

The solution of the time dependent Schrödinger equation by the (t, t') method: The use of global polynomial propagators for time dependent Hamiltonians

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Using the (t, t') method as introduced in Ref. 1 [J. Chem. Phys. **99**, 4590 (1993)] computational techniques which originally were developed for time independent Hamiltonians can be used for propagating an initial state for explicitly time dependent Hamiltonians. The present paper presents a time dependent integrator of the Schrödinger equation based on a Chebychev expansion, of the operator $\hat{U}(x, t', t_0 \rightarrow t)$, and the Fourier pseudospectral method for calculating spatial derivatives $[(\partial^2/\partial x^2), (\partial/\partial t')]$. Illustrative numerical examples for harmonic and Morse oscillators interacting with CW and short pulsed laser fields are given.

I. INTRODUCTION

Solving the time dependent Schrödinger equation has become one of the main tools of modeling and simulating molecular encounters. Time dependent quantum methods have been able to reconstruct the reactive scattering experiment of D+H₂.² They became popular in molecular surface encounters^{3(a)} and found useful in photochemistry,^{3(b)} mentioning only a few examples. Therefore it is not surprising that great effort has been devoted in the molecular dynamics community to finding efficient and accurate numerical procedures to solve the time dependent Schrödinger equation.⁴⁻⁶

An important step in the establishment of time dependent quantum mechanical methods has been the introduction of pseudospectral methods.^{7,8} The change is more than a technical improvement on algorithms. An elementary statement is that quantum mechanics is a nonlocal theory. This characteristic has to be reflected in the methods used to describe the quantum world. The foundation of the pseudospectral methods is a global functional base,⁹ therefore the nonlocal character of the representation is built in the formulation. The basic attributes of quantum mechanics such as the commutation relations between conjugate operators are preserved in the pseudospectral description. It can be shown that pseudospectral methods⁹ have exponential convergence characteristics with respect to the number of grid points or basis functions.

Initially in the development,^{7,10} the crude methods of time propagation were unbalanced with respect to the very high quality of the spatial representation. It was the introduction of the Chebychev polynomial expansion of the evolution operator¹¹ which first created a balanced method where both the spatial representation and the evolution operator possessed exponential convergence. The method gains its optimal efficiency for very high order polynomial expansions. Polynomial orders of a few thousand terms are not uncommon in current applications. For encounters described by a stationary Hamiltonian the extreme accuracy and stability of the Chebychev expansion have been found to be superior to other propagation techniques.¹²

For explicitly time dependent problems the construction

of the propagator is more involved due to the problem of time ordering. The customary solution to the problem is to segment the propagation into small intervals for which the time variation of the Hamiltonian is small. The short time intervals mean that the Chebychev expansion is far from optimal. Therefore new methods for propagation of explicitly time dependent problems have been developed. These methods have been based on short iterative polynomial expansions and the use of the Magnus series to overcome the time ordering problem.¹³⁻¹⁵ The method has been found satisfactory but could not reach the high degree of accuracy and efficiency of the Chebychev expansion. In particular that any segmented propagation scheme is bound to accumulate errors.

Explicitly time dependent descriptions are extremely useful for simulating light matter interaction in high fields.¹⁶ A typical example is harmonic generation and above-threshold-ionization spectra obtained in a system composed of noble gas atoms in the presence of high-intensity laser fields.¹⁷ It has been found that accurate determination of ionization rates require a very careful numerical study.¹⁴ Another important example is the control of chemical reactions by a sequence of shaped pulses. The control is obtained by temporal and spatial interference of matter waves and thus is sensitive to accurate determination of the phase. This means that the iterative numerical procedures used to solve the control problem¹⁸ have to be of high quality.

A new approach for the solution of explicitly time dependent problems was introduced in Ref. 1. This approach overcomes the time ordering problem by embedding the problem in an extended Hilbert space which includes an additional "time-coordinate." This embedding transforms the problem to a stationary evolution equation thus overcoming the time ordering problem. In Ref. 19 a (t, t') propagation algorithm was introduced based on a Taylor expansion of the evolution operator in the extended Hilbert space. Fourier basis functions were used to represent the spatial and temporary coordinates x and t' , respectively. The algorithm was found to be powerful in the study of photoionization/detachment of atomic or molecular systems in strong laser

TABLE I. Grid and canonical variables.

Canonical variables	Δ	min	max	Volume
x	$\Delta x = \frac{L}{N_{xp}}$	$x_{\min}=0$	$x_{\max}=L$	$\mathcal{V}_{xp} = hN_{xp}$
p	$\Delta p = \frac{h}{L}$	$p_{\min} = \frac{h}{2\Delta x}$	$p_{\max} = \frac{h}{2\Delta x}$	$\mathcal{V}_{xp} = 2Lp_{\max}$
t'	$\Delta t' = \frac{T}{N_{t'\epsilon}}$	$t'_{\min}=0$	$t'_{\max}=T$	$\mathcal{V}_{t'\epsilon} = hN_{t'\epsilon}$
ϵ	$\Delta \epsilon = \frac{h}{T}$	$\epsilon_{\min} = \frac{h}{2\Delta t'}$	$\epsilon_{\max} = \frac{h}{2\Delta t'}$	$\mathcal{V}_{t'\epsilon} = 2T\epsilon_{\max}$
t	$\Delta t = t_{\text{final}} - t_0$	$t_{\min} = t_0$	$t_{\max} = t_{\text{final}}$	$\mathcal{V}_{tE} = \pi \Delta E \Delta t$
E	$\Delta E = E_{\max} - E_{\min}$	E_{\min}	E_{\max}	$N_{\text{ch}} > \Delta E \Delta t / 2\hbar$
		$V_{\min} + \epsilon_{\min}$	$V_{\max} + \epsilon_{\max} + p_{\max}^2 / 2m$	

fields. The decaying system was represented by complex-scaled time dependent Hamiltonians.

In the present work a new propagation algorithm is developed based on the (t, t') method in which the Chebychev global polynomial expansion of the evolution operator is used for explicitly time dependent problems.

II. THE (t, t') METHOD

The solution of the time dependent Schrödinger equation by the (t, t') method is given for an initial state $\Psi(x, 0)$ as

$$\Psi(x, t) = \int_{-\infty}^{\infty} dt' \delta(t' - t) \Phi(x, t', t), \quad (2.1)$$

where t' acts like additional coordinate in the generalized Hilbert space²⁰ and $\Phi(x, t', t)$ is the solution of the time dependent Schrödinger equation represented by the (t, t') formalism,

$$i\hbar \frac{\partial}{\partial t} \Phi(x, t', t) = \mathcal{H}(x, t') \Phi(x, t', t). \quad (2.2)$$

The $\mathcal{H}(x, t')$ operator is defined for a general time dependent Hamiltonian by,

$$\mathcal{H}(x, t') = H(x, t') - i\hbar \frac{\partial}{\partial t'}. \quad (2.3)$$

The validity of Eq. (2.1) was discussed by Pflifer and Levine²¹ using the time ordering operator, a simple proof has been derived by Peskin and Moiseyev.¹⁹ As shown in Ref. 19 the fact that $\mathcal{H}(x, t')$ is time (i.e., t) independent implies that the time dependent solution of Eq. (2.2) is given by

$$\Phi(x, t', t) = \hat{U}(x, t', t_0 \rightarrow t) \Psi(x, t_0), \quad (2.4)$$

where

$$\hat{U}(x, t', t_0 \rightarrow t) = e^{-(i/\hbar)\mathcal{H}(x, t')(t-t_0)}. \quad (2.5)$$

The present paper presents a time dependent integrator of the Schrödinger equation based on a Chebychev expansion of the operator $\hat{U}(x, t', t_0 \rightarrow t)$, and Fourier or pseudospectral method for calculating the spatial x, t' derivatives.

As noted above [Eq. (2.1)] the wave function $\Phi(x, t', t)$ carries all the dynamical information. The wave function is then represented on a finite grid of sampling points in the x and t' space. The size of the grid is determined by the requirement that $\Phi(x, t', t)$ is effectively band-limited meaning that at the boundaries of the grid the wave functions amplitude is exponentially small or periodic. Periodic boundary condition are usually chosen for the t' coordinate. Another requirement is that the maximum "momentum" is well represented on the grid meaning $p_{\max} = h/2\Delta x$, $\epsilon_{\max} = h/2\Delta t'$, where ϵ_{\max} is the maximum change in energy induced by the time dependent process (see Table I).

The propagation method is based on an iterative scheme generated by the embedded $\mathcal{H}(x, t')$ Hamiltonian. The key step is to perform the operation of $\mathcal{H}(x, t')$ on a generalized vector $\psi(x, t', t)$,

$$\phi(x, t', t) = \mathcal{H}(x, t') \psi(x, t', t). \quad (2.6)$$

The operation is performed by regrouping $\mathcal{H}(x, t')$ to operators local in "coordinate" space x, t' and operators local in "momentum" space $i\hbar(\partial/\partial x)$, $i\hbar(\partial/\partial t')$,

$$\mathcal{H}(x, t') = V_0(x) + V_t(x, t') - \frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} - i\hbar \frac{\partial}{\partial t'}, \quad (2.7)$$

where V_t stands for the time dependent potential term in the Hamiltonian. The potential part of the operation is carried out in coordinate space by multiplying the value of ψ at each grid point by the value of the potential at each grid point in x and t' . The operation local in "momentum" is obtained by transforming $\psi(x, t', t)$ to its "momentum" representation $\psi(k_x, k_{t'}, t)$ multiplying by $\hbar^2 k_x^2 / 2m + \hbar k_{t'}$ at each grid point in momentum and transforming the result back to coordinate space. The transformation to the discrete momentum space and back is performed by the fast Fourier transform algorithm (FFT).^{7,22}

Once the basic operation $\phi = \mathcal{H}\psi$ is defined, it is used in an iterative scheme to calculate the operation of an arbitrary analytic function of the Hamiltonian, $\phi = f(\mathcal{H})\psi$, by a polynomial expansion. In the present study the function corresponding to the evolution operator, i.e., Eq. (2.5) becomes $f(z) = \exp[-(i/\hbar)z(t-t_0)]$. For unitary evolutions for extended propagation periods the optimal polynomial expansion

sion is based on the Chebychev orthogonal polynomials.¹¹ In order to add flexibility with an eye to future nonunitary evolutions problems, the Chebychev expansion was cast into the Newtonian interpolation polynomial.²³ For the application presented here the traditional Chebychev method using the recurrence relation to generate the polynomials would lead to identical results.²⁴

The analytic function $f(z)$ is calculated at a set of support points $\{z_k, f_k\}$, where $f_k = f(z_k)$. The interpolation polynomial is used to approximate the function $f(z)$,

$$f(z) \approx P_{N_{\text{ch}}}(z) \equiv \sum_{n=0}^{N_{\text{ch}}} a_n R_n(z), \quad (2.8)$$

where $R_n(z)$ are the Newtonian polynomials of degree n defined by

$$R_n(z) \equiv \prod_{j=0}^{n-1} (z - z_j) \quad (2.9)$$

and $R_0(z) = 1$. The coefficients a_n is the n th divided difference coefficient²⁵ defined as

$$a_0 = f_0 \quad a_1 = \frac{f_1 - f_0}{z_1 - z_0}, \quad (2.10)$$

and in general for $n > 1$,

$$a_n = \frac{f_n - P_{n-1}(z_n)}{R_n(z_n)}. \quad (2.11)$$

Since the \mathcal{H} Hamiltonian is Hermitian the support points z_k are chosen on the real axis. For a Chebychev based interpolation scheme the points z_k are chosen as the zeros of the $N+1$ Chebychev polynomial $z_k = 2 \cos[\pi(2k+1)/(N+1)]$, which defines points on the interval $\{-2, 2\}$. This choice of support interval ensures stability of the divided difference coefficients. The specific choice of interval has to be reflected in the spectrum of the Hamiltonian which should be renormalized to the $\{-2, 2\}$ interval. This is done by estimating the highest eigenvalue of \mathcal{H} as $E_{\text{max}} \approx p_{\text{max}}^2/(2m) + \epsilon_{\text{max}} + V_{\text{max}}$ and the lowest eigenvalue as $E_{\text{min}} \approx -\epsilon_{\text{max}} + V_{\text{min}}$. V_{min} and V_{max} are the lowest and highest values of the potential $V = V_0 + V_t$ on the x, t' grid. Then the normalized Hamiltonian becomes

$$\mathcal{H}_N = 4 \frac{\mathcal{H} - E_{\text{min}}}{\Delta E} - 2, \quad (2.12)$$

where $\Delta E = E_{\text{max}} - E_{\text{min}}$. \mathcal{H}_N is then used to generate the interpolation polynomials. The normalization of the Hamiltonian is compensated by calculating the function $f(z')$ used to calculate the divided difference coefficients at the points $f[\Delta E(z+2)/4 + E_{\text{min}}]$. Physically this operation means rescaling the time by $4/\Delta E$ and shifting the zero of energy which only changes the total phase.

The combination of the following pseudospectral algorithms: Fourier representation of the x and t' variables and the Newtonian interpolation polynomials using Chebychev sampling points has exponential convergence characteristics with respect to the phase space volume \mathcal{V} containing the

problem. This phase space is the direct product of the phase space volumes of the three pairs of canonical variables,

$$\mathcal{V} = \mathcal{V}_{x,p} \otimes \mathcal{V}_{t',\epsilon} \otimes \mathcal{V}_{t,E}. \quad (2.13)$$

The minimum number of sampling points is determined by this volume as $N > \mathcal{V}/h$. The minimum phase volume can be predetermined. The $\mathcal{V}_{x,p}$ volume is determined by the extent of the spatial grid L containing the significant portion of the wave function and by the maximum momentum required. Optimal results are obtained by balancing the maximum of the kinetic and potential energies by using the virial theorem.²² For an oscillator $p_{\text{max}} = 2m\sqrt{V_{\text{max}}}$ leading to $N_{xp} = \mathcal{V}_{x,p}/h = 2Lp_{\text{max}}/h$ and $\Delta x = L/N_{xp}$. The $\mathcal{V}_{t',\epsilon}$ volume is determined by the period T and the expected excitation energy ϵ_{max} . Finally the order of the Newtonian interpolation polynomial is determined by $N_{\text{ch}} > \Delta E \Delta t / 2\hbar$, where $\Delta t = t - t_0$ is the propagation time per time step. Table I summarizes the convergence characteristics described above.

III. ILLUSTRATIVE NUMERICAL EXAMPLES: FORCED HARMONIC OSCILLATOR

The time dependent Hamiltonian for the forced harmonic oscillator can be written as

$$H(x, t) = -\frac{1}{2} \frac{\partial^2}{\partial x^2} + \frac{x^2}{2} + S(t)x. \quad (3.1)$$

In this case an analytical solution of the time dependent Schrödinger equation is known for a system prepared in the m th eigenstate of the unforced harmonic oscillator.^{26,27} Two cases are analyzed here. In the first case the forcing function $S(t)$ is periodic in time. This case models an atom/molecule interacting with a high intensity CW laser. In the second case $S(t)$ is chosen as a narrow Gaussian to mimic the interaction of a system with an intense short pulsed laser.

A. Continuously driven harmonic oscillator

The quantum adiabatic approach has been suggested as a method for obtaining an eigenfunction of a complicated Hamiltonian by adiabatically switching on an interaction, starting from a known reference Hamiltonian.^{26,29} The accuracy of the method depends on two factors (a) the numerical accuracy of propagating the initial wave function with an explicitly time dependent Hamiltonian; (b) the compliance of the actual switching function with the adiabatic theorem. Since in the (t, t') method the accuracy of propagation can be saturated the method allows the study of the convergence properties of the adiabatic approach for different switching functions. Motivated by the recent study of this quantum adiabatic switching problem by Kohen and Tannor²⁶ the properties of the t, t' method are demonstrated.

Let the adiabatic switching function be defined as

$$S(t) = \sin^2\left(\frac{\Omega}{4} t\right). \quad (3.2)$$

By using the Chebychev expansion of the (t, t') evolution operator $\hat{U}(x, t', t_0 \rightarrow t)$, and Fourier method for calculating the "spatial" (x, t') derivatives the numerical time depen-

TABLE II. Parameters of propagation for the driven harmonic oscillator in a.u.

Grid for CW	$\Delta x=0.313$	$\Delta t'=2\pi/128\Omega$	$N_{xp}=64$	$N_{t'e}=128$
Time propagation for CW	$T=\Delta t=2\pi/\Omega$	$N_{ch}=8792$	$\Omega=0.1-1$	
Grid for pulse	$\Delta x=0.222$	$\Delta t'=2\pi/20$	$N_{xp}=128$	$N_{t'e}=20$
Time propagation for pulse	$\Delta t=\pi/10$	$N_{ch}=64$	$\alpha=0.8$	

dent solution, $\Psi(x, t)$ of the time dependent Schrödinger equation was obtained. Table II summarizes the grid parameters used to converge the calculation.

The expectation value $E(t) = \langle \Psi(t) | H(x, t) | \Psi(t) \rangle$ determines the adiabatic energy of the system as function of time. The standard deviation of this energy is a measure of the adiabaticity of the propagation. In Fig. 1 the standard deviation $\Delta E(t) = \sqrt{\langle H^2 \rangle - \langle H \rangle^2}$ is shown as a function of Ω for the final switching time $t=T=2\pi/\Omega$, as one can see for $\Omega=0.4$ $\Delta E(T)=10^{-8}$ in the numerical calculation. It implies that for $\Omega=0.4$ the wave function $\Psi(x, t=T)$ is an eigenfunction of the adiabatic Hamiltonian $H(x, t=T)$. Since the exact ground state energy of the shifted harmonic oscillator is exactly zero [when $S=1$ in Eq. (3.1)] then the deviation of the adiabatic energy $E(t=T)$ from the analytical result defines the error, i.e., $\text{Error} = |E(t=T)|$. As expected a zero error to the machine accuracy 10^{-16} was obtained for $\Omega=0.4$ (see Fig. 2). This result should be explained since on the basis of the adiabatic theorem one may expect that as Ω is decreased (and thereby T is increased) the Error (T) should be reduced correspondingly. We propose here that the adiabatic theorem provides the exact result when the particle is initially located at the bottom of the original potential well (i.e., $x=0$ when $S=0$) and propagates to the bottom of the shifted potential well (i.e., $x=-1$ and $S=1$) as time passes from 0 to T , with zero momentum $\langle p \rangle$ (i.e., zero velocity) and with zero $d\langle p \rangle/dt$ (i.e., zero acceleration). The expecta-

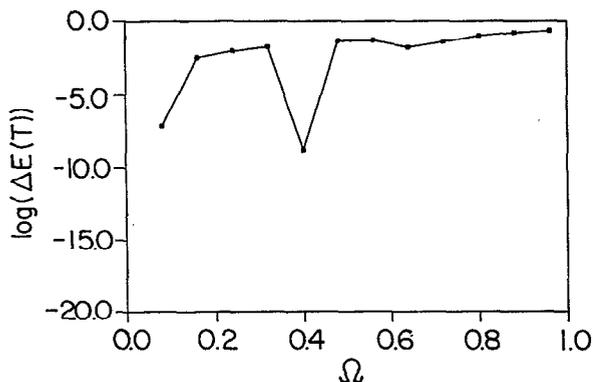


FIG. 1. The standard deviation in the calculated adiabatic energy $\Delta E = [\langle (H - \langle H \rangle)^2 \rangle]^{1/2}$ obtained for $t=T$ and $S(T)=1$ as function of the switch function parameter Ω [see Eq. (3.2)]. The minimal error is obtained for $\Omega=0.4$. The calculations were carried out using 128 t' -grid points and 64 grid points for x . Converged results were obtained with 8792 sampling points for t .

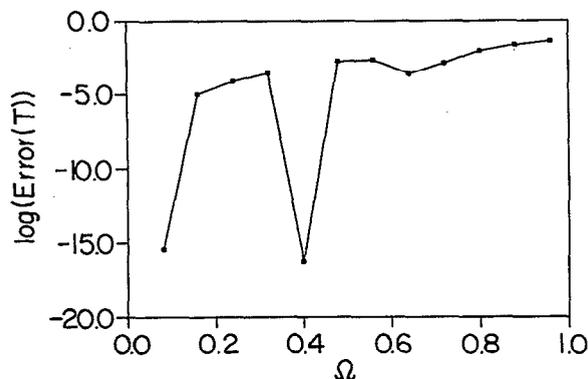


FIG. 2. The error defined as $\text{Error}(T) = |E_{\text{anal}}(T) - E_{\text{num}}(T)| = \langle H(T) \rangle$ as a function of the switching function parameter Ω .

tions $\langle x(t) \rangle$ and $\langle p(t) \rangle$ are associated with the imaginary and real part of $z(t)$ which in this case can be analytically obtained,

$$z(t) = -e^{i\omega t} \left[\int_0^t S(t') e^{-i\omega t'} dt' \right]. \quad (3.3)$$

Therefore the Error (T)=0 when the two following conditions are fulfilled:

$$z(t=T) = -1, \quad (3.4)$$

$$\frac{d}{dt} z(t) \Big|_{t=T} = 0. \quad (3.5)$$

The results presented in Figs. 3 and 4 show clearly that for $\Omega=0.4$ these two conditions are satisfied. Careful analysis of the figures shows that for this particular system an accidental fulfillment of the adiabatic theorem is obtained for $\Omega=0.4$ (also for $\Omega=0.1$). Under these conditions the numerical method was able to reconstruct the adiabatically switched eigenfunction to machine accuracy. Examining the general trend in Figs. 1 and 2 excluding the special points, it is seen

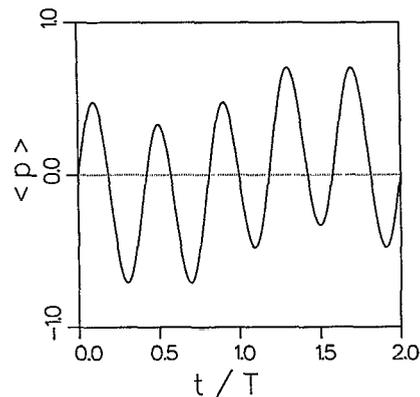


FIG. 3. The expectation value of the momentum $\langle p \rangle$ as function of time for the continuously driven harmonic oscillator defined in Eqs. (3.1), (3.2) for $\Omega=0.4$. When $t=T$ and $S=1$ then $\langle p \rangle=0$ and $d\langle p \rangle/dt=0$ (the last equality is associated with the saddle point shown for $t=T$). See also Fig. 4.

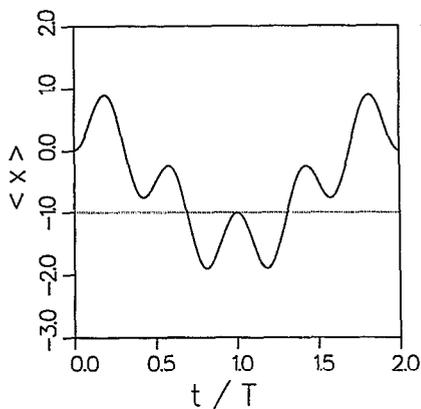


FIG. 4. The expectation of the position $\langle x \rangle$ as function of time for the continuously driven harmonic oscillator defined in Eqs. (3.1), (3.2) for $\Omega=0.4$. For $t=T$ the position $\langle x \rangle = -1$ is obtained which corresponds to $d\langle p \rangle/dt = -\langle dV/dx \rangle = -\langle x \rangle - 1 = 0$.

that the convergence of the propagated wave function to the eigenfunction as a function of the adiabatic parameter Ω is very slow. Since the numerical accuracy is saturated the slow convergence is an intrinsic property of the adiabatic approach. The same disappointing conclusion was also found in Ref. 26 for different choices of $S(t)$.

The performance of the (t, t') method was also compared to the Short iterative Lanczos (SIL) algorithm with a second order Magnus expansion.¹³ The numerical effort to obtain converged results was approximately the same. This is a result of the specific switching function $S(t)$ [Eq. (3.2)] for which the second order Magnus approximation is very accurate.¹³

B. Pulsed driven harmonic oscillator

Let the switching function $S(t)$ be defined as,

$$S(t) = e^{-(t-T)^2/\alpha} \tag{3.6}$$

then $\sqrt{\alpha/2}$ defines the width of the excitation pulse. The exact values of the expectations $\langle x(t) \rangle$ and $\langle p(t) \rangle$ can be obtained by substituting Eq. (3.6) into Eq. (3.3). The (t, t') polynomial procedure was used to generate the same expectation values numerically. Illustrations of the propagated wave function $\Phi(x, t, t')$ are shown in Fig. 5 for the computation parameters of Table II. Figure 6 shows the error in calculating the expectation $\langle x(t=T) \rangle$ for the final time $T = \pi$ and width parameter $\alpha = 0.8$, as a function of the numerical effort. The numerical effort is defined as the number of times the Hamiltonian $\mathcal{H}(x, t')$ operates on a vector during the calculations which is the order of the interpolation polynomial multiplied by the extra effort required by adding the t' variable. This extra effort is estimated as $\approx N_{t'} \log N_{t'}$. The new algorithm is compared to the SIL where the time ordering was treated up to second order in the Magnus series,²⁸

$$U(t) \approx \exp\left(-\frac{i}{\hbar} \int_0^t dt' H(t')\right)$$

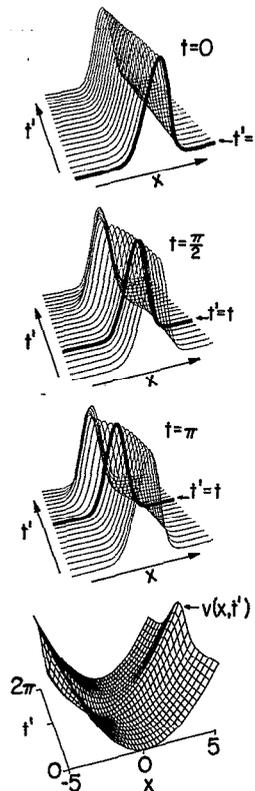


FIG. 5. Snapshots of $\Phi(x, t', t)$ are represented in the first three upper plots for $t=0, \pi/2, \pi$ for the pulsed driven oscillator defined in Eqs. (3.1) and (3.6). The fourth plot shows the interaction potential as function of x and t' . The physical solution, $\Psi(x, t)$, is marked by a solid line for $t'=t$.

$$-\frac{1}{2\hbar^2} \int_0^t dt' \int_0^{t'} dt'' [H(t'), H(t'')] + \dots \tag{3.7}$$

For the switching function of Eq. (3.6) the integrals can be

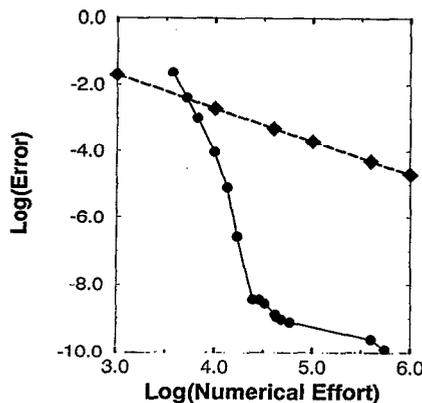


FIG. 6. Log-log plot of the error in $\langle x \rangle$ (defined as the difference between the analytical and the numerical values) for the pulsed driven oscillator defined in Eqs. (3.1) and (3.6), for $t = \pi$ as function of the numerical effort. The numerical effort is defined as the number of operations of the Hamiltonian on a vector during the propagation procedure. The solid line stands for the results obtained by the (t, t') method whereas the dashed line for the results obtained with the SIL and Magnus propagator.

TABLE III. Parameters used for propagation of the forced Morse oscillator (a.u.).

Potential parameters	$D=0.225\ 1$	$\alpha=1.174\ 1$	$\mu=1\ 745$
Forcing parameters	$A=0.011\ 025$	$\omega=0.017\ 87$	$\tau=351$
Grid	$\Delta x=0.08$	$x_0=0.8$	$N_{xp}=64$
	$\Delta t'=34.437\ 5$	$T=351$	$N_{t'}\epsilon=16$
Time propagation	$\Delta t=351$	$N_{ch}=256$	$N_t=1\ 000^a$
	$\Delta t=35\ 100$	$N_{ch}=32\ 768$	$N_t=10^a$

^a N_t is the total number of time steps.

calculated in closed form. A fifth order SIL procedure was used which means that the numerical effort per time step is approximately 10 units since the commutation relation in Eq. (3.7) doubles the numerical effort. The results presented in Fig. 6 show a slow convergence of the SIL method with the numerical effort. However, the combination of the (t, t') method with the Chebychev expansion of the time evolution operator $\hat{U}(x, t', t=0 \rightarrow T)$ provides drastic reduction in the error of the calculated expectation $\langle x(t=T) \rangle$ which has been obtained to the machine accuracy. That is, an error approximately 10^{-10} ! This means that the (t, t') method is about six orders of magnitude more accurate than the conventional SIL+Magnus procedure for the same numerical effort. We should emphasize that the results which are presented in Fig. 6 are universal in the sense that the same behavior has been obtained when the Gaussian width parameter α was varied. It is important to notice that the SIL+Magnus method shows very different convergence properties between the CW and the pulsed driven oscillator. While for the CW case fast convergence was obtained¹³ the pulsed case shows very slow convergence (Fig. 6). A possible explanation is that the pulsed case involves many frequency components which the second order Magnus expansion is not able to account for. The (t, t') method on the other hand shows uniform convergence characteristics for both cases.

C. Forced Morse oscillator

Recently a classical Hamiltonian structure has been identified in wave packet dynamics.³⁰ Utilizing this structure a new class of symplectic propagation techniques has been developed. These algorithms have been applied to the model of Walker and Preston of a diatomic molecule in a strong laser field.³¹ The Hamiltonian becomes

$$H = \frac{1}{2\mu} \frac{\partial^2}{\partial x^2} + V(x) + Ax \cos(\omega t), \quad (3.8)$$

where $V(x)$ is a Morse potential, $V(x) = D[1 - \exp(-\alpha x)]^2$. This system can serve as a good test to the (t, t') method by comparing to the detailed calculations in Ref. 30. The parameters used are consistent with the ones used by Ref. 30, modeling the HF molecule. Also the same grid parameters were used. Table III summarizes the parameters used in the calculation by the (t, t') method. Using a time step of one period of the field $\tau = 2\pi/\omega$, the propagation was executed with a polynomial of order 256 with an error of less than $\text{Error} = 10^{-14}$ for a total period of 100 cycles of the field. The use of a Chebychev polynomial means that the error is uni-

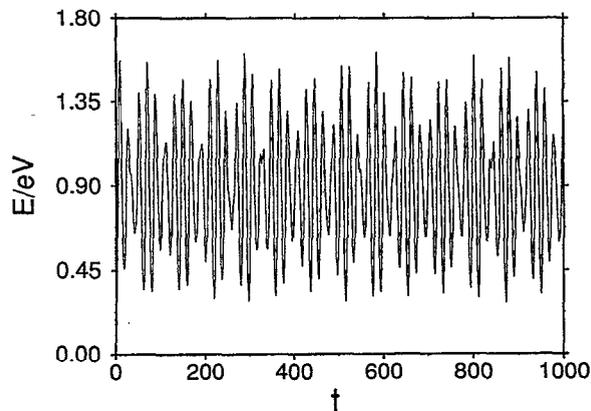


FIG. 7. The mean energy of the Morse oscillator over the $(0, 1000\tau)$ time span ($\tau = 8.505$ fs). The calculation was done with a time step of $1\ \tau$ to an accuracy of 10^{-13} .

formly distributed in the eigenvalue space. Therefore a practical measure of the error is to base it on a conserved quantity such as the deviation of the expectation of embedded Hamiltonian, $\text{Error} = |\langle \mathcal{H} \rangle_{t_{\text{final}}} - \langle \mathcal{H} \rangle_{t=0}|$, where the expectation is on the x, t' space. A more sensitive choice is the local conservation (in t') of norm $|\langle \psi(t) \rangle^2 - \langle \psi(0) \rangle^2|$ since this quantity is sensitive to the size and density of the t' grid. The two estimations of the error became the same for the converged results. This result should be compared to the best results of Ref. 30 which were of the order of 10^{-3} and a typical time step was of the order of $\pi/139$. Moreover using a polynomial of order 32 768 we were able to propagate with a time step of 100 cycles of the field, with accuracy of $\text{Error} < 10^{-13}$. The ability to use extremely high order polynomial expansions is a demonstration of the stability of the Newtonian-Chebychev algorithm which is the result of random cancelation of round of errors. The extremely long time steps mean that the problem of accumulation of errors due to small time steps inherent for prolonged calculations can be eliminated. Figure 7 shows the energy as a function of time for up to 1000 cycles of the field which is identical to Fig. 6 of Ref. 30 displaying the converged results.

It is a point of interest that very accurate time dependent wave functions of a continuous driven HF molecule are obtained by the (t, t') approach even when classical calculations show³² a chaotic dynamics. The driven HF molecule exhibits a classical chaotic motion in spite of the fact that photodissociation of low energy states cannot take place. It seems therefore that the (t, t') method should be used in the study the quantum dynamics of systems which illustrate a classical chaotic motion.

IV. CONCLUSIONS

The combination of the (t, t') formulation and the Newtonian polynomial expansion has great potential. The exponential convergence characteristics which were manifested above allow very long propagation times without accumulation of errors. This is in contrast to all existing methods used to overcome the time ordering problem which rely on small

time steps. Another feature which is not well appreciated is the uniform convergence of the Chebychev polynomial approach. The result is that once one observable is converged all other observables have also converged to the same accuracy. This is in contrast to other propagation techniques where the errors may differ orders of magnitude between different observables.¹² It is commonly found that the amplitude converges much before the phase.

The use of the (t, t') -Newtonian polynomial method has a built in flexibility which allows utilization beyond the ones demonstrated in the present work. The first extension is to choose the support points z_k in the complex plane. This extension allows the study of non-Hermitian Hamiltonian operators which naturally arise in the complex scaled coordinate approach.³⁵ For example the calculation of the dissociation rate out of the Morse well driven by the radiation field can be obtained by this method or by using absorbing boundary conditions³⁶ which will also create a non-Hermitian Hamiltonian. The other natural extension is to replace the exponential function $f(z) = e^{z^2}$ used for propagating in time by other functions for example $f(z) = 1/(z - E - i\epsilon)$ representing the Green's function $G^+(E) = (1/\mathcal{H} - E - i\epsilon)$.^{33,34,37} This choice of functions represents a scattering theory from a time dependent potential.^{19,20,21,38}

This work can be summarized by the statement that the (t, t') method enables the use of powerful global methods which were originally developed for time independent Hamiltonians for explicitly time dependent operators, even for processes which are not time periodic.

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