A Dual-Level State-Specific Time-Dependent Density-Functional Theory

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Abstract: A highly efficient new algorithm for time-dependent density-functional theory (TDDFT) calculations is presented. In this algorithm, a dual-level approach to speed up DFT calculations (Nakajima and Hirao, J Chem Phys 2006, 124, 184108) is combined with a state-specific (SS) algorithm for TDDFT (Chiba et al., Chem Phys Lett 2006, 420, 391). The dual-level SS-TDDFT algorithm was applied to excitation energy calculations of typical small molecules, the Q bands of the chlorophyll A molecule, the charge-transfer energy of the zincbacteriochlorin–bacteriochlorin model system, and the lowest-lying excitation of the circumcoronene molecule. As a result, it was found that the dual-level SS-TDDFT gave correct excitation energies with errors of 0.2–0.3 eV from the standard TDDFT approach, with much lower CPU times for various types of excitation energies of large-scale molecules.


Key words: dual-level approach; state-specific scheme; time-dependent density-functional theory; excitation energy; excited state

Introduction

Time-dependent density-functional theory (TDDFT) is one of the most useful methods for investigating electronic excited states of large molecules. This is because TDDFT gives accurate excitation energies equivalent to ab initio correlation methods with much lower computational times. Although TDDFT using pure exchange-correlation functionals underestimates Rydberg excitation and charge-transfer energies, it has already been proposed that these are efficiently improved by a long-range correction for exchange functionals. Therefore, it is expected that TDDFT will become the most powerful tool for studying the photochemistry of large systems. To carry out TDDFT calculations for large systems in practice, however, we require a highly sophisticated algorithm that makes the TDDFT procedure much more efficient.

Many techniques have been suggested for achieving a highly efficient TDDFT algorithm. By using a density-fit such as resolution of the identity, the scaling of TDDFT is reduced from $O(N^3)$ to $O(N^2)$. Several linear-scaling algorithms for DFT, e.g., fast multipole methods for Coulomb integral calculations and weight methods for numerical quadratures, are also efficient in reducing the scaling of the pure TDDFT algorithm to $O(N)$. Recently, a state-specific (SS) algorithm was developed for TDDFT calculations. In this algorithm, TDDFT calculations are performed after screening transitions contributing to a specific excitation. It was found that TDDFT using this algorithm gave accurate excitation energies with much lower computational times. In this study, it was also suggested that combining it with a linear-scaling DFT algorithm may decrease the computational order of a state-of-the-art TDDFT procedure close to $O(N)$. As a computational algorithm for DFT, a dual-level algorithm was recently proposed. In this algorithm, Kohn–Sham (KS) self-consistent-field (SCF) calculations using a high-level basis set are carried out with a Fock matrix, which is calculated using a lower-level basis set. This dual-level DFT algorithm uses the idea of the Harris-function approach, and is based on the dual-basis approach of HF and DFT, and single-reference and multireference second-order Möller–Plesset perturbation theories. In DFT calculations on large systems, the bottleneck is often the poor convergence in the SCF procedure, because large systems generally contain many near-degenerate energy levels in the vicinity of the Fermi level. The KS-SCF process requires a high computational cost: the number of SCF...
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For which it is difficult to achieve linear-scaling computational

drastically reduces the number of exchange integral operations,
for which it is difficult to achieve linear-scaling computational order, it is presumed that this algorithm is more useful for hybrid DFT calculations.

In this study, we propose a highly efficient new TDDFT algorithm for calculations on large systems by combining the dual-level DFT approach with the SS-TDDFT algorithm. The dual-level approach has so far been applied to ground state DFT calculations. By using this approach together with such a sophisticated DFT algorithm, the SS algorithm for TDDFT will be more efficient. If the combined algorithm performs well in TDDFT calculations, it becomes possible to carry out excited state calculations in significantly less computational time. In Dual-Level SS-TDDFT Algorithm section, we briefly review the dual-level SS-TDDFT algorithm. Detailed calculations are explained in Computational Details section, and calculated results using the new TDDFT approach are shown in Results and Discussion section. Finally, we conclude this study under Conclusions section.

Dual-Level SS-TDDFT Algorithm

In the dual-level TDDFT approach, TDDFT calculations are carried out using MOs that are evaluated in the SCF process using low-level basis sets. Different exchange-correlation functionals can also be used for the first step (with a low-level basis) and second step (with a high-level basis) of the dual-level DFT.

The dual-level TDDFT approach proceeds as follows:

1. First, the dual-level DFT is performed. After the KS equation is solved using a low-level basis set, the Fock matrix is constructed with a high-level basis set using the reference density matrix as

\[
F_{pq} = h_{pq} + \sum_{PQ} D_{pq}^P(pq|PQ) - t_{HB} D_{pq}^P(pQ|Pq) \\
+ t_{XC}^{\text{vir}}(\rho_j) - t_{HB}(\text{long-range}) D_{pq}^P(pQ|Pq)^{\text{Long}} \\
- t_{XC}(\text{short-range})^{\text{XC}}(\rho_j) 
\]

where capital letter terms \(P, Q, \ldots\) indicate atomic orbitals (AOs), which are represented by the low-level basis set, and the terms \(p, q, \ldots\) indicate AOs consisting of the high-level basis set. \(D^P\) is the density matrix, which is calculated using the low-level basis set. In eq. (1), \(h_{pq}\) and \(r_{pq}^{XC}\) are the elements of the one-electron Hamiltonian and exchange-correlation potential matrix, respectively, which are estimated using the high-level basis set. The coefficients \(t_{HB}\) and \(t_{XC}\) control the proportion of the Hartree–Fock exchange integral and the exchange-correlation functional of electron density \(\rho_j(r)\), respectively. In case of the long-range corrected (LC) exchange functional, a long-range part of two-electron integrals are combined with a short-range part of exchange functional in eq. (1).22

2. After constructing the Fock matrix element, the Fock matrix in eq. (1) is diagonalized to give the occupied KS orbitals and the orbital energies corresponding to the high-level basis set. The Fock matrix projected to the occupied orbital space is written as

\[
F_{pq}^{\text{occ}} = \sum_{rs} (SD)_{pq} F_{rs}(DS)_{pq},
\]

where \(S\) is the overlap matrix between the two original (high-level) basis functions. On the other hand, the virtual KS orbitals and the orbital energies are given by diagonalizing

\[
F_{pq}^{\text{vir}} = \sum_{rs} (1 - SD)_{pq} F_{rs}(1 - DS)_{pq},
\]

which is the Fock matrix projected to the virtual orbital space.

3. Next, the TDDFT equation is solved using the KS orbitals of the dual-level DFT. The TDDFT excitation energy \(\omega_0^{(0)}\) is given by

\[
\begin{pmatrix} A & B \\ B & A \end{pmatrix} \begin{pmatrix} X \\ Y \end{pmatrix} = \omega^{(0)} \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \begin{pmatrix} X \\ Y \end{pmatrix},
\]

where \(X\) and \(Y\) are the response eigenfunctions. Equation (4) can be transformed into an Hermitian eigenvalue equation,

\[
(A - B)^{1/2} (A + B)(A - B)^{-1/2} T = (\omega^{(0)})^2 T,
\]

where

\[
T = (A - B)^{-1/2} |X + Y|.
\]

The elements of matrices \(A\) and \(B\) are

\[
A_{i \sigma, j \sigma'} = \delta_{ij} \delta_{\sigma \sigma'} + K_{i \sigma, j \sigma'},
\]

and

\[
B_{i \sigma, j \sigma'} = K_{i \sigma, j \sigma'},
\]

respectively, where the \(i\)- and \(j\)-th orbitals are occupied and the \(\sigma\)- and \(\sigma'\)-th orbitals are unoccupied, and \(\sigma\) and \(\sigma'\) indicate spins. \(I\) and \(J\) are the occupied molecular orbitals, which are described using the low-level basis set. The matrix elements \(K_{i \sigma, j \sigma'}\) are given by

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2. The exchange-correlation potential and the AO-based integral

\[ K_{\text{int},j} = \langle j\sigma | \hat{H} | j\sigma \rangle + \sum_{\alpha} \left\{ \langle j\sigma | \delta^2 E_{\text{XC}} \frac{\delta}{\delta \rho_{\alpha}} \frac{\delta}{\delta \rho_{\alpha}} \rangle | j\sigma \rangle - \text{tr} \left\{ \hat{H} | j\sigma \rangle \langle j\sigma | \right\} \right\} \]

(9)

4. Now it should be noted that this dual-level TDDFT does not satisfy the Brillouin condition, because the SCF process is omitted for the high-level basis set in the dual-level DFT (step 2). Therefore, the excitation energy \( \omega^{(0)} \) should be corrected for the non-Brillouin terms. Using the KS orbitals and orbital energies, the correction to the excitation energy is evaluated perturbatively as

\[ \omega^{(1)} = \sum_{\alpha} \sum_{\mu} \sum_{\rho} C_{\alpha\mu} C_{\beta\mu} \left\{ F_{\mu\alpha} C_{\beta\alpha} + F_{\mu\beta} C_{\alpha\beta} \right\} \]

(10)

where \( C \) is the zero-order response eigenfunction of the dual-level TDDFT. Because the calculation of all the non-Brillouin corrections of the CIS(D) method requires more computational cost than the TDDFT process itself, \( \omega^{(1)} \) is a part of the non-Brillouin correction to the CIS(D) method. Consequently, the excitation energy of the dual-level SS-TDDFT is given as

\[ \omega = \omega^{(0)} + \omega^{(1)}. \]

(11)

For the scaling of computational cost, diagonalization of the \( A + B \) and \( A - B \) matrices is \( O(N_{\text{occ}} N_{\text{virt}}^3) \), in which \( N_{\text{occ}} \) and \( N_{\text{virt}} \) are the numbers of occupied and virtual molecular orbitals. Providing that \( N_{\text{virt}} \) is reduced to a constant for large systems, the order of the SS-TDDFT calculation is expected to become equivalent to that of one SCF routine in the KS calculation as described later. In the SS-TDDFT algorithm, there are four main time-consuming calculating processes.

1. The inequality condition for given excitations is given as

\[ \left| \frac{\Omega_{E,\text{int},\alpha}}{(e_{\alpha} - e_{\beta})^2} \right| > \theta, \]

where the main transition of the specific excitation is from the \( k \)-th occupied to the \( c \)-th virtual orbital. \( \theta \) is a threshold for the reduced subspace and \( 1.0 \times 10^{-8} \) was used in ref. 9.

In eq. (12), the matrix element \( \Omega_{E,\text{int},\alpha} \) is given as

\[ \Omega_{E,\text{int},\alpha} = \frac{\delta_{\alpha} \delta_{\beta} (e_{\alpha} - e_{\beta})}{(e_{\alpha} - e_{\beta})^2} \]

(13)

Matrix \( \Omega \) of eq. (13) is \((A - B)^{1/2}(A + B)(A - B)^{1/2}\) of the exact form for pure exchange-correlation functionals and an hybrid for functional hybrids. We note that the specific \( kc \) transition is fixed, because \( kc \) is input as a given transition prior to the calculation.

2. The exchange-correlation potential and the AO-based integral in the matrix–vector products, \((A + B) b_n\) and \((A - B)b_n\), are given as

\[ [(A + B)b]_{Q_s\sigma\alpha} = \sum_{R} N \sum_{Q} [D'_{R,s\tau,R}] \langle Q_s | R | Q_s \rangle - \text{tr} [(Q_s | R)] \]

(14)

and

\[ [(A - B)b]_{Q_s\sigma\alpha} = \sum_{R} N \sum_{Q} \langle (Q_s | R) - (Q_s | Q) \rangle \text{tr} [D'_{R,s\tau,R}], \]

(15)

where \( b_n \) is the \( n \)-th zeroth-order orthonormal subspace and \( E_{\text{XC}} \) is the exchange-correlation potential in the adiabatic approximation, and \( N_o \) and \( N_v \) are the numbers of the high-level and low-level basis functions and the density matrix \( D' \) is given as

\[ D'_{R,s\tau,R} = \sum_{i=1}^{N_v} C_{R,s\tau,L} \cdot C_{R,s\tau,L} \cdot b_{i}', \]

(16)

where \( i' \) and \( d' \) are a pair of occupied orbital and virtual orbitals of the reduced subspace.

3. The reduced \((A + B)\) and \((A - B)\) matrices are obtained by transformation of the AO-base form to MO-base form and the addition of the diagonal elements \((e_{\alpha} - e_{\beta})\) as

\[ (A + B)_{n,m} = \sum_{\alpha,\beta} \sum_{\mu,\rho} \delta_{\alpha\mu} \delta_{\beta\rho} \delta_{\tau} b_{\mu,\rho}^{\alpha} (e_{\alpha} - e_{\beta}) b_{\beta,\rho}^{\alpha} \]

(17)

and

\[ (A - B)_{n,m} = \sum_{\alpha,\beta} \sum_{\mu,\rho} \delta_{\alpha\mu} \delta_{\beta\rho} \delta_{\tau} b_{\mu,\rho}^{\alpha} (e_{\alpha} - e_{\beta}) b_{\beta,\rho}^{\alpha} \]

(18)

4. Finally, the Davidson algorithm excluding matrix–vector product calculations is employed.

The computational order of process 1 is equivalent to that of one matrix–vector product calculation of standard TDDFT, because the \( kc \) transition is fixed. Therefore, it is almost equal to the order of the Fock matrix elements calculation in one SCF routine. This process is, therefore, scaled as \( N_{o}^3/8 \) without any scaling approach. The scaling is changed to \( N_{o}^2 \times (N_{o}^3)^2/4 \) in the dual-level SS-TDDFT using the effective two-electron integral algorithm, because the two-electron integral consists of high- and low-level basis functions. For process 2, the scaling of the
numerical integral of the exchange-correlation potential $E_{\text{XC}}$ is $(N')^3$, in which $N'$ is the number of atoms in the system. The most time-consuming step, calculation of the $(A + B)b$ and $(A - B)b$ terms in the effective two-electron integral algorithm, is scaled as $N^4/8$. The scaling of $(A + B)b$ and $(A - B)b$ calculations is changed to $N^2 \times (N^2)^2/4$ in the dual-level SS-TDDFT. The transformation in process 3 requires a computational cost of $O(N)$, because the number of contributing AO pairs is constant for a fixed $N_{\text{trans}}$. Finally, the Davidson iterative subspace algorithm in process 4 is independent of $N$. Overall, the SS-TDDFT calculation is scaled as $N^2 \times (N^2)^2/4$ as a result of processes 1 and 2.

Computational Details

The dual-level SS-TDDFT algorithm was applied to excitation energy calculations of C$_2$H$_4$, H$_2$CO, C$_6$H$_6$, a chlorophyll A model molecule$^{24}$ (see Fig. 1), zincbacteriochlorin–bacteriochlorin (ZnBC-BC, Fig. 2),$^{27,28}$ and circumcoronene (see Fig. 3). For comparison, we also carried out standard TDDFT and dual-level SS-TDDFT calculations. The geometries of the C$_2$H$_4$, H$_2$CO, and C$_6$H$_6$ molecules were optimized by the LC Becke 1988 (B) exchange$^{29}$ one-parameter progressive (OP) correlation functional$^{30,31}$ with the 6-31$^{11}$G$^{**}$ basis set (LC-BOP/6-31$^{11}$G$^{**}$). The circumcoronene and ZnBC-BC molecules were optimized using the B3LYP$^{35}$ exchange-correlation functional using the 6-31G* basis set (B3LYP/6-31G*). For the chlorophyll A molecule, we used the optimized structure of Sundholm,$^{26}$ for which the Cartesian coordinates are shown in ref. 24. In the numerical quadrature for the exchange-correlation functional calculations, we used the Lebedev (32, 194)$^{36}$ grid, having 32 radial shells and 194 angular points per shell for all molecules. We implemented the Lebedev (32, 194) grid into the GAMESS program.$^{37}$ For calculations on C$_2$H$_4$, H$_2$CO, and C$_6$H$_6$, we used LC-BOP/6-31++G** and BOP/6-31++G** as the high-level set and BOP/6-31G as the low-level set. We also calculated TDDFT excitation energies using the high- and low-level sets through the whole process for comparison. In the calculations on chlorophyll A, ZnBC-BC, and circumcoronene molecules, the high- and low-level sets are set as LC-BOP/6-31G*, BOP/6-31G*, and BOP/6-31G, respectively. It has been proved that LC functional gave accurate excitation energies for not only valence excitations, but Rydberg and charge-transfer excitations.$^4$ Therefore, LC functional was used as a high-level set for all molecules in this study. Similarly, we also calculated excitation energies by using these sets through the whole process for these molecules. The CPU times (wall clock times) were evaluated for the calculations of these molecules in the dual-level SS-TDDFT and standard TDDFT calculations. In eq. (12), $\theta$ is a threshold for the reduced subspace and it was set as $1.0 \times 10^{-5}$ in ref. 9. For the dual-level SS-TDDFT, we examined various $\theta$ values ($1.0 \times 10^{-3}$, $1.0 \times 10^{-4}$, $1.0 \times 10^{-5}$, $1.0 \times 10^{-6}$, and $10^{-10}$) in calculating the first valence and Rydberg excitation energies of C$_2$H$_4$ molecule using LC-BOP, BOP, and B3LYP functional. As a result, functional calculations, we used the Lebedev (32, 194)$^{36}$ grid, having 32 radial shells and 194 angular points per shell for all molecules. We implemented the Lebedev (32, 194) grid into the GAMESS program.$^{37}$ For calculations on C$_2$H$_4$, H$_2$CO, and C$_6$H$_6$, we used LC-BOP/6-31++G** and BOP/6-31++G** as the high-level set and BOP/6-31G as the low-level set. We also calculated TDDFT excitation energies using the high- and low-level sets through the whole process for comparison. In the calculations on chlorophyll A, ZnBC-BC, and circumcoronene molecules, the high- and low-level sets are set as LC-BOP/6-31G*, BOP/6-31G*, and BOP/6-31G, respectively. It has been proved that LC functional gave accurate excitation energies for not only valence excitations, but Rydberg and charge-transfer excitations.$^4$ Therefore, LC functional was used as a high-level set for all molecules in this study. Similarly, we also calculated excitation energies by using these sets through the whole process for these molecules. The CPU times (wall clock times) were evaluated for the calculations of these molecules in the dual-level SS-TDDFT and standard TDDFT calculations. In eq. (12), $\theta$ is a threshold for the reduced subspace and it was set as $1.0 \times 10^{-5}$ in ref. 9. For the dual-level SS-TDDFT, we examined various $\theta$ values ($1.0 \times 10^{-3}$, $1.0 \times 10^{-4}$, $1.0 \times 10^{-5}$, $1.0 \times 10^{-6}$, and $10^{-10}$) in calculating the first valence and Rydberg excitation energies of C$_2$H$_4$ molecule using LC-BOP, BOP, and B3LYP functional. As a result,
we confirmed that $0 = 1.0 \times 10^{-5}$ gave adequate excitation energies within the errors of 0.1 eV for every types of functionals in the dual-level SS-TDDFT calculations. Therefore, we used $0 = 1.0 \times 10^{-5}$ in all calculations. All these calculations were performed on the GAMESS program.\textsuperscript{37}

Results and Discussion

Low-Lying Electronic Excitations of Typical Molecules

First, we applied the dual-level SS-TDDFT algorithm to calculations of the low-lying valence and Rydberg excitation energies of three typical molecules: $\text{C}_2\text{H}_4$, $\text{H}_2\text{CO}$, and $\text{C}_6\text{H}_6$. Table 1 summarizes the calculated excitation energies of the dual-level SS-TDDFT using LC-BOP/6-31$^+$$+G^{**}$ for the high-level and BOP/6-31G for the low-level. The calculated excitation energies of standard TDDFT with LC-BOP/6-31$^+$$+G^{**}$ or BOP/6-31G are also shown for comparison.

From Table 1, we found that there are small differences in the calculated excitation energies between the results of dual-level and standard TDDFT algorithms: the maximum error is 0.20 eV for the valence $^1\text{B}_1$ excitation of $\text{H}_2\text{CO}$ (LC-BOP/6-31$^+$$+G^{**}$; BOP/6-31G) and 0.11 eV for the Rydberg $^1\text{B}_{1u}$ excitation of $\text{C}_2\text{H}_4$ (BOP/6-31$^+$$+G^{**}$; BOP/6-31G). The dual-level TDDFT tends to slightly underestimate excitation energies in comparison with standard TDDFT. In particular, the dual-level algorithm gave more correct excitation energies for valence excitations than for Rydberg excitations, although the maximum error was given for a valence excitation. This may come from the small discrepancies between LC-BOP and BOP results for valence excitations. Because the dual-level TDDFT results are much closer to the results of high-level calculations for both valence and Rydberg excitations, this indicates that the dual-level algorithm is useful in preparing KS MOs for TDDFT calculations of typical small molecules.

It is also seen from the table that the dual-level SS-TDDFT results are close to the dual-level TDDFT values: the maximum error is 0.21 eV for the valence $^1\text{A}_2$ and Rydberg $^1\text{A}_1$ and $^2\text{I}_2$ excitations of the $\text{H}_2\text{CO}$ molecule (LC-BOP/6-31$^+$$+G^{**}$; BOP/6-31G) and 0.23 eV for the Rydberg $^2\text{I}_{2u}$ excitation of the $\text{H}_2\text{CO}$ molecule (BOP/6-31$^+$$+G^{**}$; BOP/6-31G). The SS algorithm also resulted in underestimation of the excitation energies. Furthermore, the dual-level SS-TDDFT provided large errors for the BOP calculations of the Rydberg excitations of $\text{H}_2\text{CO}$. As shown in the table, this may be because the MOs contributing to these Rydberg excitations were insufficiently given as the result of the poorly reproduced MOs by BOP/6-31G.

Comparing the dual-level SS-TDDFT results with standard TDDFT results, we found considerable errors: the maximum error is 0.39 eV for the Rydberg $^2\text{I}_{2u}$ excitation of the $\text{H}_2\text{CO}$ molecule (LC-BOP/6-31$^+$$+G^{**}$; BOP/6-31G) and 0.32 eV for the valence $^1\text{B}_1$ excitation of the $\text{H}_2\text{CO}$ molecule (BOP/6-31$^+$$+G^{**}$; BOP/6-31G). There are two possible reasons for these errors: one is because of the SCF process omitted for the high-level case of the dual-level algorithm, and another is because of the perturbation selection of the SS algorithm, which may not pick up enough contributing transitions.

Next, the dual-level SS-TDDFT algorithm was applied to calculations of the Q bands of the chlorophyll A molecule. The chlorophyll molecule is one of the most important molecules in photosynthesis. It is known that the photosynthesis reactions of plants proceed through visible light absorption by the chlorophyll A molecule. Chlorophyll A is a porphyrin derivative, which emits Q- and B bands stemming from $\pi$-$\pi^*$ excitations: Q bands show a weak intensity around 500–700 nm (1.8–2.5 eV) and B bands show a strong intensity around 350–400 nm (3.0–3.5 eV). Many investigations have been carried out on these bands by TDDFT\textsuperscript{25,26} and SAC-CI\textsuperscript{38} calculations. Hence, this molecule is an appropriate benchmark system for discussing the applicability of the dual-level SS-TDDFT algorithm.

In Table 2, calculated Q-band energies of the chlorophyll A molecule (see Fig. 1) are shown for the dual-level (SS-)TDDFT algorithm. We used LC-BOP/6-31G* and BOP/6-31G* as the high-level sets of this algorithm and BOP/6-31G* as the low-level set, respectively. The table shows that the dual-level algorithm hardly changes the excitation energies, especially in the case that the same pure functional is used for high- and low-level sets: the errors are 0.04 eV at most. For the case that different functional and basis sets are used in the dual-level algorithm (LC-BOP/6-31G*; BOP/6-31G case), the errors are slightly larger than the aforementioned one. However, these error values are equivalent to or smaller than those of small molecules. Although calculated oscillator strengths seem to have large errors in comparison with those of excitation energies, the errors are not so great as to affect the analyses. We therefore suppose that this algorithm is usable for calculations on $\pi$-$\pi^*$ transitions in such large molecules.

To discuss the efficiency of the dual-level SS-TDDFT algorithm, we compare the CPU times of this algorithm with those of the standard and dual-level TDDFT in Table 3. Comparing the CPU times, we found that the dual-level process requires much less time than those of the standard DFT. However, the CPU time of the dual-level TDDFT is not much different than those of the standard TDDFT. This is because the dual-level DFT process requires only the low-level calculation plus one iteration of high-level calculation and the bottleneck of the TDDFT process is solving the TDDFT equation. The SS algorithm clearly overcomes this situation. By using the SS algorithm, the CPU time of TDDFT is obviously reduced to one-third of the standard TDDFT time: 3577–1204 min for LC-BOP/6-31G* and 2632–834 min for BOP/6-31G*. As shown in the table, the excitation energy and oscillator strength were not so varied through both the dual-level and SS processes. This may suggest that the dual-level SS-TDDFT algorithm is useful in $\pi$-$\pi^*$ excitation energy calculations of such biomolecular systems.

Low-Lying Valence and Charge-Transfer Excitations of a ZnBC-BC Model System

Next, we examined the dual-level SS-TDDFT algorithm for charge-transfer energy calculations of ZnBc-BC. As mentioned in Introduction section, TDDFT usually fails to give correct charge-transfer energies and two of the authors have already
Table 1. Calculated Vertical Valence and Rydberg Excitation Energies (in eV) of the C$_2$H$_4$, H$_2$CO, and C$_6$H$_6$ Molecules by Dual-Level State-Specific (SS) and Standard TDDFT.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Excitation</th>
<th>Main transition</th>
<th>Dual-level TDDFT</th>
<th>Dual-level SS-TDDFT</th>
<th>Standard TDDFT</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>LC-BOP/6-31++G**; BOP/6-31G</td>
<td>LC-BOP/6-31++G**; BOP/6-31G</td>
<td>LC-BOP/6-31++G**; BOP/6-31G</td>
</tr>
<tr>
<td>C$_2$H$_4$</td>
<td>V $^1$B$_1u$</td>
<td>$\pi \to \pi^*$</td>
<td>7.61 (−0.02) 7.41 (0.04)</td>
<td>7.53 (−0.10) 7.30 (−0.07)</td>
<td>7.63 7.37 8.46</td>
</tr>
<tr>
<td></td>
<td>R $^1$B$_1$</td>
<td>$\pi \to 3s$</td>
<td>7.02 (−0.12) 6.37 (0.00)</td>
<td>6.93 (−0.21) 6.26 (−0.11)</td>
<td>7.14 6.37 9.15</td>
</tr>
<tr>
<td></td>
<td>R $^2$B$_1$</td>
<td>$\pi \to 3p\tilde{A}$</td>
<td>7.67 (−0.12) 6.88 (0.01)</td>
<td>7.59 (−0.20) 6.77 (−0.10)</td>
<td>7.79 6.87 9.46</td>
</tr>
<tr>
<td></td>
<td>R $^1$B$_2$</td>
<td>$\pi \to 3p\tilde{A}$</td>
<td>7.81 (−0.12) 6.90 (−0.01)</td>
<td>7.72 (−0.21) 6.79 (−0.12)</td>
<td>7.93 6.91 10.20</td>
</tr>
<tr>
<td>H$_2$CO</td>
<td>V $^1$A$_2$</td>
<td>$\pi \to \pi^*$</td>
<td>3.75 (−0.09) 3.86 (−0.05)</td>
<td>3.54 (−0.30) 3.66 (−0.25)</td>
<td>3.84 3.91 3.91</td>
</tr>
<tr>
<td></td>
<td>V $^1$B$_1$</td>
<td>$\sigma \to \pi^*$</td>
<td>8.85 (−0.20) 8.64 (−0.24)</td>
<td>8.76 (−0.29) 8.54 (−0.32)</td>
<td>9.05 8.86 8.94</td>
</tr>
<tr>
<td></td>
<td>R $^1$B$_2$</td>
<td>n $\to 3\text{va}_1$</td>
<td>6.66 (−0.15) 5.86 (0.03)</td>
<td>6.46 (−0.35) 5.64 (−0.19)</td>
<td>6.81 5.83 8.32</td>
</tr>
<tr>
<td></td>
<td>R $^1$A$_3$</td>
<td>n $\to 3\text{pb}_2$</td>
<td>7.68 (−0.17) 6.78 (0.07)</td>
<td>7.47 (−0.38) 6.56 (−0.15)</td>
<td>7.85 6.71 9.70</td>
</tr>
<tr>
<td></td>
<td>R $^1$B$_2$</td>
<td>n $\to 3\text{pa}_1$</td>
<td>7.57 (−0.18) 7.19 (0.07)</td>
<td>7.36 (−0.39) 6.96 (−0.16)</td>
<td>7.75 7.12 11.35</td>
</tr>
<tr>
<td></td>
<td>V $^1$B$_{3u}$</td>
<td>$\pi \to \pi^*$</td>
<td>5.47 (−0.02) 5.23 (−0.01)</td>
<td>5.49 (0.00) 5.18 (−0.06)</td>
<td>5.49 5.24 5.45</td>
</tr>
<tr>
<td></td>
<td>V $^1$B$_{3u}$</td>
<td>$\pi \to \pi^*$</td>
<td>6.37 (0.05) 5.99 (0.04)</td>
<td>6.32 (0.00) 5.91 (−0.04)</td>
<td>6.32 5.95 6.33</td>
</tr>
<tr>
<td></td>
<td>V $^1$E$_{3u}$</td>
<td>$\pi \to \pi^*$</td>
<td>7.14 (0.01) 6.89 (0.05)</td>
<td>7.06 (−0.07) 6.81 (−0.03)</td>
<td>7.13 6.84 7.40</td>
</tr>
<tr>
<td></td>
<td>R $^1$E$_{1g}$</td>
<td>$\pi \to 3\gamma$</td>
<td>6.69 (−0.09) 5.71 (0.01)</td>
<td>6.62 (−0.16) 5.60 (−0.10)</td>
<td>6.78 5.70 7.80</td>
</tr>
<tr>
<td></td>
<td>R $^1$A$_{2u}$</td>
<td>$\pi \to 3\rho\tilde{A}$</td>
<td>7.32 (0.07) 6.24 (0.02)</td>
<td>7.31 (0.06) 6.13 (−0.09)</td>
<td>7.25 6.22 9.13</td>
</tr>
</tbody>
</table>

The dual-level SS-TDDFT uses a high-level set of exchange-correlation functional and basis function (upper) and a low-level set (lower). “V” and “R” indicate valence and Rydberg excitations. The differences in calculated excitation energies from standard TDDFT values are also shown in parentheses.
Table 2. Calculated Excitation Energies (in eV) of the Q Bands of the Chlorophyll A Model Molecule.

<table>
<thead>
<tr>
<th>State</th>
<th>Dual-level TDDFT</th>
<th>Dual-level SS-TDDFT</th>
<th>Standard TDDFT</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>LC-BOP/6-31G*;</td>
<td>BOP/6-31G*;</td>
<td>LC-BOP/6-31G*;</td>
</tr>
<tr>
<td></td>
<td>BOP/6-31G</td>
<td>BOP/6-31G</td>
<td>BOP/6-31G*</td>
</tr>
<tr>
<td>2A</td>
<td>1.94 (0.02)</td>
<td>1.99 (0.01)</td>
<td>1.92</td>
</tr>
<tr>
<td>3A</td>
<td>2.30 (0.13)</td>
<td>2.04 (0.06)</td>
<td>2.43</td>
</tr>
</tbody>
</table>

The differences in calculated excitation energies from standard TDDFT values are also shown in parentheses.

Table 3. CPU Timings of the Dual-Level SS-TDDFT Calculations on the Chlorophyll A Molecule.

<table>
<thead>
<tr>
<th></th>
<th>Dual-level TDDFT</th>
<th>Dual-level SS-TDDFT</th>
<th>Standard TDDFT</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>LC-BOP/6-31G*;</td>
<td>BOP/6-31G*;</td>
<td>LC-BOP/6-31G*;</td>
</tr>
<tr>
<td></td>
<td>BOP/6-31G</td>
<td>BOP/6-31G</td>
<td>BOP/6-31G*</td>
</tr>
<tr>
<td>Excitation energy (eV)</td>
<td>2.30 (0.13)</td>
<td>2.04 (0.06)</td>
<td>2.43</td>
</tr>
<tr>
<td>Oscillator strength (a.u.)</td>
<td>0.035</td>
<td>0.032</td>
<td>0.034</td>
</tr>
<tr>
<td>CPU timing (min)</td>
<td>2937</td>
<td>2014</td>
<td>758</td>
</tr>
<tr>
<td>Low-level calculation</td>
<td>154 (SCF cycle 25)</td>
<td>154 (SCF cycle 25)</td>
<td>704 (SCF cycle 26)</td>
</tr>
<tr>
<td>1 iteration of High-level calculation</td>
<td>41</td>
<td>32</td>
<td>1927 (SCF cycle 26)</td>
</tr>
<tr>
<td>Dual-level DFT PT TDDFT</td>
<td>2937</td>
<td>2014</td>
<td>758 (SCF cycle 26)</td>
</tr>
<tr>
<td>(root = 2; trial vector 30)</td>
<td>2937</td>
<td>2014</td>
<td>758 (SCF cycle 26)</td>
</tr>
<tr>
<td>Dual-level SS-TDDFT PT</td>
<td>3132</td>
<td>2200</td>
<td>3577</td>
</tr>
<tr>
<td>Total time</td>
<td>3132</td>
<td>2200</td>
<td>3577</td>
</tr>
</tbody>
</table>

Calculated excitation energies and oscillator strengths are also displayed for each set. For the name of the dual-level (SS-)TDDFT, the upper and lower lines indicate the high-level and low-level sets, respectively. The differences in calculated excitation energies from standard TDDFT values are also shown in parentheses. All CPU timings were clocked on an HP Workstation zx6000 (Intel Itanium 21.50 GHz).
solved this problem by developing LC-TDDFT. For ZnBc-Bc, Dreuw and Head-Gordon suggested that the intermolecular charge-transfer energies are obviously underestimated in comparison to the Q-band energies, and this was already overcome by using a long-range correction method. However, it provides no assurance that accurate charge-transfer energies are given for the dual-level SS-TDDFT calculation, in which the LC-BOP functional is used as the high-level functional. Here, we confirm that the dual-level SS-TDDFT using an LC functional is available in charge-transfer energy calculations.

Figure 4 illustrates the calculated charge-transfer energies of the ZnBc-Bc model system (see Fig. 2) for intermolecular distances of 4.0–10.0 Å. As shown in the figure, the dual-level SS-TDDFT gave almost the same curve as the standard TDDFT curve. Because the figure shows that all these curves are approximately identical to the curve for standard TDDFT using the LC-BOP functional, it was confirmed that the dual-level SS-TDDFT algorithm using the LC-BOP functional gave the correct behavior for this long-range charge-transfer energy. This result suggests that both the dual-level and SS algorithms have no adverse effects on the behavior of long-range charge transfers.

In Table 4, the calculated excitation energies and oscillator strengths are summarized for the 10 lowest-lying electronic states of the ZnBc-Bc system with intermolecular distances R = 10.0 Å. The four lowest states are Q bands of independent Bc and ZnBc molecules, and there are four π → π* and two CT bands above these Q bands. The calculated results of the excitation energies indicated that the dual-level algorithm gave errors within 0.07 eV except for the lowest π → π* state of the independent ZnBc molecule (the error is 0.22 eV). For the SS algorithm, the maximum error in the excitation energy is 0.13 eV for two intermolecular CT states between ZnBc and Bc besides that of the Q3 band of independent Bc. This may indicate that the perturbation selection in eq. (10) is less satisfactory for such long-range CT excitations, because this selection is assured for the case that the excitation energy is adequately expressed by the perturbation expansion. However, the error is so small that the SS algorithm is usable in, at least, qualitative discussions of long-range CT excitations. Furthermore, the table shows
that both the dual-level and SS algorithms gave much worse oscillator strengths only for two \( \pi-\pi^* \) excitations of the ZnBc-Bc dimer (7th and 9th excitations in Table 4). This may be because these states are degenerate and mixed with each other, and DFT essentially gives poor results for such degenerate excitations. Therefore, we suppose that the oscillator strengths of these two excitations may be poorly reproduced in standard TDDFT calculations.

Similar to the calculations of chlorophyll A, we measured the CPU times for the lowest CT excitation of the ZnBc-Bc system with \( R = 10.0 \) Å (the 8th excitation). In Table 5, the CPU times are displayed for each step of the dual-level SS-TDDFT algorithm. For pure functionals, it is known that this CT excitation energy is significantly underestimated.27 The table also indicates that the dual-level TDDFT using a pure BOP functional +6-31G* basis set for the high-level set gave a very small CT excitation energy in comparison with other Q band and \( \pi-\pi^* \) excitation energies in Table 4. What we should notice is that the dual-level SS-TDDFT algorithm using an LC-BOP functional + large 6-31G* basis set required very short CPU times (303 min), which are equivalent to the time of a pure BOP functional + small 6-31G basis set (268 min), although it also estimated the accurate excitation energy for this CT excitation. This result may indicate that the dual-level SS-TDDFT algorithm using a LC functional is very powerful for calculating specific CT excitation energies.

**Lowest-Lying Excitation of Circumcoronene**

Finally, we calculated the first excitation energy of the circumcoronene molecule (see Fig. 3), which has a planar structure containing a broad delocalized \( \pi \) bonding. Because long-range exchange interactions obviously play a significant role in the electronic excitations of such systems, it is presumed that the LC scheme is required for exchange functionals, especially in TDDFT calculations.

Table 6 shows the calculated excitation energies. As expected, the LC scheme clearly increased the excitation energies of the pure BOP functional from 1.95 to 2.65 eV in the calculations of standard TDDFT using the 6-31G* basis set. This result suggests that long-range exchange interaction is important in this excitation. The table indicates that the dual-level and SS algorithms maintain the accuracy even for the excitation, which is considerably affected by a long-range interaction; the error is 0.23 eV from the dual-level algorithm and 0.04 eV from the SS algorithm in TDDFT calculations using LC-BOP/6-31G*: BOP/6-31G. Putting together the earlier discussions, it is reasonable to consider that dual-level SS-TDDFT keeps the accuracy of excitation energies within the errors of 0.2–0.3 eV for large molecules.

The CPU times of the dual-level SS-TDDFT calculations are also shown in Table 6. Because this excitation is the lowest, only one excitation should be calculated even in the standard TDDFT calculation. Nevertheless, the CPU times were reduced to less than half of the standard TDDFT times in the dual-level SS-TDDFT: 2746–1298 min for LC-BOP/6-31G*: BOP/6-31G and 1792–766 min for BOP/6-31G*: BOP/6-31G. Considering that the accuracy of the excitation energy was maintained in this
Table 6. CPU Timings of the Dual-Level SS-TDDFT Calculations for the First Excitation Energy of Circumcoronene.

<table>
<thead>
<tr>
<th>Method</th>
<th>Excitation energy (eV)</th>
<th>CPU timing (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Low-level calculation</td>
</tr>
<tr>
<td>LC-BOP/6-31G*</td>
<td>2.42 (0.23)</td>
<td>1.85 (0.10)</td>
</tr>
<tr>
<td>BOP/6-31G</td>
<td>2.18 (0.27)</td>
<td>1.85 (0.10)</td>
</tr>
<tr>
<td>BOP/6-31G*</td>
<td>1.95 (0.00)</td>
<td>1.85 (0.10)</td>
</tr>
<tr>
<td>BOP/6-31G</td>
<td>1.92 (0.10)</td>
<td>1.85 (0.10)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>High-level calculation</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dual-level SS-TDDFT</td>
<td></td>
<td></td>
</tr>
<tr>
<td>LC-BOP/6-31G*</td>
<td>2.65</td>
<td>2.57</td>
</tr>
<tr>
<td>BOP/6-31G</td>
<td>2.32</td>
<td>2.25</td>
</tr>
<tr>
<td>BOP/6-31G*</td>
<td>2.10</td>
<td>2.03</td>
</tr>
<tr>
<td>BOP/6-31G</td>
<td>1.98</td>
<td>1.91</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
| Calculated excitation energies (eV) are also displayed. For the name of the dual-level SS-TDDFT, the upper and lower lines indicate the high-level and low-level sets, respectively. The differences in calculated excitation energies from standard TDDFT values are also shown in parentheses. All CPU timings were clocked on an HP Workstation zx6000 (Intel Itanium 21.50 GHz). The dual-level SS-TDDFT is also useful in investigating a broad π bonding in large-scale systems.

Conclusions

As a highly efficient TDDFT algorithm for large-scale systems, we propose a method combining the dual-level DFT approach with the SS-TDDFT algorithm. The dual-level DFT approach was applied to TDDFT calculations: (1) after carrying out the SCF calculation using a low-level set of exchange-correlation functional and basis set, the Fock matrix is constructed using the potential of the low-level set and a high-level set, (2) the Fock matrix is diagonalized to give KS orbitals, (3) the TDDFT equation is solved using the orbitals and excitation energies are obtained, and (4) the calculated excitation energies are corrected for the non-Brillouin term resulting from the neglect of the SCF process in the second step. For the TDDFT procedure (the third step), we applied the SS algorithm, in which transitions contributing to a specific excitation energy are theoretically screened by a perturbation selection in eq. (10). We applied this dual-level SS-TDDFT algorithm to the excitation energy calculations of various systems and recorded the CPU times.

First, we calculated the low-lying valence and Rydberg excitation energies of typical small systems: C$_2$H$_4$, H$_2$CO, and C$_6$H$_6$. As a result, we found that both the dual-level and SS algorithms maintain the accuracy of excitation energies within errors of 0.23 eV. However, the total errors are doubled in the dual-level SS-TDDFT for such small systems, with the maximum error of 0.39 eV. We presumed that the neglect of the SCF process in the dual-level algorithm causes insufficient perturbation selection in the SS algorithm.

Next, we applied this algorithm to calculations of the Q bands (π-π* excitations) of the chlorophyll A molecule. Consequently, both the dual-level and SS algorithms accurately reproduced the excitation energies of the standard TDDFT (the error is 0.04 eV at most) with much lower CPU times (1/3 of the standard time). This result may suggest that this algorithm is efficient for calculations of the π-π* excitation energy of such biomolecular systems.

This algorithm was then applied to the charge-transfer energy calculations of ZnBe-Bc dimer. By plotting the charge-transfer energy in terms of the intermolecular distance, we found that the dual-level SS-TDDFT gives the correct behavior for the long-range charge transfer if LC functional is used as the high-level functional of the dual-level approach. Calculated excitation energies and oscillator strengths also suggested that the dual-level and SS algorithms keep the accuracy of the standard TDDFT results. Moreover, the dual-level SS-TDDFT drastically reduced the CPU time to less than 1/30 of the standard TDDFT time. We therefore concluded that the dual-level SS-TDDFT using LC functional is very useful in CT calculations.

Finally, we calculated the first excitation energy of the circumcoronene molecule, which contains a broad delocalized π bonding. For such a system, it is known that the LC scheme significantly affects the excitation energy. As a result, the dual-level SS-TDDFT gave a correct excitation energy maintaining
the accuracy with less than half of the CPU time in comparison with the standard TDDFT approach. It is therefore suggested that the dual-level SS-TDDFT is also useful in calculating a broad π bonding of large molecules.

In summary, we conclude that the dual-level SS-TDDFT is a powerful tool for investigating various types of excitation energies of large-scale systems. However, we also found that this method gives slightly poorer results for small molecules. There is room for further investigation.

Acknowledgments

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References

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