Communication: An exact short-time solver for the time-dependent Schrödinger equation

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The short-time integrator for propagating the time-dependent Schrödinger equation, which is exact to machine's round off accuracy when the Hamiltonian of the system is time-independent, was applied to solve dynamics processes. This integrator has the old Cayley's form [i.e., the Padé (1,1) approximation], but is implemented in a spectrally transformed Hamiltonian which was first introduced by Chen and Guo. Two examples are presented for illustration, including calculations of the collision energy-dependent probability passing over a barrier, and interaction process between pulse laser and the I₂ diatomic molecule. © 2011 American Institute of Physics. [doi:10.1063/1.3549570]

The understanding of many phenomena in atomic and molecular physics requires an explicit quantum mechanical treatment. Accurate and efficient numerical methods for solving the quantum equations of the processes are powerful ways to understand the realistic molecular encounters. Quantum wave packet studies based upon pseudospectral method are now common in chemical physics because of the good scaling law and the clearly physical picture it provides.¹ Along with the rapid development of the computer power, a broad range of investigations into the efficiency of various algorithms for the solution of time-dependent Schrödinger equation (TDSE) have appeared.^{1–10}

The key stages for modeling of the TDSE on grid are how to represent the wave function on limited grid points and how to integrate the wave function along with its time evolution. Solutions for the later stage [atomic units (a.u.) are adopted unless specified],

$$\Psi(t) = \hat{U}(t)\Psi(0) = \hat{T} \exp\left(-i \int_0^t \hat{H}(\tau) d\tau\right) \Psi(0), \quad (1)$$

(for Ψ on chosen grid points) can be obtained by recursively applying the elementary mapping step, by a short time interval method,³

$$\hat{U}(t) = \prod_{n=0}^{N-1} \hat{U}(\Delta t + n\Delta t, n\Delta t), \quad (2)$$

or by a polynomial expansion method,

$$\hat{U}(t) = \exp(-i\hat{H}t) \approx \sum_{n=0}^N a_n P_n(-i\hat{H}t). \quad (3)$$

We ignore the time-ordering operator $\hat{T}$ because it is irrelevant when the Hamiltonian is time-independent.³

Many short time interval methods are available to solve the TDSE, such as the finite difference method,^{1,2,11} the ex-

ponential split operator method,¹² the propagators in Cayley's form (CF) associated with the operator splitting method or alternating directions implicit (ADI) method,¹³ and the short iterative Lanczos (SIL) method.¹⁴ Usually the convergence of these methods has low orders, except the SIL method which expands the wave function to be evaluated in the Krylov subspace.² Such as the propagator in the CF, which is accurate up to the second order of time-step, can be derived as

$$\begin{aligned} \hat{U}(\Delta t, 0) &= \sin \Delta t \hat{H} - i \cos \Delta t \hat{H}, \\ \hat{U}(-\Delta t, 0) &= \sin \Delta t \hat{H} + i \cos \Delta t \hat{H}, \end{aligned} \quad (4)$$

therefore,

$$\frac{\hat{U}(\Delta t, 0)}{\hat{U}(-\Delta t, 0)} \equiv \hat{U}(2\Delta t, 0) = \frac{1 - i \tan \Delta t \hat{H}}{1 + i \tan \Delta t \hat{H}}. \quad (5)$$

By retaining the first Taylor expansion term of $\tan(x)$, we obtain

$$\hat{U}(\Delta t, 0) \approx \frac{1 - i \Delta t \hat{H}/2}{1 + i \Delta t \hat{H}/2}. \quad (6)$$

The propagator in the CF associated with the finite difference method treating with the space variable(s) is the Crank–Nicolson (CN) method,¹⁵ which has general applications and is typical example in many numerical physics textbooks.^{13,16,17} Currently, it is quite popular for solving the TDSE involving atomic Coulomb potential, Maxwell equation describing electromagnetic propagation, and the time-dependent Gross–Pitaevskii equation describing the properties of Bose–Einstein condensates at ultralow temperature.^{18–26} This method is unconditionally stable and unitary. However, due to its large dispersive error and the low efficiency of the lower order finite difference method,^{1,27} the propagator in the CF has not arisen much interest in chemical physics field so far.

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On the other hand, from Eq. (5) we may define a spectrally transformed Hamiltonian (STH) $\hat{\Theta}$ as

$$\hat{\Theta} = 2 \arctan \left(\frac{\Delta t \hat{H}}{2} \right). \quad (7)$$

$\hat{\Theta}$ has the same eigenfunctions as the original $\hat{H}$, as first proposed by Chen and Guo.²⁸ Then the TDSE with $\hat{\Theta}$ becomes

$$i \frac{\partial \Psi}{\partial \tau} = \hat{\Theta} \Psi \quad (8)$$

and for this TDSE with above spectrally transformed Hamiltonian (TDSE-STH), we have exact short time interval propagator in Cayley's form,

$$\hat{U}_\tau(1, 0) = \exp(-i\hat{\Theta}) \equiv \frac{1-i \tan(\hat{\Theta}/2)}{1+i \tan(\hat{\Theta}/2)} \equiv \frac{1-i \Delta t \hat{H}/2}{1+i \Delta t \hat{H}/2}. \quad (9)$$

The last term in above equation is exactly same as the right side of Eq. (6). Now the propagator in Cayley's form is an exact time integrator for the TDSE with the spectral transformed Hamiltonian Θ . Now τ is the time in the TDSE-STH, corresponding to t in the TDSE. We will name this propagator as Chen–Guo (CG) propagator due to the original idea given in Ref. (6), where this propagator was introduced for a high-resolution spectral calculation.

Realizing this property of the propagator in the CF in Eq. (6), we can model many atomic and molecular dynamics processes following the TDSE using *huge* time-step, which but are exact with respect to the time propagation stage. The idea in this method, in spirit, shares some similarity with the recently proposed Chebyshev real wave packet approach.⁶

The spectrally transformed Hamiltonian Θ has the same eigenfunctions as the original Hamiltonian Θ but different eigenenergies. These eigenenergies have one-to-one relationship and are connected with each other in a simple analytic form. Therefore a simply analytic form can be found to relate the calculated observable of Hamiltonian Θ and H . Finally we note that CG propagator does not require any special grid method, and the finite-difference method used in the traditional CN method or the (pseudo-)spectral method, such as discrete variable representation method, used in quantum dynamics calculations can be straightforward applied, which may result in different numerical efficiencies. The novelty of the CG propagator is how we calculate the desired observable using the concept of the spectrally transformed Hamiltonian, since the CG propagator is still in the CF.

We first consider (i) the particle scattering from a one-dimensional potential barrier, which is illustrated in the left panel of Fig. 1. The potential barrier is given as $V(r) = V_0 X^3/(1 - X^3)$, where $X = \exp(-a_0(r - r_0))$ with $a_0 = 0.5$, $r_0 = 0$, and $V_0 = 2.0$ eV. The initial wave packet, which describes the particle before reaching barrier, comes from the right side to the barrier, with Gaussian shape as

$$\Psi(r; 0) = A \exp \left(\frac{-(r - r_c)^2}{2\sigma_w^2} \right) \exp(-ir k_0), \quad (10)$$

where r_c defines the central position of the initial wave packet. σ_w , k_0 , and A are the width, momentum, and normalization factor of the initial wave packet. The transmission

FIG. 1. Left panel: One-dimensional scattering process of a moving wave packet. Right panel: The convergence of the CG propagator, the propagator in the original CF, and the SESO method. The CG propagator has exponential convergence and its slow convergence at smaller time-step is due to the quality of the applied absorption potential.

scattering matrix is thus obtained in the TDSE as

$$S(E_c) = \frac{1}{2\pi} \frac{1}{C(E_c)C^*(E_c)} \frac{i}{2m} [\Psi(E_c) \nabla \Psi^*(E_c) - \Psi^*(E_c) \nabla \Psi(E_c)], \quad (11)$$

where time-independent energy-resolved $\Psi(E_c)$ and $\nabla \Psi(E_c)$ are calculated by the Fourier transform with respect to time t . $C(E_c)/C^*(E_c)$ is the Fourier transform of the initial/final wave packet $\Psi(r; 0/t)$ with respect to r . m is the reduced mass of the system. When $S(E_c)$ is evaluated in the TDSE-STH by the CG propagator, we have

$$\bar{S}(\theta_c) = \frac{1}{2\pi} \frac{f(\theta_c)}{C(E_c)C^*(E_c)} \frac{i}{2m} [\Psi(\theta_c) \nabla \Psi^*(\theta_c) - \Psi^*(\theta_c) \nabla \Psi(\theta_c)] \equiv \bar{S}(E_c), \quad (12)$$

where time-independent energy-resolved $\Psi(\theta_c)$ and $\nabla \Psi(\theta_c)$ are calculated by the Fourier transform again, but with respect to time τ . The relation between θ and E_c is given by

$$E_c = \frac{2 \arctan(\theta \Delta t / 2)}{\Delta t}. \quad (13)$$

The continuum wave function with the spectrally transformed Hamiltonian must be normalized accordingly to that in its original Hamiltonian, which gives the factor $f(\theta_c)$. $f(\theta_c)$ is expressed as

$$f(\theta_c) = \left[\frac{dE_c}{d\theta} \right]^2 = \frac{1}{(1 + \Delta t E_c \Delta t E_c)^2} \quad (14)$$

and the square comes from the multiplication of t and $\hat{H}$ in Eq. (7).

The right panel of Fig. 1 presents the comparison of the convergence behaviors of three different propagators, including the CG propagator which has the CF but using the spectrally transformed Hamiltonian, the propagator which has the CF but using the original Hamiltonian, and the popular second-order exponential split operator (SESO). The convergence behaviors of the results S_c calculated by the propagators is defined as

$$\sigma_s = \frac{|S_c - S_c^A|}{|S_c^A| N_c}, \quad (15)$$

where S_c is calculated between $[0.1, 1.0]$ eV and S_c^A is the accurate results. N_c is the number of the collision energy points. It is observed that the CG propagator in Eq. (12) converges exponentially due to the requirement of the Fourier transform between energy and time space (the initial wave packet has a broad energy distribution). Both the propagators in the CF in Eq. (11) and the SESO converge in second order way, but the SESO is more accurate on this problem. The CG propagator is most impressive. With time-step $\Delta t = 100$ a.u., it can give results with error less than 1%, contrast with that the old CF propagator with time-step small as $\Delta t = 2$ a.u. can obtain results with such accuracy.

It is then straightforward to calculate the absorption spectrum by the autocorrelation function method using the CG propagator.²⁹ The initial wave function can be taken as the ground vibrational state $\Psi(0)$ of the ground electronic state. Using the propagator in the CF, the absorption spectrum can be calculated as

$$\begin{aligned}\sigma(\omega) &\sim \int_{-\infty}^{\infty} C(t) \exp(-\Gamma t) \\ &= \int_{-\infty}^{\infty} \langle \Psi(0) | \Psi(t) \rangle \exp(-\Gamma t).\end{aligned}\quad (16)$$

When the CG propagator is used, the absorption is expressed as

$$\bar{\sigma}(\theta) \sim \int_{-\infty}^{\infty} C(\tau) \exp(-\Gamma' \tau) \equiv \sigma(\omega), \quad (17)$$

with $\omega = 2 \tan(\theta/2)/\Delta t$. The above equation is true because the eigenstates of the original Hamiltonian and spectrally transformed Hamiltonian are same. Γ and Γ' are applied to simulate the lifetime effect to the absorption spectrum and to reduce the propagation time. In the work by Chen and Guo, the CG propagator has been applied to calculate the spectral profile so we do not show similar results here.

Currently there is much interest in investigating efficient numerical method for describing the interaction processes between few-cycle laser pulses and atoms and molecules. Due to the Coulomb potential, there are many works which adopt the propagator in the CF associated with the finite difference method to solve the TDSE. However, it is not so straightforward to carry out numerical simulations using the CG propagator for the system involving explicitly time-dependent Hamiltonian. Anyway, illuminated by the idea using the STH, the propagator in the CF using the concept of the STH may be substantially improved in some way. We will calculate (ii) the excitation procession of the diatomic I_2 molecule, which was used in the above example, by a laser pulse to explore this issue.

The time-dependent pulses applied in the calculation can be expressed as, without invoking rotating wave approximation,

$$E(t) = E_0 \exp\left(-\frac{4 \ln 2}{\sigma_p^2}(t - t_0)^2\right) \cos(\omega_0 t + \psi), \quad (18)$$

where $E_0 = 1 \times 10^{13}$ W cm⁻² is the peak amplitude, $\sigma_p = 20$ fs defines the full-width at half-maximum, and t_0 and $\omega_0 = 0.085$ a.u. ($\lambda = 536$ nm) are the central time and photon

FIG. 2. Left panel: The convergence of the population P_e on the excited state calculated by the propagator in the original CF, by the CG propagator and by the SESO method. CG propagator has the best convergence. Right Panel: The time-dependent population on the ground (P_g) and excited state (P_e), which exhibits several Rabi oscillations. It may be a tough example for a method testing.

energy of the pulse, respectively. The laser pulse is explicitly time-dependent, which must be transformed accordingly in the STH. One choice to define the time-dependent pulse in the STH is to rescale the pulse frequency ω_0 as

$$\bar{\omega}_0 = 2 \arctan \frac{(\omega_0 \Delta t/2)}{\Delta t}, \quad (19)$$

but keeping other parameters. This method is not rigorous because the envelope variation of the pulse in the STH cannot be considered. The other choice is that we first calculate the Fourier transform $E(\omega)$ of the time-dependent pulse; then, we can calculate the time-dependent laser pulse $E(\tau)$ by another Fourier transform from the $E(\bar{\omega})$, where $\bar{\omega}$ is related with ω according to Eq. (19). In order to keep the laser pulse area in the STH, we need to include a frequency dependent factor $f(\bar{\omega}) = 1/\sqrt{1 + \Delta t^2 \omega^2/4}$ before we calculate $E(\tau)$ from $E(\bar{\omega})$.

The former approximate method has no improvement comparing with the original CF propagator. So we only present some results using the later choice, which improve much the convergence of the original CF propagator. In the calculation the nonperturbation method is used and the dipole approximation is adopted. The Franck-Condon approximation is applied and the transition dipole is simply assumed as constant of 1.0. In the calculation, the time-ordering operator $\hat{T}$ is ignored, so the CG propagator using spectrally transformed pulse is not exact integrator for this model any more.

The convergence behaviors of the CF, the CG, and the SESO propagators are plotted in the left panel of Fig. 2. The right panel presents the time-dependent population of both electronic ground and excited states under the pulse laser excitation. There are several Rabi oscillations in the time-dependent population due to the slow motion of the nuclei and intense intensity of the pulse, which may indicate that this example is a tough test for the propagators. It can be seen in the left panel that the CG propagator is the most accurate one among these three methods. The three methods have same order of convergence this time, because the error now is solely caused by the negligence of the time-ordering operator $\hat{T}$. This fact also explains why the CG propagator is only slightly better than the SESO method—due to the flat nature

of the excited state potential energy curve, the error in the SESO for this system is extremely small.

When the model has more than one degree of freedom, propagator in the CF can be conveniently applied with the ADI method or the operator splitting method.¹³ A typical implementation of it with the operator splitting method can be written as

$$\hat{U}(\Delta t, 0) = \exp(-i\Delta t \hat{H}) \\ \approx \exp\left(\frac{-i\Delta t \hat{H}_x}{2}\right) \exp(-i\Delta t \hat{H}_y) \exp\left(\frac{-i\Delta t \hat{H}_x}{2}\right) \quad (20)$$

$$\approx \frac{1 - i\Delta t \hat{H}_x/4}{1 + i\Delta t \hat{H}_x/4} \exp(-i\Delta t \hat{H}_y) \frac{1 - i\Delta t \hat{H}_x/4}{1 + i\Delta t \hat{H}_x/4}. \quad (21)$$

It has been argued that the later propagator in Eq. (21) has better numerical performance than the former in Eq. (20) with only exponential ones for treating with atomic electron dynamics.³⁰ As we have shown

$$\exp\left(\frac{-i\Delta t \hat{H}_x}{2}\right) \exp(-i\Delta t \hat{H}_y) \exp\left(\frac{-i\Delta t \hat{H}_x}{2}\right) \\ \equiv \frac{1 - i \tan(\Delta t \hat{H}_x/4)}{1 + i \tan(\Delta t \hat{H}_x/4)} \exp(-i\Delta t \hat{H}_y) \frac{1 - i \tan(\Delta t \hat{H}_x/4)}{1 + i \tan(\Delta t \hat{H}_x/4)}, \quad (22)$$

therefore the propagator in Eq. (21) definitely has larger errors. The better performance of Eq. (21) for treating atomic electron dynamics is due to the $\tan(x) = \tan(\Delta t \hat{H}_x/4)$ transform in Eq. (22) which restrains the artificial “hole” around the Coulomb potential singularity. Otherwise unphysical numerical results will be observed when a relative large time-step Δt is applied, in contrast with the SESO method in Eq. (20) which requires smaller time-step for treating the strong potential around this region. Even the propagator in Eq. (21) is stable with large time-step for treating the Coulomb singularity, from Eq. (22) we may know that it never produces accurate results when the SESO using the same time-step cannot correctly describe the strong potential around the singularity point.

The CG propagator may be not so helpful when the propagator in Cayley’s form is applied in combination with the operator splitting method and the ADI method. However, the total Hamiltonian matrix is quite sparse in most quantum

dynamics calculation. The iterative generalized minimum residual method therefore can be effectively used to solve the propagator in Eq. (9) with a good preconditioner.²⁰ Combining the idea of spectrally transform Hamiltonian, the old propagator in Cayley’s form, which is unitary and unconditionally stable, would be expected to acquire much more applications.

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