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Efficient method for simulating quantum electron dynamics under the time-dependent Kohn-Sham equation

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A numerical scheme for solving the time evolution of wave functions under the time-dependent Kohn-Sham (TDKS) equation has been developed. Since the effective Hamiltonian depends on the wave functions, the wave functions and the effective Hamiltonian should evolve consistently with each other. For this purpose, a self-consistent loop is required at every time step for solving the time evolution numerically, which is computationally expensive. However, in this paper, we develop a different approach, expressing a formal solution of the TDKS equation, and prove that it is possible to solve the TDKS equation efficiently and accurately by means of a simple numerical scheme without the use of any self-consistent loops.

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I. INTRODUCTION

Since the innovative work on the density functional theory (DFT) [1] and the Kohn-Sham equation [2], many kinds of static or adiabatic quantum electronic phenomena have been investigated based on first principles. As an extension of the DFT to nonadiabatic dynamical phenomena, the time-dependent density functional theory (TDDFT) has been developed [3,4]. By using the TDDFT, some excitation phenomena have been analyzed more accurately than by using the DFT [5]. However, the formulation of the TDDFT is too complicated to solve the wave functions numerically in order to see electron dynamics directly. So a considerable approximation called the TD Kohn-Sham (TDKS) equation has been applied for numerical simulations [6,7].

The difficulty in numerically solving the TDKS equation is the treatment of the density-dependent Hamiltonian. The wave functions and the Hamiltonian should always be self-consistent with each other. A fourth order self-consistent field (SCF) iterative scheme was proposed by Sugino and Miyamoto [6]. However, the use of a SCF loop at every time step is computationally expensive.

In this paper, we propose a different formalism for the numerical solution of the TDKS equation. Based on it, we prove that a simple formula without SCF loops can solve the TDKS equation with sufficient accuracy. We find that computational techniques [9,10] previously developed by us for the one-electron TD Schrödinger equation in real space and real time are also useful for the TDKS equation.

II. CONVENTIONAL METHOD

The TDKS equation is a mean field approach used for describing the time evolution of the electron density ρ via one-electron wave functions ψ_n under an effective Hamiltonian $\mathcal{H}$,

$$i\frac{\partial \psi_n(t)}{\partial t} = \mathcal{H}[\rho,t]\psi_n(t), \quad \mathcal{H}[\rho,t] = -\frac{\triangle}{2} + V[\rho,t], \tag{1}$$

$$V[\rho,t] = V_{\mathrm{int}}[\rho] + V_{\mathrm{ext}}(t), \quad \rho(t) = \sum_{n=1}^{N} |\psi_n(t)|^2.$$

Here, $V[\rho,t]$ is an effective potential which represents the internal mutual interactions $V_{\mathrm{int}}[\rho]$ and the external time-dependent potential $V_{\mathrm{ext}}(t)$. Throughout this paper, we use atomic units $\hbar = 1$, $m = 1$, and $e = 1$ for equations and values.

Because of the time dependence of the Hamiltonian, the solution of the TDKS equation can be formally expressed in terms of a time-ordering exponential operator:

$$\psi_n(t) = \mathcal{T}\exp\left[-i\int_0^t dt'\,\mathcal{H}[\rho,t'] \right]\psi_n(0). \tag{2}$$

There are many numerical methods for computing Eq. (2). The simplest method discretizes the elapsed time t into small time slices Δt, and approximates Eq. (2) as

$$\psi_n(t+\Delta t) \approx \exp(-i\Delta t\mathcal{H}[\rho,t])\psi_n(t), \tag{3}$$

and it is computed using the Runge-Kutta method, or by the split operator technique:

$$\psi_n(t+\Delta t) \sim \exp\left[\frac{i\Delta t}{2}\frac{\triangle}{2}\right]\exp\left[\frac{\Delta t}{i}V[\rho,t]\right]\exp\left[\frac{i\Delta t}{2}\frac{\triangle}{2}\right]\psi_n(t). \tag{4}$$

However, this is not sufficiently accurate, because it ignores the time dependence of the Hamiltonian during the small time slice, while the splitting reduces accuracy to an even lower level.

Another well-known computational method for Eq. (2) uses a Hamiltonian in the middle of the steps,

$$\psi_n(t+\Delta t) \simeq \exp\left(-i\Delta t\mathcal{H}\left[\rho, t+\frac{\Delta t}{2}\right]\right)\psi_n(t). \tag{5}$$

Equation (5) is also computed by the split operator technique:

$$\psi_n(t+\Delta t) \sim \exp\left[\frac{i\Delta t}{2}\frac{\triangle}{2}\right]\exp\left(\frac{\Delta t}{i}V\left[\rho, t+\frac{\Delta t}{2}\right]\right) \times \exp\left[\frac{i\Delta t}{2}\frac{\triangle}{2}\right]\psi_n(t). \tag{6}$$

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Here, $V[\rho,t+\Delta t/2]$ is estimated from an interpolation between $V[\rho,t]$ and $V[\rho,t+\Delta t]$. Therefore, they have to be solved by a SCF loop. This scheme is accurate enough; however, it is computationally expensive to perform the SCF loop at every time step.

III. FORMULATION

To avoid the use of a SCF loop, we first express the time evolution of the wave functions using a Taylor development in exponential form as

$$\psi_n(t+\Delta t)=\sum_{k=0}^{\infty}\frac{\Delta t^k}{k!}\frac{\partial^k}{\partial t^k}\psi_n(t)=\exp\left[\Delta t\frac{\partial}{\partial t}\right]\psi_n(t). \qquad (7)$$

We consider a quantity $f(\{\psi\},\{\psi^*\},t)$ which depends on the wave functions ψ and time t explicitly. The time derivative of this quantity is expanded by the chain rule,

$$\frac{\partial f}{\partial t}=\frac{\partial\psi}{\partial t}\frac{\delta f}{\delta\psi}+\frac{\partial\psi^*}{\partial t}\frac{\delta f}{\delta\psi^*}+\frac{\partial f}{\partial t_{\mathrm{ex}}}. \qquad (8)$$

Here, we have used the following notation:

$$\frac{\partial\psi}{\partial t}\frac{\delta f}{\delta\psi}\equiv\sum_{m=1}^{N}\int d\mathbf{r}\frac{\partial\psi_m(\mathbf{r})}{\partial t}\frac{\partial f}{\partial\psi_m(\mathbf{r})}, \qquad (9)$$

and $\partial/\partial t_{\mathrm{ex}}$ means an explicite time-derivative operator, which operates on only explicitly time-dependent quantities.

By substituting the TDKS equation (1) into Eq. (8), the time differential is generally expressed as

$$i\frac{\partial}{\partial t}=(\mathcal{H}[\rho,t]\psi)\frac{\delta}{\delta\psi}-(\mathcal{H}[\rho,t]\psi)^*\frac{\delta}{\delta\psi^*}+i\frac{\partial}{\partial t_{\mathrm{ex}}}. \qquad (10)$$

For example, it operates on a wave function ψ_n as

$$\begin{aligned} i\frac{\partial\psi_n}{\partial t}&=(\mathcal{H}[\rho,t]\psi)\frac{\delta\psi_n}{\delta\psi}-(\mathcal{H}[\rho,t]\psi)^*\frac{\delta\psi_n}{\delta\psi^*}+i\frac{\partial\psi_n}{\partial t_{\mathrm{ex}}}\\ &=\mathcal{H}[\rho,t]\psi_n, \qquad (11)\end{aligned}$$

because ψ_n does not depend on ψ_m^* and t explicitly.

Another example concerns the density ρ:

$$\begin{aligned} i\frac{\partial\rho}{\partial t}&=(\mathcal{H}[\rho,t]\psi)\frac{\delta\rho}{\delta\psi}-(\mathcal{H}[\rho,t]\psi)^*\frac{\delta\rho}{\delta\psi^*}+i\frac{\partial\rho}{\partial t_{\mathrm{ex}}}\\ &=\sum_m\,(\mathcal{H}[\rho,t]\psi_m)\psi_m^*-(\mathcal{H}[\rho,t]\psi_m)^*\psi_m, \qquad (12)\end{aligned}$$

because ρ also does not depend on t explicitly.

By substituting Eq. (10) into Eq. (7), we can formally write the solution without employing the time-ordering operator as

$$\begin{aligned}\psi_n(t+\Delta t)=\exp\frac{\Delta t}{i}\Bigg[&(\mathcal{H}[\rho,t]\psi)\frac{\delta}{\delta\psi}-(\mathcal{H}[\rho,t]\psi)^*\frac{\delta}{\delta\psi^*}\\ &+i\frac{\partial}{\partial t_{\mathrm{ex}}}\Bigg]\psi_n(t). \qquad (13)\end{aligned}$$

However, this does not describe the algorithm for computations. To show the method of computation of Eq. (13), we decompose the exponential operator as

$$\begin{aligned}\psi_n(t+\Delta t)\simeq{}&\exp\left[\frac{\Delta t}{2}\frac{\partial}{\partial t_{\mathrm{ex}}}\right]\\ &\times\exp\frac{i\Delta t}{4}\left[(\triangle\psi)\frac{\delta}{\delta\psi}-(\triangle\psi)^*\frac{\delta}{\delta\psi^*}\right]\\ &\times\exp\frac{\Delta t}{i}\left[(V[\rho,t]\psi)\frac{\delta}{\delta\psi}-(V[\rho,t]\psi)^*\frac{\delta}{\delta\psi^*}\right]\\ &\times\exp\frac{i\Delta t}{4}\left[(\triangle\psi)\frac{\delta}{\delta\psi}-(\triangle\psi)^*\frac{\delta}{\delta\psi^*}\right]\\ &\times\exp\left[\frac{\Delta t}{2}\frac{\partial}{\partial t_{\mathrm{ex}}}\right]\psi_n(t). \qquad (14)\end{aligned}$$

Equation (14) is correct up to the second order of Δt.

To clarify the meaning of the exponential operator that contains the Laplacian appearing in Eq. (14), we expand it in a Taylor development as

$$\begin{aligned}&\exp\frac{i\Delta t}{4}\left[(\triangle\psi)\frac{\delta}{\delta\psi}-(\triangle\psi)^*\frac{\delta}{\delta\psi^*}\right]\psi_n\\ &\quad=\sum_{k=0}^{\infty}\frac{(i\Delta t)^k}{k!4^k}\left[(\triangle\psi)\frac{\delta}{\delta\psi}-(\triangle\psi)^*\frac{\delta}{\delta\psi^*}\right]^k\psi_n. \qquad (15)\end{aligned}$$

The first term $(k=1)$ of the series operates on ψ_n as

$$\left[(\triangle\psi)\frac{\delta}{\delta\psi}-(\triangle\psi)^*\frac{\delta}{\delta\psi^*}\right]\psi_n=\triangle\psi_n. \qquad (16)$$

The second term $(k=2)$ operates as

$$\begin{aligned}&\left[(\triangle\psi)\frac{\delta}{\delta\psi}-(\triangle\psi)^*\frac{\delta}{\delta\psi^*}\right]^2\psi_n\\ &\quad=\left[(\triangle\psi)\frac{\delta}{\delta\psi}-(\triangle\psi)^*\frac{\delta}{\delta\psi^*}\right]\triangle\psi_n\\ &\quad=(\triangle\psi)\frac{\delta\triangle\psi_n}{\delta\psi}\\ &\quad=\triangle\frac{\delta\psi_n}{\delta\psi}(\triangle\psi)=\triangle\triangle\psi_n. \qquad (17)\end{aligned}$$

Generally,

$$\left[(\triangle\psi)\frac{\delta}{\delta\psi}-(\triangle\psi)^{*}\frac{\delta}{\delta\psi^{*}}\right]^{k}\psi_n=\triangle^{k}\psi_n . \tag{18}$$

Thus, we obtain the following identity:

$$\exp\frac{i\Delta t}{4}\left[(\triangle\psi)\frac{\delta}{\delta\psi}-(\triangle\psi)^{*}\frac{\delta}{\delta\psi^{*}}\right]\psi_n=\exp\left[\frac{i\Delta t}{4}\triangle\right]\psi_n . \tag{19}$$

Similarly, we expand the exponential operator that contains the effective potential appearing in Eq. (14) as

$$\begin{aligned}\exp\frac{\Delta t}{i}&\left[(V[\rho,t]\psi)\frac{\delta}{\delta\psi}-(V[\rho,t]\psi)^{*}\frac{\delta}{\delta\psi^{*}}\right]\psi_n\\&=\sum_{k=0}^{\infty}\frac{(\Delta t)^k}{k!\,i^k}\left[(V[\rho,t]\psi)\frac{\delta}{\delta\psi}-(V[\rho,t]\psi)^{*}\frac{\delta}{\delta\psi^{*}}\right]^{k}\psi_n .\end{aligned}\tag{20}$$

The first term $(k=1)$ of the series operates ψ_n as

$$\left[(V[\rho,t]\psi)\frac{\delta}{\delta\psi}-(V[\rho,t]\psi)^{*}\frac{\delta}{\delta\psi^{*}}\right]\psi_n=V[\rho,t]\psi_n . \tag{21}$$

The second term $(k=2)$ operates as

$$\begin{aligned}&\left[(V[\rho,t]\psi)\frac{\delta}{\delta\psi}-(V[\rho,t]\psi)^{*}\frac{\delta}{\delta\psi^{*}}\right]V[\rho,t]\psi_n\\&\quad=V[\rho,t]V[\rho,t]\psi_n+\left((V[\rho,t]\psi)\frac{\delta V[\rho,t]}{\delta\psi}\right)\psi_n\\&\qquad-\left((V[\rho,t]\psi)^{*}\frac{\delta V[\rho,t]}{\delta\psi^{*}}\right)\psi_n\\&\quad=V[\rho,t]V[\rho,t]\psi_n+\left((V[\rho,t]\psi)\psi^{*}\frac{\delta V[\rho,t]}{\delta\rho}\right)\psi_n\\&\qquad-\left((V[\rho,t]\psi)^{*}\psi\frac{\delta V[\rho,t]}{\delta\rho}\right)\psi_n\\&\quad=V[\rho,t]V[\rho,t]\psi_n .\end{aligned}\tag{22}$$

Thus, we obtain the following identity:

$$\begin{aligned}\exp\frac{\Delta t}{i}&\left[(V[\rho,t]\psi)\frac{\delta}{\delta\psi}-(V[\rho,t]\psi)^{*}\frac{\delta}{\delta\psi^{*}}\right]\psi_n\\&=\exp\left[\frac{\Delta t}{i}V[\rho,t]\right]\psi_n .\end{aligned}\tag{23}$$

Substituting Eqs. (19) and (23) into Eq. (14), we obtain

$$\begin{aligned}\psi_n(t+\Delta t)\simeq{}&\exp\left[\frac{\Delta t}{2}\frac{\partial}{\partial t_{\rm ex}}\right]\exp\left[\frac{i\Delta t}{2}\frac{\triangle}{2}\right]\exp\left[\frac{\Delta t}{i}V[\rho,t]\right]\\&\times\exp\left[\frac{i\Delta t}{2}\frac{\triangle}{2}\right]\exp\left[\frac{\Delta t}{2}\frac{\partial}{\partial t_{\rm ex}}\right]\psi_n(t).\end{aligned}\tag{24}$$

By the way, $V_{\rm int}[\rho]$ does not depend on time explicitly, because the density ρ does not depend on time explicitly as shown in Eq. (12). Meanwhile, $V_{\rm ext}(t)$ does depend on time explicitly,

$$\frac{\partial V_{\rm int}[\rho]}{\partial t_{\rm ex}}=0,\qquad\frac{\partial V_{\rm ext}(t)}{\partial t_{\rm ex}}\neq 0. \tag{25}$$

Therefore, the exponential of the explicit time-derivative operator appearing in Eq. (24) affects only the external time-dependent potential $V_{\rm ext}(t)$ as

$$\exp\left[\frac{\Delta t}{2}\frac{\partial}{\partial t_{\rm ex}}\right]V_{\rm ext}(t)=V_{\rm ext}\left(t+\frac{\Delta t}{2}\right). \tag{26}$$

As a result, we obtain the desired formula:

$$\begin{aligned}\psi_n(t+\Delta t)\simeq{}&\exp\left[\frac{i\Delta t}{2}\frac{\triangle}{2}\right]\exp\left\{\frac{\Delta t}{i}\left[V_{\rm int}[\rho']\right.\right.\\&\left.\left.+V_{\rm ext}\left(t+\frac{\Delta t}{2}\right)\right]\right\}\exp\left[\frac{i\Delta t}{2}\frac{\triangle}{2}\right]\psi_n(t).\end{aligned}\tag{27}$$

Here, $V_{\rm ext}(t+\Delta t/2)$ is the external force in the middle of the steps. Meanwhile, ρ' in $V_{\rm int}[\rho']$ is not the density in the middle of the steps, but the density after the preceding operation, namely,

$$\rho'(\mathbf{r})=\sum_{n=1}^{N}\left|\exp\left[\frac{i\Delta t}{2}\frac{\triangle}{2}\right]\psi_n(\mathbf{r},t)\right|^2 . \tag{28}$$

Therefore, the formula (27) can be explicitly computed without employing any SCF loops.

The present non-self-consistent-field (non-SCF) formula (27) is quite similar to the conventional non-SCF formula (4) and the conventional SCF formula (6). However, in this paper, we have derived the formula based on the strict solution (13) by considering the time dependence of the Hamiltonian, while the conventional non-SCF formula did not consider the time dependence. We can easily show that the present non-SCF formula is as accurate as the conventional SCF formula by associating ρ' with $\rho(t+\Delta t)$ as

$$\begin{aligned}\rho'&=\sum_{n=1}^{N}|\psi_n(t)|^2+i\frac{\Delta t}{2}\left(\psi_n^{*}\frac{\triangle}{2}\psi_n-\psi_n\frac{\triangle}{2}\psi_n^{*}\right)_t+O(\Delta t^2)\\&=\sum_{n=1}^{N}|\psi_n(t)|^2+\frac{\Delta t}{2}\left(\psi_n^{*}\frac{\partial\psi_n}{\partial t}-\psi_n\frac{\partial\psi_n^{*}}{\partial t}\right)_t+O(\Delta t^2)\\&=\rho(t)+\frac{\Delta t}{2}\left.\frac{\partial\rho}{\partial t}\right|_t+O(\Delta t^2)=\rho\left(t+\frac{\Delta t}{2}\right)+O(\Delta t^2).\end{aligned}\tag{29}$$

Therefore, both the non-SCF formula and the SCF formula are correct up to the second order of Δt.

IV. COMPUTATIONAL TECHNIQUE

Computational techniques previously developed by us for the one-electron TD Schrödinger equation [9,10] are also beneficial for formula (27). We discretize the wave functions in real space, and use the finite element method for spatial derivatives. The only difference between the schemes for the TDKS equation and TD Schrödinger equation is the exponential of the effective potential:

$$\psi_n'(\mathbf{r}) = \exp\left[\frac{\Delta t}{i} V_{\text{int}}[\rho]\right]\psi_n(\mathbf{r}). \tag{30}$$

By this operation, the phase of the wave functions is altered at each point, but the density $\rho(\mathbf{r})$ is not altered. Therefore, we take the value of $V_{\text{int}}[\rho](\mathbf{r})$ as a constant during the computation; it is calculated just before the computation.

It is quite easy to improve the accuracy of formula (27) to the fourth order. The fourth order accurate formula is given by Suzuki's exponential product theory [8] as

$$\begin{aligned}\psi_n(t+\Delta t) \simeq {} & S_2(s\Delta t; t+(1-s)\Delta t)\\ & \times S_2(s\Delta t; t+(1-2s)\Delta t)\\ & \times S_2((1-4s)\Delta t; t+2s\Delta t)\\ & \times S_2(s\Delta t; t+s\Delta t) S_2(s\Delta t; t)\psi_n(t).\end{aligned} \tag{31}$$

Here, s and $S_2(\Delta t;t)$ are given by

$$s = 1/(4-\sqrt[3]{4}), \tag{32}$$

$$S_2(\Delta t;t) = \exp\left[\frac{i\Delta t}{2}\frac{\triangle}{2}\right]\exp\left[\frac{\Delta t}{i}V[\rho',t]\right]\exp\left[\frac{i\Delta t}{2}\frac{\triangle}{2}\right], \tag{33}$$

where ρ' is the density after the preceding operations.

V. EXAMPLE

In this section, we perform a simple simulation to verify the efficiency and accuracy of the present method. The model system we use here is a one-dimensional isolated system in which two electrons interact by a δ-function interaction under an oscillating electric field. The two-body wave function $\Psi(x_1,x_2;t)$ in this system obeys the following TD Schrödinger equation:

$$\begin{aligned}i\frac{\partial}{\partial t}\Psi(x_1,x_2;t) = \Bigg[& -\frac{1}{2}\frac{\partial^2}{\partial x_1^2} - \frac{1}{2}\frac{\partial^2}{\partial x_2^2} + \alpha\,\delta(x_1-x_2)\\ & + (x_1+x_2)E_0\sin(\omega_0 t)\Bigg]\Psi(x_1,x_2;t),\end{aligned} \tag{34}$$

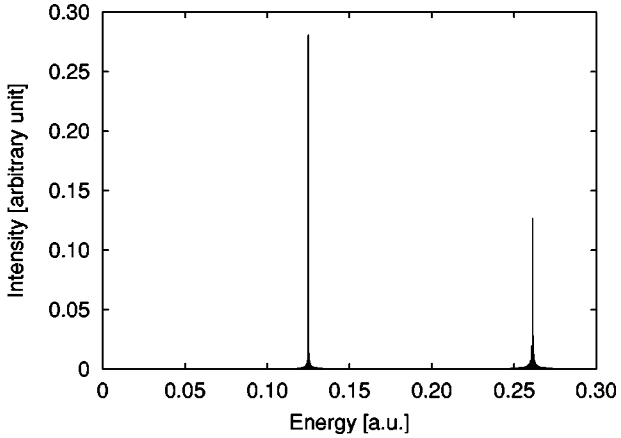

FIG. 1. Spectrum of the scattered light. The sharp peak found at 0.125 a.u. corresponds to the Rayleigh scattering. The sharp peak found at 0.261 a.u. corresponds to the emission from the first excited state to the ground state; this energy includes many-body and nonlinear effects.

where α is the coupling constant of the interaction, and E_0 is an external electric field to perturb this system.

We suppose that $\Psi(x_1,x_2;t)$ is expressed by a common one-electron orbital wave function $\psi(x,t)$ as

$$\begin{aligned}\Psi(x_1,x_2;t) = \psi(x_1,t)\psi(x_2,t)\frac{1}{\sqrt{2}}[& \chi(\uparrow,\sigma_1)\chi(\downarrow,\sigma_2)\\ & - \chi(\downarrow,\sigma_1)\chi(\uparrow,\sigma_2)].\end{aligned} \tag{35}$$

Thus, the TDKS equation is derived exactly:

$$\begin{aligned}i\frac{\partial}{\partial t}\psi(x,t) &= \left[-\frac{1}{2}\frac{\partial^2}{\partial x^2} + \alpha\rho(x,t) + xE_0\sin(\omega_0 t)\right]\psi(x,t),\\ \rho(x,t) &= |\psi(x,t)|^2.\end{aligned} \tag{36}$$

We use the following parameters for computation:

Size of the system	$L = 8.0$
Number of grid points	$N_p = 64$
Mutual interaction	$\alpha = 0.5$
External force	$E_0 = 1/64$
Frequency	$\omega_0 = 1/8$
Small time slice	$\Delta t = 1/16$
Total time steps	$N_t = 256 \times 1024$

First, we compute the lowest eigenstate of this system using the time-independent Kohn-Sham equation:

$$E\psi_0(x) = \left[-\frac{1}{2}\frac{\partial^2}{\partial x^2} + \alpha\rho(x)\right]\psi_0(x). \tag{37}$$

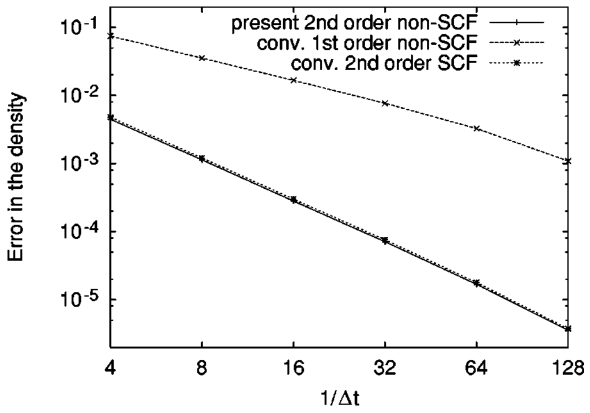

FIG. 2. Errors in the density obtained by three methods on some small time slices. The conventional non-SCF method is accurate up to the first order of Δt, while the present non-SCF method and the conventional SCF method are accurate up to the second order of Δt. In this test case, the error of the non-SCF method is almost the same as that of the SCF method.

We use this state as the initial state.

Second, we compute the time evolution using Eq. (27). Third, by Fourier transforming the time fluctuation of the polarization, we obtain the spectrum of the scattered light as shown in Fig. 1.

The peak appearing at energy $\omega_0 = 0.125$ (a.u.) comes from the injected light. The peak appearing at energy $\omega = 0.261$ (a.u.) is expected to be the excitation energy between the first excited state and the ground state.

We have calculated the excitation energy by certain other methods: Method A solves the eigenstates by the non-TDKS equation (37), method B modifies the result of method A by using the random-phase approximation (RPA), and method C diagonalizes the non-TD Schrödinger equation. The results are listed below.

Excitation energies a.u. calculated by various methods.

(A) Non-TDKS equation	$\omega_{\mathrm{KS}} = 0.199$
(B) Non-TDKS equation with RPA	$\omega_{\mathrm{RPA}} = 0.255$
(C) Non-TD Schrödinger equation	$\omega_{\mathrm{Sch}} = 0.260$
TDKS equation	$\omega = 0.261$

We found that the peak obtained by the present method, i.e., the TDKS equation, reproduces fairly accurately the excitation energy calculated by means of the exact diagonalization of the non-TD Schrödinger equation. That is, by solving the TDKS equation, dynamical phenomena can be described more accurately than by using the RPA as long as the effective Hamiltonian is correct.

Next, to evaluate the error of the method, we estimate the error of the $\mathcal{E}$ density $\rho(x,T)$ at a specified time $T = 256$ a.u.

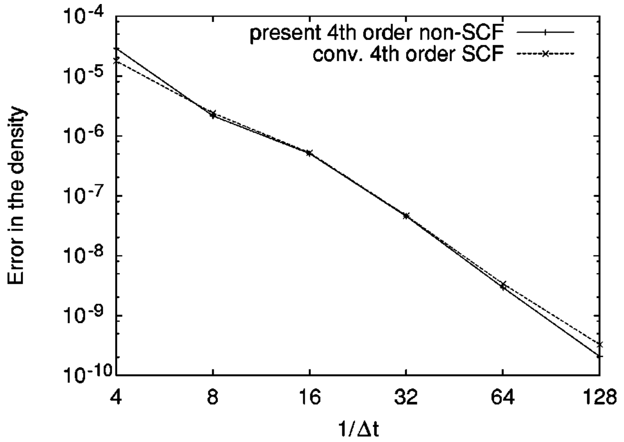

FIG. 3. Errors in the density obtained by the fourth order methods. Both errors are roughly proportional to Δt^4, and they are much less than those of the second order methods. In this test case, the error of the non-SCF method is almost the same as that of the SCF method.

$$\mathcal{E} = \int_0^L dx \left| \rho(x,T) - \rho_{\mathrm{exact}}(x,T) \right|, \tag{38}$$

here the exact value $\rho_{\mathrm{exact}}(x,T)$ is prepared in advance by performing the same simulation on an extremely small time slice $\Delta t = 1/256$ a.u.

Figure 2 shows the errors on some time slices obtained by three methods: the present non-SCF method (27), the conventional non-SCF method (4), and the conventional SCF method (6).

All methods are accurate enough in this result. However, the conventional non-SCF method is stable only within a specific short time span, e.g., $T = 512$ a.u. for all Δt in this test. Meanwhile, the present non-SCF method and the conventional SCF method are stable even over a long time span, e.g., $T = 64 \times 1024^2$ a.u., $\Delta t = 1/16$ a.u., in this test. Therefore, these methods are suitable for long time span simulations.

We have also tested the simulation using the present fourth order non-SCF method (31) and the fourth order SCF method proposed in the literature [6]. Figure 3 shows the errors. Both errors are much less than those of the second order methods.

VI. CONCLUSION

We have proved that simulation of the wave function using the TDKS equation can be performed by a simple scheme and that there is no need for the use of SCF loops to maintain the self-consistency of the effective Hamiltonian. Our proposed non-SCF method is competitive in accuracy with the SCF method, and also it is superior in computational efficiency. We are convinced that our method is helpful for investigating nonadiabatic and nonlinear quantum electron dynamics.

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