gray's procedure is that the operator parts in Eq. (11) act only on the real part of the wave function $\psi_r(t)$ at each propagation step. If the initial wave function is real, this procedure can reduce computational effort by a factor of 2.

By first splitting Eq. (4) into real and imaginary parts, and further using the relations between Hermite and Laguerre polynomials [5],

$$H_{2n}(x)=(-1)^n 2^{2n} n! L_n^{-1/2}(x^2),$$
$$H_{2n+1}(x)=(-1)^n 2^{2n+1} n! x L_n^{1/2}(x^2), \tag{13}$$

we obtain the following results for $\cos(\tau\hat{H})\psi_r(t)$ and $\sin(\tau\hat{H})\psi_r(t)$:

TABLE I. Potential parameters (a.u. throughout).

Harmonic	Morse
$\frac{1}{2}\mu\omega^2x^2$	$De(1-e^{-\beta x})^2$
$\mu=918.491$	$\mu=918.491$
	$\beta=1.02764$
	$De=0.17444$
$\omega=\omega_0$	$\omega_0=\beta\sqrt{2De/\mu}$

$$\cos(\tau\hat{H})\psi_r(t)=e^{-(t/2\lambda)^2}\sum_{n=0}^{\infty}\frac{(-1)^n}{(2n)!}\left(\frac{t}{2\lambda}\right)^{2n}H_{2n}(\lambda\hat{H})\psi_r(t)$$
$$=\sum_{n=0}^{\infty}C_n(\tau)\phi_n^{(r,c)}(t),$$
$$\sin(\tau\hat{H})\psi_r(t)=e^{-(t/2\lambda)^2}\sum_{n=0}^{\infty}\frac{(-1)^n}{(2n+1)!}\left(\frac{t}{2\lambda}\right)^{2n+1}\times H_{2n+1}(\lambda\hat{H})\psi_r(t)$$
$$=\sum_{n=0}^{\infty}\frac{2}{2n+1}C_n(\tau)\phi_n^{(r,s)}(t), \tag{14}$$

where $C_n(\tau)=e^{-(t/2\lambda)^2}[2^n/(2n-1)!!](\tau/2\lambda)^{2n}$, $\phi_n^{(r,c)}(t)=L_n^{-1/2}(\lambda^2\hat{H}^2)\psi_r(t)$, and $\phi_n^{(r,s)}(t)=\lambda\hat{H}L_n^{1/2}(\lambda^2\hat{H}^2)\psi_r(t)$, which satisfy the recurrence relations [5]

$$(n+1)\phi_{n+1}^{(r,c)}(t)=(2n+1/2-\lambda^2\hat{H}^2)\phi_n^{(r,c)}(t)-(n-1/2)\phi_{n-1}^{(r,c)}(t),$$
$$\phi_0^{(r,c)}(t)=\psi_r(t),\quad \phi_1^{(r,c)}(t)=1/2\phi_0^{(r,c)}(t)-\lambda^2\hat{H}^2\psi_r(t),$$
$$\phi_n^{(r,s)}(t)=\lambda\hat{H}\phi_n^{(r,c)}(t)+\phi_{n-1}^{(r,s)}(t),\quad \phi_0^{(r,s)}(t)=\lambda\hat{H}\psi_r(t). \tag{15}$$

Note that the recurrence relation for $\phi_n^{(r,s)}(t)$ does not need extra evaluation of Hamiltonian operation on $\phi_n^{(r,c)}(t)$, and can just take the intermediate result from the recurrence relation for $\phi_n^{(r,c)}(t)$ because the Hamiltonian operation is squared in the recurrence relation for $\phi_n^{(r,c)}(t)$. Since the Laguerre polynomials have been used in expansion (14), the present propagation scheme is called the *Laguerre scheme*.

Numerical tests in this paper have been carried out on the one-dimensional harmonic and Morse oscillators. The spatial derivative in the Hamiltonian is evaluated using fast Fourier transform, and hence there is no need to go beyond more than one dimension to test the present scheme because, within the Fourier spectral framework, the present scheme numerically shares the same advantages and disadvantages with the Chebyshev scheme. To make a parallel comparison, Gray's procedure [Eqs. (11) and (12)] has also been adopted for the Chebyshev scheme. Following Tal-Ezer and Kosloff [2], the eigenfunctions of the harmonic and Morse oscillators are propagated, and the results are compared to their corresponding analytical solutions of the Schrödinger equation. Errors can be estimated or measured by the norm of the propagated wave functions and the deviations of the propagated wave functions from their exact ones, i.e.,

TABLE II. Comparison of numerical results for the harmonic oscillator between the Laguerre and Chebyshev schemes. For each time step τ the total propagation time $t=10\,000\tau$. The parameter $S=9$ is used.

			Laguerre			Chebyshev		
	n	τ	N	Norm	Error	N	Norm	Error
		5	8	$1.\overbrace{0\cdots0}^{12}$	2.3×10^{-20}	10	$1.\overbrace{0\cdots0}^{12}$	2.4×10^{-20}
		15	15	$1.\overbrace{0\cdots0}^{13}$	1.7×10^{-19}	15	$1.\overbrace{0\cdots0}^{12}$	3.7×10^{-19}
	0	25	21	$1.\overbrace{0\cdots0}^{13}$	3.3×10^{-19}	19	$1.\overbrace{0\cdots0}^{11}$	1.3×10^{-19}
M=32		40	31	$1.\overbrace{0\cdots0}^{12}$	3.1×10^{-19}	25	$1.\overbrace{0\cdots0}^{11}$	3.2×10^{-19}
Δx=0.107		5	9	$1.\overbrace{0\cdots0}^{11}$	2.1×10^{-16}	9	$1.\overbrace{0\cdots0}^{11}$	2.1×10^{-16}
		15	16	$1.\overbrace{0\cdots0}^{11}$	2.6×10^{-16}	15	$1.\overbrace{0\cdots0}^{11}$	2.6×10^{-16}
	5	25	23	$1.\overbrace{0\cdots0}^{11}$	2.7×10^{-16}	19	$1.\overbrace{0\cdots0}^{11}$	6.1×10^{-16}
		40	34	$1.\overbrace{0\cdots0}^{11}$	5.0×10^{-16}	23	$1.\overbrace{0\cdots0}^{11}$	5.6×10^{-16}
		5	11	$1.\overbrace{0\cdots0}^{13}$	2.9×10^{-22}	12	$1.\overbrace{0\cdots0}^{11}$	1.8×10^{-20}
		15	23	$1.\overbrace{0\cdots0}^{13}$	2.6×10^{-21}	21	$1.\overbrace{0\cdots0}^{12}$	2.8×10^{-18}
	0	25	38	$1.\overbrace{0\cdots0}^{12}$	2.2×10^{-21}	28	$1.\overbrace{0\cdots0}^{11}$	1.1×10^{-19}
M=64		40	66	$1.\overbrace{0\cdots0}^{11}$	1.6×10^{-21}	38	$1.\overbrace{0\cdots0}^{11}$	6.8×10^{-20}
Δx=0.07		5	11	$1.\overbrace{0\cdots0}^{13}$	8.5×10^{-25}	12	$1.\overbrace{0\cdots0}^{13}$	1.4×10^{-22}
		15	22	$1.\overbrace{0\cdots0}^{12}$	1.4×10^{-22}	21	$1.\overbrace{0\cdots0}^{12}$	3.4×10^{-20}
	5	25	38	$1.\overbrace{0\cdots0}^{12}$	1.5×10^{-21}	28	$1.\overbrace{0\cdots0}^{11}$	8.8×10^{-20}
		40	67	$1.\overbrace{0\cdots0}^{11}$	5.5×10^{-21}	38	$1.\overbrace{0\cdots0}^{11}$	2.1×10^{-20}

$$\int dx|\psi_{\text{calc}}(x,t)|^2=1, \quad \int dx|\psi_{\text{anal}}(x,t)-\psi_{\text{calc}}(x,t)|^2, \tag{16}$$

where $\psi_{\text{calc}}(x,t)$ denotes the propagated wave function and $\psi_{\text{anal}}(x,t)$ the corresponding analytical one whose form is $\psi_n(x,t)=\psi_n(x,0)e^{-iE_nt}$ where E_n and $\psi_n(x,0)$ are the nth energy level and its corresponding eigenfunction of the harmonic or Morse oscillator.

All details of numerical computation are very simple in this paper. The integrations in Eq. (16) are approximately computed simply by the direct summation form, i.e., for any integrable function $g(x)$, $\int_a^b dx\, g(x)\approx\Sigma_{i=0}^{M}g(x_i)\Delta x_i$ which is the poorest numerical quadrature, but it is enough for our present purpose (see Table II and III). The arbitrary parameter λ introduced in the present propagation scheme can be adjusted to avoid multiplications between large and small numbers in the computer, and to accelerate the convergence of expansions (5), (7), and (14) depending on the systems under study. For the real time propagation, the empirical formula $\lambda=S/H_{\max}$ has been used in our present calculations, in which $H_{\max}=T_{\max}+V_{\max}$ represented on the grid and $S=8-10$ depending on the system considered. Unlike the Chebyshev scheme, the underestimated or overestimated $H_{\max}$ does not cause the numerical instability in the present scheme.

In Table I are listed the potential parameters for the harmonic and Morse oscillators used in this paper. In Tables II and III, Δx and M denote the grid spacing and the number of Fourier grid points, respectively. The parameter τ indicates the propagation time step and, the total propagation time t is $10\,000\tau$ in the calculations. It is necessary to point out that the parameter N in Table II and III is the highest order of expansion determined by the convergence criterion, which is set to be $|R_{N+1}-R_N|<10^{-14}$ for double precision, where R_N represents the Nth term in expansion (14). The number of calls to Hamiltonian acting on the wave function is $2N$ at

TABLE III. Comparison of numerical results for the Morse oscillator between the Laguerre and Chebyshev schemes. For each time step τ the total propagation time $t=10\,000\tau$. The parameter $S=9$ is used.

			Laguerre			Chebyshev		
	n	τ	N	Norm	Error	N	Norm	Error
		5	12	$1.0\overbrace{\cdots0}^{12}$	4.1×10^{-24}	13	$1.0\overbrace{\cdots0}^{12}$	3.1×10^{-22}
		15	26	$1.0\overbrace{\cdots0}^{12}$	5.3×10^{-22}	22	$1.0\overbrace{\cdots0}^{11}$	1.4×10^{-20}
	0	25	42	$1.0\overbrace{\cdots0}^{12}$	1.8×10^{-21}	30	$1.0\overbrace{\cdots0}^{11}$	4.3×10^{-19}
M=64		40	72	$1.0\overbrace{\cdots0}^{12}$	1.2×10^{-20}	41	$1.0\overbrace{\cdots0}^{12}$	1.9×10^{-20}
Δx=0.075		5	12	$1.0\overbrace{\cdots0}^{12}$	6.7×10^{-20}	13	$1.0\overbrace{\cdots0}^{12}$	6.7×10^{-20}
		15	26	$1.0\overbrace{\cdots0}^{12}$	8.0×10^{-20}	22	$1.0\overbrace{\cdots0}^{13}$	1.0×10^{-20}
	5	25	43	$1.0\overbrace{\cdots0}^{13}$	7.3×10^{-20}	30	$1.0\overbrace{\cdots0}^{12}$	7.3×10^{-20}
		40	72	$1.0\overbrace{\cdots0}^{11}$	8.6×10^{-20}	41	$1.0\overbrace{\cdots0}^{12}$	9.0×10^{-20}

each propagation step. Two energy levels $n=0$ and 5 for both oscillators are considered.

The numerical tests for these two model systems have shown the following: First, the accuracy of the method is very high and the error is almost uniformly distributed over different time steps. Second, compared with the Chebyshev scheme, the expansion coefficient $C_n(\tau)$ in Eq. (14) can be easily and accurately calculated through its recurrence relation $C_{n+1}(\tau)=[2/(2n+1)](\tau/2\lambda)^2C_n(\tau)$, which is extremely stable numerically. Third, the method is not unitary, that is, it does not preserve the energy and the norm, but because of its high accuracy, the deviation from the unitarity can be kept as small up to the convergence criterion during the propagation. Finally, we have to mention a numerical drawback of the present scheme. The number of expansion terms needed to converge the sum increases more quickly than that in the Chebyshev scheme as the propagation time step becomes large.

In conclusion, the present scheme can be regarded as an equivalent to the Chebyshev scheme. It shares almost all the advantages and disadvantages except for the drawback mentioned above. However, it also possesses other favorable points that do not exist in the Chebyshev scheme. One is the calculation for the expansion coefficient $C_n(\tau)$. Another is that the present scheme, in principle, does not need to scale the Hamiltonian. Only for numerical reasons we introduced an arbitrary parameter λ in the expansion in order to reduce the operation error between large and small numbers in the computer and to adjust the convergence rate. The empirical formula $\lambda=S/H_{\max}$, with $S=8-10$, aims at balancing between the calculations of $C_n(\tau)$ and $\phi_n(t)$. All these are not strictly restrictive. Therefore, combined with an appropriate interpolation scheme for spatial derivatives instead of the Fourier grid, a potential and promising application of this nonscaling property for the Hamiltonian would be the generalization of the present scheme to any shape of spatial region and irregular (scattered) grids which are important for high-dimensional problems, which is just the motivation for the present paper. A recently developed method, reproducing the kernel Hilbert space [6], would be a good way of doing this. Of course, the Chebyshev scheme could also be extended to this case with our interpolation scheme for spatial derivatives, as long as the scaling of the Hamiltonian could be correctly done.

[1] (a) D. H. Zhang and John Z. H. Zhang, in *Dynamics of Molecules and Chemical Reactions*, edited by R. E. Wyatt and J. Z. H. Zhang (Dekker, New York, 1996), pp. 231–276; (b) R. Kosloff, in *Dynamics of Molecules and Chemical Reactions, ibid.* pp. 185–230; (c) R. Kosloff, Annu. Rev. Phys. Chem. **45**, 145 (1994); (d) *Time-Dependent Quantum Molecular Dynamics*, edited by J. Broeckhove and L. Lathouwers (Plenum, New York, 1992); (e) C. Leforestier *et al.*, J. Comput. Phys. **94**, 59 (1991).

[2] H. Tal-Ezer and R. Kosloff, J. Chem. Phys. **81**, 3967 (1984).

[3] S. K. Gray, J. Chem. Phys. **96**, 6543 (1992).

[4] G. Arfken, *Mathematical Methods of Physicists*, 3rd ed. (Academic, New York, 1985).

[5] I. S. Gradshteyn and I. M. Ryzhik, *Table of Integrals, Series, and Products* (Academic, New York, 1980).

[6] X.-G. Hu, T.-S. Ho, and H. Rabitz, Chem. Phys. Lett. **288**, 719 (1998); Comput. Phys. Commun. **113**, 168 (1998); Phys. Rev. A (to be published).