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Citation	Journal Of Chemical Physics, 2007, v. 126 n. 13, p. 134104
Issued Date	2007
URL	http://hdl.handle.net/10722/70419
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Density matrix based time-dependent density functional theory and the solution of its linear response in real time domain

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(Received 20 December 2006; accepted 15 February 2007; published online 3 April 2007)

A density matrix based time-dependent density functional theory is extended in the present work. Chebyshev expansion is introduced to propagate the linear response of the reduced single-electron density matrix upon the application of a time-domain δ -type external potential. The Chebyshev expansion method is more efficient and accurate than the previous fourth-order Runge-Kutta method and removes a numerical divergence problem. The discrete Fourier transformation and filter diagonalization of the first-order dipole moment are implemented to determine the excited state energies. It is found that the filter diagonalization leads to highly accurate values for the excited state energies. Finally, the density matrix based time-dependent density functional is generalized to calculate the energies of singlet-triplet excitations. © 2007 American Institute of Physics.
 [DOI: 10.1063/1.2715549]

I. INTRODUCTION

Time-dependent density functional theory¹ (TDDFT) is nowadays one of the most popular methods in the calculation of excitation energies due to its accuracy and efficiency. Most such calculations^{2–11} are in the frequency domain and use the fact that the first-order change of electronic density has poles when the frequency of the external time-dependent potential is equal to the excitation energy. The excitation energies are determined through solving an eigenvalue equation which does not depend explicitly on the form of the external potential as the following:^{2,3}

$$\Omega F_I = \omega_I^2 F_I, \quad (1)$$

where ω_I is the excitation energy to be determined. Canonical molecular orbitals have to be used to build the matrix Ω . The dimension of matrix Ω is of $O(N^2)$, where N is the number of the basis functions. To diagonalize the whole matrix, the computational effort will scale as $O(N^6)$. In most cases only the transitions with low excitation energies are needed and iteration methods such as Lanczos method¹² or Davidson's algorithm¹³ are used to obtain the lowest few excitations. In these iteration methods, the whole matrix is not constructed explicitly, instead the multiplication between matrix Ω and trial vectors is carried out. This multiplication is almost the same as constructing Fock matrix in self-consistent cycle using canonical molecular orbitals as basis set. However, for large systems, this method is inefficient since the number of transitions may be too large even in a small energy range and delocalized canonical molecular orbitals have to be used. In addition, this type of methods has the difficulty to decide the transition energies to the highly

excited states, such as plasmon resonance. The difficulty can be partially circumvented by calculating directly the frequency dependent polarizability.^{14–17} The frequency dependent polarizability can be calculated most efficiently in canonical molecular orbital basis.¹⁴ Otherwise, a nonsymmetrical linear equation has to be solved.¹⁷ The computational time of these methods scales as $O(N^{3-6})$.

An alternative is to propagate the time-dependent Kohn-Sham orbitals in the real time domain^{18–22} with the system subjected to an external electric field. The time-dependent polarizability can be calculated directly, and the electronic absorption spectra in the entire energy range can be obtained through its Fourier transformation. The resulting spectrum covers thus all excited states, and the time-dependent properties can be simulated directly using this approach. However, this approach is not as efficient compared to Davidson's algorithm when only the lowest several transitions are needed.

Instead of Kohn-Sham orbitals, an equation of motion (EOM) for the linear response of the reduced single-electron density matrix due to an external time-dependent potential can be integrated as well in the real time domain, and the first-order change of time-dependent polarizability can be calculated directly. By making use of the nearsightedness of the density matrix,²³ the computational time of this approach scales linearly with the system size.²⁴ The resulting method, the localized density matrix (LDM) method, was implemented at the semiempirical level to calculate the absorption spectra and excited state energies of large systems such as polymer aggregates,^{25,26} carbon nanotubes,²⁷ semiconducting nanowires,²⁸ and light harvesting systems.²⁹ Recently the LDM method was implemented at TDDFT level,^{30,31} and the first $O(N)$ TDDFT calculation was carried out to calculate absorption spectra of long polyene oligomers. In the LDM method the fourth-order Runge-Kutta algorithm is employed

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to integrate the EOM in the time domain. Although it has no particular advantage over the Davidson's solution of TDDFT for small molecules, the LDM method can be applied to much larger systems because of its $O(N)$ nature, and can be used to calculate all excited states instead of the lowest few of medium to large sized molecules. In principle it can also be applied to calculate the absorption spectra of periodic systems.

In the present work we extend the LDM method by introducing Chebyshev expansion^{32,33} to propagate the reduced single-electron density matrix in time domain. In addition, two spectral analysis algorithms, the discrete Fourier transformation³⁴ and filter diagonalization method,³⁵⁻³⁷ are implemented to extract the excited state properties from the time-dependent induced dipole moment.

II. THEORY

Let us consider that a system in its ground state is perturbed by the following external potential:

$$V^{\text{pert}}(\mathbf{r}, t) = V^{\text{ext}}(\mathbf{r}) \delta(t). \quad (2)$$

The first-order change of the wave function for the system after this perturbation can be written as

$$\Psi^{(1)}(t) = -i \sum_i e^{-iE_i t} \langle \Psi_i | \hat{V}^{\text{ext}} | \Psi_0 \rangle \Psi_i, \quad (3)$$

where Ψ_0 is the ground state wave function, Ψ_i is the i th excited state wave function, E_0 is the ground state energy and E_i is the energy of the i th excited state. The time-dependent first-order change of any operator \hat{A} , such as the dipole moment operator, can thus be calculated based on the following equation:

$$\begin{aligned} \langle \hat{A}^{(1)}(t) \rangle &= \langle \Psi_0(t) | \hat{A} | \Psi^{(1)}(t) \rangle + \langle \Psi^{(1)}(t) | \hat{A} | \Psi_0(t) \rangle \\ &= -i \sum_i (\langle \Psi_0 | \hat{A} | \Psi_i \rangle \langle \Psi_i | \hat{V}^{\text{ext}} | \Psi_0 \rangle e^{-i(E_i - E_0)t} - c.c.). \end{aligned} \quad (4)$$

It can be seen from the above equations that the excitation energy $E_i - E_0$ for Ψ_i can be determined through spectral analysis once the first-order time evolution of the expectation value of operator \hat{A} is known if $\langle \Psi_0 | \hat{A} | \Psi_i \rangle$ and $\langle \Psi_0 | \hat{V}^{\text{ext}} | \Psi_i \rangle$ are nonzero. To make sure that no excited states will miss due to $\langle \Psi_0 | \hat{A} | \Psi_i \rangle = 0$, \hat{A} is preferably chosen as the same operator as \hat{V}^{ext} .

The time-dependent first-order expectation value of any one-electron operator can be decided through TDDFT. In TDDFT and with orthogonal basis set, the time-dependent first-order change of reduced single-electron density matrix for a system subjected to a perturbation described by Eq. (2) satisfies

$$i \frac{d}{dt} P_\sigma^{(1)} = [h_\sigma^{(0)}, P_\sigma^{(1)}] + [h_\sigma^{(1)}, P_\sigma^{(0)}], \quad (5)$$

$$P_\sigma^{(1)}(t=0) = -i[V_\sigma^{\text{ext}}, P_\sigma^{(0)}], \quad (6)$$

where σ is the index for spin, $P_\sigma^{(0)}$ and $h_\sigma^{(0)}$ is the ground state density matrix and Fock matrix, respectively, $P_\sigma^{(1)}$ and $h_\sigma^{(1)}$ is the first-order change of the density matrix and Fock matrix, respectively, and V_σ is the external potential for spin σ electrons. These matrices satisfy the following relations:

$$[h_\sigma^{(0)}, P_\sigma^{(0)}] = 0, \quad (7)$$

$$P_\sigma^{(0)} P_\sigma^{(0)} = P_\sigma^{(0)}, \quad (8)$$

$$P_\sigma^{(0)} P_\sigma^{(1)} + P_\sigma^{(1)} P_\sigma^{(0)} = P_\sigma^{(1)}, \quad (9)$$

$$\begin{aligned} h_{pq,\sigma}^{(1)} &= \sum_{st,\sigma'} P_{st,\sigma'}^{(1)} \int \phi_{p\sigma}^*(\mathbf{r}_1) \phi_{q\sigma}(\mathbf{r}_1) \\ &\quad \times \left(\frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} + \frac{\partial V_{XC}^\sigma(\mathbf{r}_1)}{\partial \rho_{\sigma'}(\mathbf{r}_1)} \delta(\mathbf{r}_1 - \mathbf{r}_2) \right) \\ &\quad \times \phi_{s\sigma'}^*(\mathbf{r}_2) \phi_{t\sigma'}(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2. \end{aligned} \quad (10)$$

The indices p , q , s , and t in Eq. (10) are for basis functions. Note that the adiabatic approximation for the exchange-correlation (XC) kernel¹ has already been used here. Eqs. (8) and (9) are the idem-potency condition for the density matrix. To satisfy Eq. (9), the following purification scheme can be used:

$$P_\sigma^{(1),\text{new}} = P_\sigma^{(0)} P_\sigma^{(1)} + P_\sigma^{(1)} P_\sigma^{(0)} - 2P_\sigma^{(0)} P_\sigma^{(1)} P_\sigma^{(0)}. \quad (11)$$

It can be seen from Eq. (11) that $P_\sigma^{(1),\text{new}}$ satisfies Eq. (9) and that $P_\sigma^{(1),\text{new}}$ is equal to $P_\sigma^{(1)}$ if $P_\sigma^{(1)}$ satisfies Eq. (9). Actually in most cases Eq. (9) can be satisfied trivially according to Eqs. (5)–(8). Once the time-dependent first-order change of the density matrix is obtained, the time-dependent first-order change of any one-electron operator can thus be determined through $\langle \hat{A}^{(1)}(t) \rangle = \text{Tr}(P^{(1)}(t)A)$ and the excitation energies can be decided through the spectral analysis for $\langle \hat{A}^{(1)}(t) \rangle$ based on Eq. (4).

According to Eq. (4), only those excitations induced by the external perturbation potential can be obtained. Usually electric field is used as the external potential and only dipole allowed transitions are obtained. To obtain dipole forbidden transitions, a different or fictitious potential can be used.^{29,38} For closed-shell systems, if the external potential is spin independent and spin-orbital coupling is not considered, the first-order changes of density matrix for α spin and β spin are the same. We can simplify Eqs. (5) and (6) by adding up the P_α and P_β part,

$$i \frac{d}{dt} (P_\alpha^{(1)} + P_\beta^{(1)}) = [h^{(0)}, P_\alpha^{(1)} + P_\beta^{(1)}] + [h^{(1)}, P_\alpha^{(0)} + P_\beta^{(0)}], \quad (12)$$

$$(P_\alpha^{(1)} + P_\beta^{(1)})(t=0) = -i[V^{\text{ext}}, P_\alpha^{(0)} + P_\beta^{(0)}], \quad (13)$$

$$h_{pq}^{(1)} = 2 \sum_{st} (P_{st,\alpha}^{(1)} + P_{st,\beta}^{(1)}) \int \phi_p^*(\mathbf{r}_1) \phi_q(\mathbf{r}_1) \times \left(\frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} + \left(\frac{\partial V_{XC}^\alpha(\mathbf{r}_1)}{\partial \rho_\alpha(\mathbf{r}_1)} + \frac{\partial V_{XC}^\alpha(\mathbf{r}_1)}{\partial \rho_\beta(\mathbf{r}_1)} \right) \delta(\mathbf{r}_1 - \mathbf{r}_2) \right) \times \phi_s^*(\mathbf{r}_2) \phi_t(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2. \quad (14)$$

Singlet-singlet excitation energies can thus be calculated through Eqs. (12)–(14). On the other hand, singlet-triplet excitations for closed-shell systems can only be retrieved with the external potential containing spin operator. Singlet-triplet excitations can be induced when magnetic field is used as external field and under the dipole approximation the interaction between the system and the magnetic field polarized along the z direction can be expressed as

$$V^{\text{ext}} = B(\mathbf{r}) \sigma_z, \quad (15)$$

where σ_z is the z component of Pauli spin matrix and $B(\mathbf{r})$ is the magnetic field. We have thus the following equations in this case:

$$i \frac{d}{dt} (P_\alpha^{(1)} - P_\beta^{(1)}) = [h^{(0)}, P_\alpha^{(1)} - P_\beta^{(1)}] + [h^{(1)}, P_\alpha^{(0)} - P_\beta^{(0)}], \quad (16)$$

$$(P_\alpha^{(1)} - P_\beta^{(1)})(t=0) = -i [V^{\text{ext}}, P_\alpha^{(0)} - P_\beta^{(0)}], \quad (17)$$

$$h_{pq}^{(1)} = 2 \sum_{st,\sigma'} (P_{st,\alpha}^{(1)} - P_{st,\beta}^{(1)}) \int \phi_p^*(\mathbf{r}_1) \phi_q(\mathbf{r}_1) \times \left(\frac{\partial V_{XC}^\alpha(\mathbf{r}_1)}{\partial \rho_\alpha(\mathbf{r}_1)} - \frac{\partial V_{XC}^\alpha(\mathbf{r}_1)}{\partial \rho_\beta(\mathbf{r}_1)} \right) \phi_s^*(\mathbf{r}_1) \phi_t(\mathbf{r}_1) d\mathbf{r}_1. \quad (18)$$

Equations (14) and (18) are exactly the same as those used for singlet-singlet and singlet-triplet excitations in conventional TDDFT calculations.⁸ We note that any potential that induces singlet-triplet excitations may be used to calculate the singlet-triplet transition energies. However, if the external potential includes σ_x or σ_y terms, a noncollinear scheme for the XC potential^{39–41} is required to recover Eq. (18) for the singlet-triplet excitations.^{42,43} Equations (12)–(14) and (16)–(18) are the basic equations to decide the time-dependent first-order change of the density matrix in the present work.

III. NUMERICAL INTEGRATION

Equations (12) and (16) are first-order differential equations and one of the most fundamental methods to solve differential equations is the fourth-order Runge-Kutta method.³⁴ Its numerical error is of the order of $(\Delta t)^4$, where Δt is the time step and very short simulation time steps are required to obtain accurate solution. Noting that the first-order change of Fock matrix depends linearly on the first order change of density matrix, we may rewrite Eqs. (12) and (16) in the following linear form:

$$i \frac{d}{dt} P^{(1)} = L P^{(1)}, \quad (19)$$

where L is a time-independent linear operator. The Runge-Kutta method with adaptive time steps, which has been shown to achieve much improvement for systems under strong laser fields,⁴⁴ is not expected to be more efficient for solving Eq. (19) due to the time-independent property of L . The formal solution for Eq. (19) can be written as

$$P(t) = e^{-iLt} P(t=0). \quad (20)$$

The most straightforward method to calculate e^{-iLt} is the Taylor expansion. It can be shown that the fourth-order Runge-Kutta method is exactly the same as Taylor expansion to the fourth order for this type of differential equations. In addition, the convergence property of the Taylor expansion behaves as a power law. Taylor expansion for e^{-iLt} is thus not very efficient and accurate. Generally speaking, to converge Taylor expansion for e^{-iLt} , a time step satisfying $\Delta t \ll k/L_{\text{max}}$ is needed, where k is the terms used in the Taylor expansion, L_{max} is the largest eigenvalue of operator L , i.e., the largest excitation energy. When a large time step is used, a numerical divergent problem could arise. The largest time step that leads to a stable expansion should satisfy

$$\left| \sum_{n=0}^k \frac{1}{n!} (-i\Delta t L_{\text{max}})^n \right| \leq 1. \quad (21)$$

According to Eq. (21), it can be seen that for $k=2$, the expansion is unstable no matter what time step is used. For $k=4$, the largest time step for stable expansion is $\sqrt{8}/L_{\text{max}}$.^{21,45} For $k=6$, an even smaller time step is needed.

A more efficient method to calculate e^{-iLt} is the Chebyshev expansion. In this approach, $P(t)$ reads^{32,33}

$$P^{(1)}(t) = e^{-iLt} P^{(1)}(t=0) = \sum_{n=0}^{\infty} (2 - \delta_{n0}) J_n(t\Delta) P_n, \quad (22)$$

$$P_n = \frac{-2i}{\Delta} L P_{n-1} + P_{n-2}, \quad P_1 = \frac{-i}{\Delta} L P_{n-1}, \quad (23)$$

$$P_0 = P^{(1)}(t=0),$$

where $J_n(\alpha)$ is Bessel function of the first kind and Δ is a positive number larger than L_{max} to converge this expansion. Unlike the Taylor expansion method, this expansion converges for any time step as long as Δ is larger than L_{max} . The numerical divergent problem is thus completely removed in the Chebyshev expansion. In our calculations, Δ is estimated through the difference between the highest virtual level and the lowest occupied level. For any time t' smaller than the time step t , $P^{(1)}(t')$ can be determined with the same expansion with little additional effort. The Chebyshev expansion converges exponentially due to the exponential decay of the Bessel function $J_n(\alpha)$ when n is larger than α .³³ The number of terms needed in Eq. (22) should only be slightly larger than $t\Delta$. To achieve high efficiency with Chebyshev approach, a large value of t is preferred. The Chebyshev approach is about 70% as costly in terms of computational time

as the fourth-order Runge-Kutta method with the largest possible time step, while leading to much more accurate results. To achieve the same accuracy, the fourth-order Runge-Kutta method or the fourth-order Taylor expansion method will be several hundred times more expensive. Using the fact that the first-order density matrix at the initial time is pure imaginary if real basis functions and real external potential are used, it can be seen that P_n will be real when n is odd and pure imaginary when n is even based on Eq. (23). For pure imaginary P_n , the first-order change of Fock matrix $h^{(1)}$, which is usually the most expensive part, will be zero if “pure” XC functional is used. This further reduces the computational effort. When a hybrid Hartree-Fock/DFT functional is used, $h^{(1)}$ has only contribution from the Hartree-Fock exchange part for the pure imaginary P_n and the computational effort can be further reduced.

In both Taylor expansion and Chebyshev expansion for e^{-iLt} , the computational effort depends on the largest excitation energy, which is a transition involving core orbitals. These core excitations are of little interest in most cases and have negligible effect on valence excitations. If the core excitations are excluded, a much larger time step can be used in the Taylor expansion or a much smaller Δ and thus much less terms are needed in the Chebyshev expansion. Core orbitals can be easily excluded in the construction of Fock matrix if the canonical molecular orbitals are used as basis functions. When other types of basis functions are used, the core orbitals can be excluded either through the use of pseudopotentials or projection operators. Caution should be taken in the calculation of excitation energies with pseudopotentials since the valence orbitals obtained in this way are different from those with the presence of core orbitals. In the present work, the following projector operator is used to project out the core orbitals:

$$(P_{\text{core}})_{\mu\nu} = 1 - \sum_{i \in \text{core}} c_{\mu i} c_{\nu i}, \quad (24)$$

where $c_{\mu i}$ is the molecular orbital coefficient, and μ and ν are indices for orthogonal basis functions. The action of the projection operator on the Fock matrix should be $P_{\text{core}} F P_{\text{core}}$. In addition, the core orbitals are highly localized and this projection operator is thus a sparse matrix. The projection increases the computational effort for $h^{(1)}$ marginally.

IV. SPECTRAL ANALYSIS

Once the time-dependent first-order density matrix is obtained, the time-dependent first-order change of one-electron operator $\langle \hat{A}^{(1)}(t) \rangle$ can be calculated. A Fourier transformation on $\langle \hat{A}^{(1)}(t) \rangle$ leads to the following equation:

$$\begin{aligned} \langle A^{(1)}(\omega) \rangle &= \int_0^\infty e^{i(\omega+i\gamma)t} \langle A^{(1)}(t) \rangle dt \\ &= - \sum_i \left(\frac{1}{(E_i - E_0) + \omega + i\gamma} + \frac{1}{(E_i - E_0) - \omega - i\gamma} \right) \\ &\quad \times \langle \Psi_0 | \hat{A} | \Psi_i \rangle \langle \Psi_i | V^{\text{ext}} | \Psi_0 \rangle, \end{aligned} \quad (25)$$

where γ is a small positive number to ensure the conver-

gence of the integral. It can be seen that if both V^{ext} and \hat{A} are dipole moment operators, Eq. (25) is just the dynamic polarizability and the imaginary part of it will be the absorption spectra. The excitation energies can be decided through the peaks of the absorption spectra. In actual calculations, a finite propagation time has to be used. To extract the spectral information embedded in $\langle \hat{A}^{(1)}(t) \rangle$ in a finite time, a straightforward method is the discrete Fourier transformation³⁴ for $\langle \hat{A}^{(1)}(t) \rangle$ on a set of even space time grid. In discrete Fourier transformation, $\langle \hat{A}^{(1)}(t) \rangle$ at $\omega = 2n\pi/T$, $n=0, \dots, N/2$ can be obtained approximately, where T is the total propagation time and N is the number of points in the time grid. The resolution is thus $2\pi/T$.

Recently the filter diagonalization³⁵⁻³⁷ method was developed with great success in the spectral analysis for a time signal $S(t) = \sum_i d_i e^{i\omega_i t}$. In this method, a filter function is introduced to filter out the components of the frequencies outside a desired range in the time signal. The frequency inside this range and the corresponding d_i can be decided by diagonalizing a small matrix. The corresponding error for the obtained frequencies can also be estimated. The propagation time to resolve fully the spectral information only needs to be proportional to the inverse of the average frequency spacing since different spectral ranges are handled separately in the filter diagonalization method. For comparison, the propagation time is proportional to the inverse of the minimum frequency spacing if one employs the discrete Fourier transformation. This means a much shorter propagation time can be used if filter diagonalization is employed for the spectral analysis. The filter diagonalization leads to more accurate frequencies embedded in the time signal than the discrete Fourier transformation. Moreover, when the time signal is not as accurate, the filter diagonalization method can still result in surprisingly accurate results.

V. COMPUTATIONAL DETAILS AND RESULTS

The above mentioned methods have been implemented into the LODESTAR program package.²⁴⁻³¹ To check the accuracy of the Chebyshev expansion and Taylor expansion methods, $\langle \hat{A}^{(1)}(t) \rangle$ can be calculated with sum-over-state method⁴⁶ through the calculation of all the excitations according to Eqs. (1) and (4) as the following:

$$\langle \hat{A}^{(1)}(t) \rangle = -2 \sum_I \omega_I \sin \omega_I t \sum_{ia} A_{ia} V_{ai}^{\text{ext}}(F_I)_{ia} / (\varepsilon_a - \varepsilon_i), \quad (26)$$

where i is the index for occupied molecular orbital, a is the index for virtual orbital, and ε_i and ε_a are their energies, respectively. The excitation energies calculated via Eq. (1) are used to calibrate the spectral analysis methods.

In our calculations, the time-dependent first order change of the dipole moment along the C-C direction for ethene and along the C_2 axis passing through two carbon atoms of benzene due to a perturbation of an electric field of the same direction is calculated both from Taylor's expansion to the fourth order and Chebyshev approach. The electric field is a time-domain δ function described by Eq. (2). This time-

dependent dipole moment is calculated via Eq. (26) as well for comparison. Since we deal with small molecules in the present work, the cutoff for the first-order change of density matrix is not applied. The excitation energies are extracted from the time-dependent dipole moment by employing the discrete Fourier transformation and the filter diagonalization methods. The singlet-triplet excitations for ethene are calculated as well using the potential specified in Eq. (15) with $B(\mathbf{r})$ polarized along the C–C direction. 6-31G basis set is employed. The local density approximation^{47,48} (LDA) for the XC potential and adiabatic local density approximation¹ (ALDA) for the XC kernel are used in the calculations. Besides LDA potential and ALDA kernel, other types of XC potentials and XC kernels such as hybrid Hartree-Fock/DFT potentials and kernels are also compatible with the present approach although the corresponding computational efforts are increased. Comparison is made with the calculated results based on Eq. (1). In the calculations the 1s orbitals of carbon atoms are kept frozen and test calculations show that the error in the excitation energies due to the frozen orbital approximation is below 0.01 eV. The time step used in the Taylor expansion is 0.02 fs, and Δ in Chebyshev expansion is set to 65 and 80 eV for ethylene and benzene, respectively. Without the frozen 1s core orbitals, a time step of 0.005 fs and Δ of about 500 eV should be used instead and the computational time increases thus four to five times. It is important to point out that the Δ value in Chebyshev expansion and the largest stable time step in Taylor expansion are related to the largest excitation energy of the system, not the highest excitation energy that can be induced by the external field. The propagation times for ethene and benzene are 5 and 15 fs, respectively, in the calculations. For medium to large systems, a propagation time of 35 fs is usually enough to obtain absorption spectra with an energy resolution of ~ 0.1 eV.

The numerical errors of the time-dependent first-order dipole moment for ethene based on the fourth-order Taylor expansion and Chebyshev expansion are plotted in Fig. 1. The numerical exact time-dependent dipole moment is calculated according to Eq. (26). It can be seen that the Chebyshev expansion method leads to much more accurate results than the fourth-order Taylor expansion. On the other hand, the total number of the LP operation based on Eq. (19) is about 550 for the Chebyshev method and 1000 in the fourth-order Taylor expansion method. The most time consuming step is to construct $h^{(1)}$ matrix. In the case of Chebyshev expansion, $h^{(1)}$ needs to be constructed 225 times while it is 1000 times for the Taylor expansion method. The Taylor expansion method is approximately three times more time consuming while lower accuracy is achieved. The total time needed to calculate $h^{(1)}$ for ethene is already comparable to that in conventional TDDFT calculations for the lowest several excitations, where $h^{(1)}$ needs to be constructed for several tenth times or even more, while the information of the absorption spectra in the whole energy range can be obtained with the present approach. The spectral analysis on the time-dependent dipole moment calculated using Chebyshev approach is performed via the discrete Fourier transformation and the filter diagonalization, and the obtained excitation en-

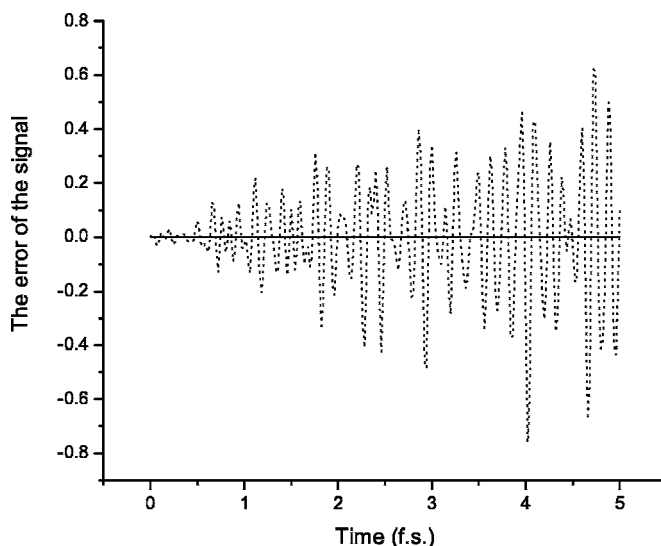


FIG. 1. The error of the first-order time-dependent dipole moment obtained from Chebyshev method and Taylor expansion to the fourth order. (Solid line: the error of Chebyshev method; dotted line: the error of Taylor expansion).

ergies lower than 20 eV are listed in Table I. The numerical exact excitation energies using Eq. (1) are tabulated for comparison. The singlet-triplet excitations are given as well. It can be seen that the excitation energies from the filter diagonalization agree very well with the numerical exact values. The discrete Fourier transformation leads to an error of ~ 0.05 eV and moreover, several weak excitations are missing. The total propagation time used for this systems is 5 fs which corresponds to an average resolution of 0.83 eV. However, it can be seen that the fifth and the sixth singlet-triplet excitation are resolved with the filter diagonalization approach although their energy gap is only 0.75 eV. We conclude thus that the filter diagonalization is an excellent method for spectral analysis.

TABLE I. The singlet-singlet and singlet-triplet excitation energies of ethene with TDDFT for transitions that are dipole allowed in the C–C direction of ethene (unit: eV).

No. of state	Numerical exact ^a	Oscillator strength	FD ^b	dFT ^c
Singlet-singlet excitations				
1	8.570	0.105	8.569	8.472
2	11.937	0.070	11.937	11.922
3	13.965	0.042	13.965	13.922
4	16.993	0.002	16.991	
5	17.813	0.023	17.812	
6	19.160	0.029	19.159	19.206
Singlet-triplet excitations				
1	4.838		4.837	4.788
2	10.451			
3	10.740		10.740	10.723
4	13.309		13.310	13.393
5	16.137		16.134	
6	16.869		16.869	
7	17.612		17.610	17.613

^aResults according to Eq. (1).

^bFilter diagonalization.

^cDiscrete Fourier transformation.

TABLE II. The singlet-singlet excitation energies of benzene with TDDFT for transitions that are dipole allowed in the direction along the C_2 axis passing through two carbon atoms of benzene (unit: eV).

No. of state	Numerical exact ^a	Oscillator strength	FD ^b	dFT ^c
1	7.415	0.230	7.415	7.395
2	11.132	$0.1E-5$		
3	11.222	0.020	11.222	11.133
4	12.022	0.046	12.018	11.970
5	12.680	0.076	12.674	12.662
6	14.275	$0.6E-5$	14.276	
7	14.367	0.039	14.368	14.339
8	15.046	0.008	15.048	
9	15.198	0.016	15.199	15.165
10	16.137	0.055	16.137	16.105
11	16.465	0.039	16.458	16.490
12	17.734	0.007	17.734	
13	17.761	$0.2E-5$		
14	17.943	0.004	17.881	
15	18.118	0.006	18.083	
16	18.587	0.083	18.581	18.599

^aResults according to Eq. (1).

^bFilter diagonalization.

^cDiscrete Fourier transformation.

The calculated results for benzene are listed in Table II. The excitation energies calculated via the filter diagonalization still agree very well with the numerical exact values, although some very weak transitions such as the second and the 13th transitions are not resolved. The discrete Fourier transformation results in much larger errors and more transitions missing. The total propagation time of 15 fs corresponds to an average resolution of 0.27 eV. Although the spacing between the sixth and seventh excited state is only about 0.1 eV, these two peaks are resolved with filter diagonalization. However, the 13th to 15th excited states are resolved partially even with filter diagonalization method, while they cannot be resolved at all with discrete Fourier transformation. To achieve a higher resolution, longer propagation time is needed. The time signals used in the above spectral analysis are calculated with the Chebyshev expansion approach and are thus highly accurate. When the time signals calculated with the fourth-order Taylor expansion are used, we find that the filter diagonalization leads to similarly accurate results.

VI. CONCLUSION

A linear response density matrix based TDDFT formalism in real time domain is extended in the present work. When the external field is a time-domain δ function, the first-order time-dependent density matrix can be written as an exponential of a time-independent operator acting on the initial density matrix. The time evolution of first-order time-dependent density matrix are calculated with two approaches, the Chebyshev expansion method and the fourth-order Runge-Kutta or fourth-order Taylor expansion method. It is found that the Chebyshev approach is much more accurate and efficient than the fourth-order Taylor expansion method. Moreover, the previous divergence problem of the

Runge-Kutta method is completely removed in the Chebyshev approach. The time-domain TDDFT formalism has been generalized to calculate the singlet-triplet excitations by introducing the polarized magnetic field.

To extract the excitation energies from the induced time-dependent dipole moment, two spectral analysis methods have been implemented: the discrete Fourier transformation and the filter diagonalization methods. The filter diagonalization method is found to be a much more powerful method, it yields more accurate values of the excitation energies and is capable of resolving more embedded signals. When the time-dependent signal is not as accurate, for instance, the time-dependent dipole moment calculated via the Taylor expansion, the filter diagonalization method can still yield the highly resolved values of the excitation energies.

Conventional TDDFT based on Eq. (1) is a powerful tool in the calculation of the lowest few excitation energies, especially for small-to-medium sized systems. However, it is difficult to apply it to large systems or to calculate the energies of highly excited states. The density matrix based time-domain TDDFT is an alternative to calculate the excited states and can circumvent such difficulties. For small systems, the present formalism is not as efficient as the conventional TDDFT method. However, since our time-domain TDDFT is an $O(N)$ method via a cutoff for density matrix, it can be applied to large systems. Moreover, the excitations in the whole energy range can be treated with this approach. This makes the present formalism a proper candidate for the study of excited states of large systems. For large systems, a propagation time of 35 fs can give rise to an energy resolution of ~ 0.1 eV. With the core orbitals kept frozen, the first-order Fock matrix need to be constructed for about 1000 times with the Chebyshev approach. This is still a very large number for large size systems with *ab initio* method. One possible means to reduce this number is to avoid the explicit construction of Fock matrix at each time step. Instead, the Fock matrix can be extrapolated from the existing ones. Work along this direction is under the way.

ACKNOWLEDGMENTS

The authors thank V. A. Mandelshtam for offering us the filter diagonalization code. Support from the Hong Kong Research Grant Council (HKU 7012/04P) and the National Science Foundation of China (NSFC 20433020) is gratefully acknowledged.

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