A long-range-corrected time-dependent density functional theory

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We apply the long-range correction (LC) scheme for exchange functionals of density functional theory to time-dependent density functional theory (TDDFT) and examine its efficiency in dealing with the serious problems of TDDFT, i.e., the underestimations of Rydberg excitation energies, oscillator strengths, and charge-transfer excitation energies. By calculating vertical excitation energies of typical molecules, it was found that LC-TDDFT gives accurate excitation energies, within an error of 0.5 eV, and reasonable oscillator strengths, while TDDFT employing a pure functional provides 1.5 eV lower excitation energies and two orders of magnitude lower oscillator strengths for the Rydberg excitations. It was also found that LC-TDDFT clearly reproduces the correct asymptotic behavior of the charge-transfer excitation energy of ethylene–tetrafluoroethylene dimer for the long intramolecular distance, unlike a conventional far-nucleus asymptotic correction scheme. It is, therefore, presumed that poor TDDFT results for pure functionals may be due to their lack of a long-range orbital–orbital interaction. © *2004 American Institute of Physics.*
[DOI: 10.1063/1.1688752]

I. INTRODUCTION

Time-dependent density functional theory (TDDFT) is becoming a popular method of calculating various molecular properties, e.g., absorption spectra.[1,2] Recently, geometrical optimization of excited states of molecules has been done by calculating energy gradients of TDDFT.[3–5] Since TDDFT incurs computational costs of the order of the configuration interaction singles method, it is presumed that TDDFT can be applied to even *ab initio* molecular dynamics calculations of photochemical reactions of large systems.

However, TDDFT calculations seem to have significant problems. One of the most severe is their poor estimation of the Rydberg excitations: They underestimate the Rydberg excitation energies and the corresponding oscillator strengths.[6–8] As is well-known, TDDFT using pure functionals generally provides several dozen percent smaller Rydberg excitation energies than experimental energies.[12] TDDFT also has difficulty to bring even the first digit of the oscillator strengths into line with the experimental value.[8] It has been suggested that the incorrect far-nucleus behavior of functionals may be responsible for these problems.[1] For most functionals, the σ-spin exchange-correlation potential, $v_{xc}^\sigma = \delta E_{xc}/\delta\rho_\sigma$ (E_{xc} is the exchange-correlation energy functional and ρ_σ is the σ-spin electron density), does not reproduce the correct far-nucleus asymptotic behavior,[9,10]

$$\lim_{R\to\infty} v_{xc}^\sigma(\mathbf{R}) = -\frac{1}{R}, \tag{1}$$

where $R=|\mathbf{R}|$ and $\mathbf{R}$ is the distance vector from the nearest nucleus, and atomic units have been used ($\hbar=e^2=m=1$, energies are in hartree, and distances are in bohr). Since this correct behavior is also given from the self-interaction exchange energy of a hydrogenlike atomic orbital,[11] this failure may be due to the self-interaction error in the functional. Van Leeuwen and Baerends suggested the LB94 functional, which improves the energy potential of the Becke 1988 exchange functional to reproduce this asymptotic behavior.[13] Instead of Eq. (1), Tozer and Handy suggested the asymptotic correction (AC) scheme, which improves functional potentials by imposing the asymptotic condition,[14,15]

$$\lim_{R\to\infty} v_{xc}^\sigma(\mathbf{R}) = -\frac{1}{R} + \epsilon_\sigma^{\text{HOMO}} + I_\sigma, \tag{2}$$

where $\epsilon_\sigma^{\text{HOMO}}$ is the eigenvalue of the highest occupied σ-spin molecular orbital and I_σ is the ionization potential of the σ-spin electron. It has been reported that the underestimation of Rydberg excitation energies is modified by using the above improvements.

Besides the above problems, it was also pointed out that TDDFT poorly reproduces charge-transfer excitations. By calculating the charge-transfer excitation energies of ethylene-tetrafluoroethylene dimer, Dreuw, Weisman, and Head-Gordon recently found that the excitation energies are significantly underestimated with increasing intermolecular

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distance by TDDFT employing conventional functionals including LB94 and Becke three parameter Lee–Yang–Parr (B3LYP).[16] Consequently, they suggested that exchange-correlation functionals should be investigated with respect to the charge-transfer problem as a benchmark for their applicability to TDDFT. Since charge transfer is essentially a single excitation that is taken into consideration in the Hartree–Fock (HF) wave function, it is presumed that this failure may come from the insufficient long-range exchange effect in the exchange functionals.[17]

We have applied the long-range correction (LC) scheme[17] to TDDFT. The LC scheme uses the standard error function to improve the exchange functional for calculating the long-range electron–electron distance with the HF exchange integral. In a previous study, it was found that the calculated dissociative energy potentials of van der Waals bonds of rare-gas dimers are obviously improved by combining the LC scheme with a van der Waals functional.[18] It is, therefore, supposed that the problems of TDDFT may be due to the insufficient exchange interaction between distant orbitals in exchange functionals rather than incorrect far-nucleus asymptotic behavior. In this paper, we confirm that the LC scheme improves the accuracy of the excitation energies and oscillator strengths of the Rydberg and charge-transfer excitations calculated by TDDFT.

II. THEORY

A. Long-range exchange correction scheme

The LC scheme explicitly incorporates the long-range orbital–orbital interaction part in the exchange functional by combining with the HF exchange integral.[17,19,20] In this scheme, electron repulsion operator $1/r_{12}$ is divided into short-range and long-range parts by using the standard error function as

$$\frac{1}{r_{12}} = \frac{1 - \mathrm{erf}(\mu r_{12})}{r_{12}} + \frac{\mathrm{erf}(\mu r_{12})}{r_{12}}, \tag{3}$$

where $r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|$ for coordinate vectors of electrons, $\mathbf{r}_1$ and $\mathbf{r}_2$, and μ is a parameter that determines the ratio of these parts. Following Eq. (3), the short-range part of exchange interaction can be incorporated by modifying the usual exchange functional form, $E_x = -(1/2)\Sigma_\sigma \times \int \rho_\sigma^{4/3} K_\sigma d^3 \mathbf{R}$, into

$$E_x^{sr} = -\frac{1}{2}\sum_\sigma \int \rho_\sigma^{4/3} K_\sigma \left\{ 1 - \frac{8}{3} a_\sigma \left[\sqrt{\pi}\, \mathrm{erf}\left(\frac{1}{2a_\sigma}\right) \right. \right.$$
$$\left. \left. + 2a_\sigma(b_\sigma - c_\sigma) \right] \right\} d^3 \mathbf{R}, \tag{4}$$

where a_σ, b_σ, and c_σ are

$$a_\sigma = \frac{\mu K_\sigma^{1/2}}{6\sqrt{\pi}\rho_\sigma^{1/3}}, \tag{5}$$

$$b_\sigma = \exp\left(-\frac{1}{4a_\sigma^2}\right) - 1, \tag{6}$$

and

$$c_\sigma = 2a_\sigma^2 b_\sigma + \tfrac{1}{2}. \tag{7}$$

We should notice that this equation is different from the previously proposed form,[17]

$$E_x^{sr} = -\frac{1}{2}\sum_\sigma \int \rho_\sigma^{4/3} K_\sigma \left\{ 1 - \frac{8}{3} a_\sigma \left[\sqrt{\pi}\, \mathrm{erf}\left(\frac{1}{2a_\sigma}\right) \right. \right.$$
$$\left. \left. + (2a_\sigma - 4a_\sigma^3)\exp\left(-\frac{1}{4a_\sigma^2}\right) - 3a_\sigma + 4a_\sigma^3 \right] \right\} d^3 \mathbf{R}, \tag{8}$$

because the $4a_\sigma^3[1 - \exp(-1/4a_\sigma^2)]$ term causes a cancellation of significant digits for large a_σ. For accuracy, b_σ should also be transformed into the Taylor expansion, provided a_σ is very large. The long-range part of the exchange interaction is expressed with the HF exchange integral,[21]

$$E_x^{lr} = -\frac{1}{2}\sum_\sigma \sum_i^{occ} \sum_j^{occ} \int \int \psi_{i\sigma}^*(\mathbf{r}_1)\psi_{j\sigma}^*(\mathbf{r}_1)$$
$$\times \frac{\mathrm{erf}(\mu r_{12})}{r_{12}} \psi_{i\sigma}(\mathbf{r}_2)\psi_{j\sigma}(\mathbf{r}_2) d^3\mathbf{r}_1 d^3\mathbf{r}_2, \tag{9}$$

where $\psi_{i\sigma}$ is the ith σ-spin molecular orbital. The parameter μ was determined so as to minimize the mean absolute deviation of the calculated equilibrium distances for the dimers of the first to third-row atoms (except rare-gas dimers) with the 6-311G++(2d,2p) basis set[22,23] and three types of exchange-correlation functionals mentioned later ($\mu = 0.33$).

B. Time-dependent density functional theory and oscillator strength

In TDDFT, the Ith excitation energy ω_I and corresponding response function $\mathbf{F}_I$ are usually obtained by solving the eigenvalue equation,[1,24]

$$(\mathbf{A}-\mathbf{B})^{1/2}(\mathbf{A}+\mathbf{B})(\mathbf{A}-\mathbf{B})^{1/2}\mathbf{F}_I = \omega_I^2 \mathbf{F}_I. \tag{10}$$

The elements of the matrices $\mathbf{A}$ and $\mathbf{B}$ are

$$A_{ia\sigma,jb\tau} = \delta_{ij}\delta_{ab}\delta_{\sigma\tau}(\epsilon_{a\sigma} - \epsilon_{i\sigma}) + K_{ia\sigma,jb\tau}, \tag{11}$$

where $\epsilon_{i\sigma}$ is the ith σ-spin orbital energy, and

$$B_{ia\sigma,jb\tau} = K_{ia\sigma,bj\tau}, \tag{12}$$

where $K_{ia\sigma,jb\tau}$ is given by

$$K_{ia\sigma,jb\tau} = (ia\sigma|jb\tau) + \int \int \psi_{i\sigma}^*(\mathbf{r}_1)\psi_{a\sigma}(\mathbf{r}_1)$$
$$\times \frac{\delta^2 E_{xc}}{\delta\rho_\sigma(\mathbf{r}_1)\delta\rho_\tau(\mathbf{r}_2)} \psi_{j\tau}(\mathbf{r}_2)\psi_{b\tau}^*(\mathbf{r}_2) d^3\mathbf{r}_1 d^3\mathbf{r}_2$$
$$+ K_{ia\sigma,jb\tau}^{HF}. \tag{13}$$

In Eq. (13), the first term of the right side is the Hartree integral,

$$(ia\sigma|jb\tau) = \int \int \psi_{i\sigma}^*(\mathbf{r}_1)\psi_{a\sigma}(\mathbf{r}_1)\frac{1}{r_{12}}$$
$$\times \psi_{j\tau}(\mathbf{r}_2)\psi_{b\tau}^*(\mathbf{r}_2) d^3\mathbf{r}_1 d^3\mathbf{r}_2, \tag{14}$$

J. Chem. Phys., Vol. 120, No. 18, 8 May 2004

Long-range-corrected TDDFT   8427

and $K^{HF}_{ia\sigma,bj\tau}$ is the mixed HF exchange integral term; for pure functionals, $K^{HF}_{ia\sigma,jb\tau}=0$, and for hybrid functionals (e.g., B3LYP[25]),

$$K^{HF}_{ia\sigma,jb\tau}=c_x\delta_{\sigma\tau}(ja\sigma|ib\tau), \tag{15}$$

where c_x is a constant mixing rate. TDDFT employing an LC exchange functional (LC-TDDFT) also gives a nonzero $K^{HF}_{ia\sigma,jb\tau}$ due to the long-range term in Eq. (9),

$$K^{HF}_{ia\sigma,jb\tau}=\delta_{\sigma\tau}\int\psi^*_{j\sigma}(\mathbf{r}_1)\psi^*_{a\sigma}(\mathbf{r}_2)\frac{\text{erf}(\mu r_{12})}{r_{12}}$$
$$\times\psi_{i\tau}(\mathbf{r}_1)\psi_{b\tau}(\mathbf{r}_2)d^3\mathbf{r}_1 d^3\mathbf{r}_2. \tag{16}$$

This $K_{ia\sigma,jb\tau}$ term brings nonzero off-diagonal elements into **A** and **B**.

The oscillator strength of the Ith excited state is generally defined as[1]

$$f_I=\tfrac{2}{3}(E_I-E_0)\sum_{\nu=x,y,z}|\langle\Psi_0|\mathbf{r}_\nu|\Psi_I\rangle|^2, \tag{17}$$

where Ψ_0 and Ψ_I are the wave functions of the ground and Ith excited states with the total energies, E_0 and E_I, respectively. In TDDFT, the oscillator strength is given by[1]

$$f_I=\tfrac{2}{3}\sum_{\nu=x,y,z}\left[\sum_{ia\sigma}d^\nu_{ia\sigma}(\epsilon_{a\sigma}-\epsilon_{i\sigma})^{1/2}F^I_{ia\sigma}\right]^2, \tag{18}$$

where $d^\nu_{ia\sigma}$ is the transition dipole moment,

$$d^\nu_{ia\sigma}=\int\psi_{i\sigma}(\mathbf{r})r_\nu\psi_{a\sigma}(\mathbf{r})d^3\mathbf{r}, \tag{19}$$

and $F^I_{ia\sigma}$ is the response function obtained by solving Eq. (10).

III. COMPUTATIONAL DETAILS

To assess LC-TDDFT, we calculated the excitation energies and oscillator strengths of five typical molecules (nitrogen, carbon monoxide, formaldehyde, ethylene, and benzene) and the charge-transfer excitation energy of ethylene–tetrafluoroethylene dimer. The calculations were carried out using the restricted Kohn–Sham (RKS)[26,27] and the restricted time-dependent Kohn–Sham (RTDKS).[1] In the RKS and RTDKS calculations, we used the following exchange-correlation functionals; Becke 1988 (B88) exchange[28] + one-parameter progressive (OP) correlation[29] (BOP), Perdew–Burke–Ernzerhof exchange[30] + OP correlation (PBEOP), B88 exchange + Lee–Yang–Parr correlation[31] (BLYP), and hybrid B3LYP,[25] functionals. The LC scheme was applied to the BOP (LC-BOP), PBEOP (LC-PBEOP), and BLYP (LC-BLYP) functional in both the RKS and RTDKS procedures. Besides the LC scheme, the AC scheme[14,15] was also adapted to the BOP functional (AC-BOP). Experimental geometries of molecules were used in the calculations of excitation energies and oscillator strengths. Only the geometry of ethylene–tetrafluoroethylene was optimized by using the RKS scheme. Augmented Sadlej pVTZ[32,33] and 6-31G*[34,35] Gaussian basis sets were employed for all constituent atoms in the calculations of typical molecules and ethylene–tetrafluoroethylene dimer, respec-

tively. All RKS and RTDKS calculations were carried out using the UTCHEM program.[36] To confirm the accuracy of LC-TDDFT, we also examined the *ab initio* symmetry adapted cluster configuration interaction (SAC-CI) method[37] with the same basis set using the GAUSSIAN 03 program,[38] except for the calculations of the charge-transfer excitation. In the SAC-CI calculations, the single- and double-R (SD-R) method was used to incorporate excitations up to doubles nonperturbatively.

IV. CALCULATIONS

We calculated the vertical excitation energies and oscillator strengths of N_2, CO, H_2CO, C_2H_4, and C_6H_6 molecules and the charge-transfer excitation energy of $C_2H_4-C_2F_4$ dimer by using a TDDFT scheme employing various types of exchange-correlation functionals.

A. Vertical excitation energies of typical molecules

Tables I–V summarize the calculated vertical excitation energies of N_2, CO, H_2CO, C_2H_4, and C_6H_6 molecules. As the tables indicate, the LC functionals (LC-BOP, LC-PBEOP, and LC-BLYP) obviously give more accurate Rydberg excitation energies, unlike the underestimates of pure functionals (BOP, PBEOP, and BLYP), regardless of functional or molecular species. The LC functionals also give accurate valence excitation energies. These schemes consequently reduce the total mean absolute deviations to half for these molecules. The tables also show that the AC scheme improves the excitation energies, although the accuracies of the calculated Rydberg excitation energies are not sufficient for C_2H_4 and C_6H_6. We should notice that this AC scheme provided much more accurate excitation energies for C_2H_4 and C_6H_6 with the mean absolute deviation of 0.06 and 0.12 eV, respectively, with the HCTH functional.[39,40] Conventional TDDFT studies have shown that pure functionals give accurate valence excitation energies and 1 to 2 eV lower Rydberg excitation energies. This conclusion is also supported by the present calculations of pure functionals. Compared with pure functionals, the hybrid B3LYP functional gives slightly worse valence excitation energies, but 0.5–1 eV better Rydberg excitation energies for all molecules. However, there is not much improvement in comparison with LC functionals. It is therefore confirmed that the accurate LC results may be due to the long-range correction rather than the hybridization of the HF exchange integral.

As a whole, the LC functionals gave the most accurate excitation energies. The AC-BOP functional also gave the comparable excitation energies. The Rydberg excitation energies of the LC and AC schemes were more accurate than the ones estimated by pure functionals, while they maintained the accuracy of the valence excitation energies.

B. Oscillator strengths of typical molecules

Tables I–V also show the calculated oscillator strengths (OS). These results should be discussed from the viewpoints of magnitude and order of magnitude.

For the N_2 molecule, only LC functionals (LC-BOP, LC-PBEOP, and LC-BLYP) give the same first digit as the experimental value, while pure functionals (BOP, PBEOP, and

TABLE I. Vertical excitation energies and oscillator strengths of N_2 molecule as calculated by TDDFT. Calculated SAC-CI and experimental results are also shown for comparison. An augmented Sadlej pVTZ basis set was employed in all calculations.

State	Transition	LC-BOP	BOP	AC-BOP	LC-PBEOP	PBEOP	LC-BLYP	BLYP	B3LYP	SAC-CI	Expt.
				Valence excitation energies (eV)							
$^3\Sigma_u^+$	$\pi_u \to \pi_g$	7.37	7.55	7.61	7.41	7.62	7.25	7.44	7.03	7.86	7.75
$^3\Pi_g$	$\sigma_g \to \pi_g$	7.79	7.50	7.55	7.78	7.50	7.70	7.41	7.54	8.36	8.04
$^3\Delta_u$	$\pi_u \to \pi_g$	8.29	8.35	8.43	8.32	8.42	8.15	8.22	7.96	9.15	8.88
$^1\Pi_g$	$\sigma_g \to \pi_g$	9.35	9.07	9.19	9.34	9.06	9.33	9.06	9.24	9.69	9.31
$^3\Sigma_u^-$	$\pi_u \to \pi_g$	9.34	9.59	9.68	9.34	9.58	9.30	9.55	9.31	10.06	9.67
$^1\Sigma_u^-$	$\pi_u \to \pi_g$	9.34	9.59	10.02	9.34	9.58	9.30	9.55	9.31	10.27	9.92
$^1\Delta_u$	$\pi_u \to \pi_g$	9.86	9.89	10.02	9.89	9.93	9.83	9.85	9.72	10.71	10.27
$^3\Pi_u$	$\sigma_u \to \pi_g$	10.79	10.27	10.58	10.77	10.33	10.64	10.31	10.62	11.59	11.19
				Rydberg excitation energies (eV)							
$^3\Sigma_g^+$	$\sigma_g \to 3s\sigma_g$	11.17	9.97	11.16	11.14	9.92	11.13	10.00	10.62	12.17	12.00
$^1\Sigma_g^+$	$\sigma_g \to 3s\sigma_g$	11.59	10.09	11.42	11.57	10.10	11.56	10.14	11.18	12.53	12.20
$^1\Pi_u$	$\sigma_g \to 3p\pi_u$	12.07	10.27	11.98	12.05	10.34	12.06	10.35	11.55	13.14	12.90
$^1\Sigma_u^+$	$\sigma_g \to 3p\sigma_u$	12.11	10.26	12.18	12.09	10.33	12.12	10.34	11.53	13.24	12.98
				Mean absolute deviations of excitation energies (eV)							
Valence		0.37	0.40	0.27	0.36	0.38	0.45	0.46	0.54	0.33	⋯
Rydberg		0.78	2.37	0.84	0.81	2.35	0.81	2.31	1.30	0.25	⋯
Total		0.51	1.06	0.46	0.51	1.03	0.57	1.07	0.79	0.30	⋯
				Oscillator strengths ($\times 10^{-2}$)							
$^1\Pi_u$	$\sigma_g \to 3p\pi_u$	11.90	0.28	2.02	11.71	0.51	13.47	0.39	1.33	8.14	24.3
$^1\Sigma_u^+$	$\sigma_g \to 3p\sigma_u$	25.90	0.69	6.07	25.69	1.14	28.63	0.94	3.84	15.67	27.9

BLYP) provide values that are mostly two orders of magnitude lower than the actual ones. Although the AC scheme has a positive effect on the calculated OSs in comparison with BOP results, these values are still one order of magnitude lower values than the experimental ones. The B3LYP functional estimates even smaller OSs. The order of OS is reproduced by all functionals.

LC functionals also give the most accurate OSs of the CO molecule. Other functionals give much smaller OSs. B3LYP gives the second-best OS, one larger than those of the pure functionals. AC-BOP gives slightly smaller OSs than BOP does. There is no experimental data for the order of OS. Compared with the SAC-CI result, only LC and AC-BOP results have the same order of magnitude.

TABLE II. Vertical excitation energies and oscillator strengths of CO molecule as calculated by TDDFT. Calculated SAC-CI and experimental results are also shown for comparison. An augmented Sadlej pVTZ basis set was employed in all calculations.

State	Transition	LC-BOP	BOP	AC-BOP	LC-PBEOP	PBEOP	LC-BLYP	BLYP	B3LYP	SAC-CI	Expt.
				Valence excitation energies (eV)							
$^3\Pi$	$\sigma \to \pi^*$	6.07	5.94	6.00	6.06	5.94	5.94	5.81	5.84	6.50	6.32
$^1\Pi$	$\sigma \to \pi^*$	8.44	8.25	8.45	8.43	8.22	8.43	8.23	8.39	8.95	8.51
$^3\Sigma^+$	$\pi \to \pi^*$	8.20	8.15	8.25	8.23	8.19	8.12	8.06	7.90	8.56	8.51
$^3\Delta$	$\pi \to \pi^*$	8.93	8.78	8.90	8.95	8.83	8.82	8.68	8.63	9.48	9.36
$^1\Sigma^-$	$\pi \to \pi^*$	9.77	9.79	9.92	9.77	9.77	9.74	9.75	9.70	10.29	9.88
$^3\Sigma^-$	$\pi \to \pi^*$	9.77	9.79	9.92	9.77	9.77	9.74	9.75	9.70	9.48	9.88
$^1\Delta$	$\pi \to \pi^*$	10.20	10.02	10.20	10.21	9.99	10.18	10.00	10.03	10.48	10.23
				Rydberg excitation energies (eV)							
$^3\Sigma^+$	$\sigma \to 3s$	9.82	8.73	9.66	8.95	8.67	9.80	8.75	9.51	10.66	10.40
$^1\Sigma^+$	$\sigma \to 3s$	10.30	8.88	9.95	10.28	8.87	10.28	8.92	9.79	11.13	10.78
$^3\Sigma^+$	$\sigma \to 3p\sigma$	10.65	9.30	10.71	9.79	8.83	10.64	9.36	10.19	11.56	11.30
$^1\Sigma^+$	$\sigma \to 3p\sigma$	10.76	9.34	10.83	10.73	9.35	10.73	9.37	10.23	11.70	11.40
$^1\Pi$	$\sigma \to 3p\pi$	10.86	9.42	10.62	10.83	9.42	10.85	9.46	10.31	11.83	11.53
$^3\Pi$	$\sigma \to 3p\pi$	10.74	9.35	10.54	10.72	9.35	10.77	9.41	10.27	11.70	11.55
$^1\Sigma^+$	$\sigma \to 3d\sigma$	11.76	9.94	11.51	11.73	10.00	11.79	10.00	10.96	12.70	12.40
				Mean absolute deviations of excitation energies (eV)							
Valence		0.19	0.28	0.17	0.18	0.28	0.25	0.35	0.36	0.26	⋯
Rydberg		0.64	2.06	0.79	0.91	2.12	0.64	2.01	1.16	0.27	⋯
Total		0.41	1.17	0.48	0.54	1.20	0.45	1.18	0.76	0.27	⋯
				Oscillator strengths ($\times 10^{-2}$)							
$^1\Pi$	$\sigma \to \pi^*$	19.92	8.66	6.68	20.02	8.87	20.20	8.78	11.24	9.63	17.6
$^1\Sigma^+$	$\sigma \to 3s$	2.45	0.00	0.35	2.40	0.00	1.82	0.00	0.06	1.16	⋯
$^1\Sigma^+$	$\sigma \to 3p\sigma$	15.13	4.06	4.69	15.15	4.68	17.25	4.68	7.12	11.15	⋯
$^1\Pi$	$\sigma \to 3p\pi$	4.07	0.47	1.70	4.04	0.58	4.56	0.61	1.39	2.46	⋯
$^1\Sigma^+$	$\sigma \to 3d\sigma$	0.67	0.42	0.16	0.63	0.29	0.67	0.44	0.49	0.31	⋯

TABLE III. Vertical excitation energies and oscillator strengths of H_2CO molecule as calculated by TDDFT. Calculated SAC-CI and experimental results are also shown for comparison. An augmented Sadlej pVTZ basis set was employed in all calculations.

State	Transition	LC-BOP	BOP	AC-BOP	LC-PBEOP	PBEOP	LC-BLYP	BLYP	B3LYP	SAC-CI	Expt.
					Valence excitation energies (eV)						
$^3A_2$	$n \to \pi^*$	3.15	3.20	3.26	3.13	3.15	3.06	3.12	3.19	3.65	3.50
$^1A_2$	$n \to \pi^*$	3.82	3.86	3.94	3.81	3.80	3.78	3.82	3.92	4.13	3.94
$^3A_1$	$\pi \to \pi^*$	5.82	5.92	5.97	5.84	5.98	5.70	5.81	5.46	6.12	5.53
$^1B_1$	$\sigma \to \pi^*$	9.11	8.84	8.96	9.10	8.81	9.07	8.80	9.03	9.56	8.68
					Rydberg excitation energies (eV)						
$^3B_2$	$n \to 3sa_1$	6.60	5.57	6.50	6.57	5.47	6.50	5.53	6.28	7.10	6.83
$^1B_2$	$n \to 3sa_1$	6.74	5.66	6.62	6.71	5.57	6.63	5.61	6.40	7.26	7.09
$^3A_1$	$n \to 3pb_2$	7.47	6.26	7.37	7.44	6.21	7.44	6.28	7.10	8.03	7.79
$^3B_2$	$n \to 3pa_1$	7.32	6.26	7.29	7.30	6.26	7.24	6.28	7.07	7.92	7.96
$^1A_1$	$n \to 3pb_2$	7.57	6.31	7.45	7.54	6.28	7.52	6.32	7.16	8.12	7.97
$^1B_2$	$n \to 3pa_1$	7.48	6.32	7.41	7.45	6.32	7.40	6.32	7.14	8.08	8.12
$^1A_2$	$n \to 3pb_1$	7.72	6.57	7.52	7.69	6.53	7.69	6.59	7.41	8.34	8.38
$^1A_2$	$n \to 3db_1$	8.70	7.16	8.50	8.67	7.20	8.73	7.20	8.11	9.32	9.22
					Mean absolute deviations of excitation energies (eV)						
Valence		0.30	0.23	0.24	0.31	0.26	0.29	0.23	0.19	0.45	$\cdots$
Rydberg		0.47	1.66	0.59	0.50	1.69	0.53	1.65	0.84	0.13	$\cdots$
Total		0.41	1.18	0.47	0.44	1.22	0.45	1.18	0.62	0.24	$\cdots$
					Oscillator strengths ($\times 10^{-2}$)						
$^1B_2$	$n \to 3sa_1$	0.08	0.04	0.06	0.08	0.04	0.07	0.04	0.05	0.06	2.8,3.2,3.8,4.13
$^1A_1$	$n \to 3pb_2$	2.21	1.68	1.02	2.20	1.91	2.17	1.95	2.71	1.88	3.2,3.6,3.8,6.05
$^1B_2$	$n \to 3pa_1$	7.17	2.11	2.62	7.17	2.46	7.81	2.49	3.64	4.26	1.7,1.9,1.7,2.81
$^1B_1$	$\sigma \to \pi^*$	6.69	1.75	2.42	6.68	1.57	7.16	1.73	2.32	2.95	$\cdots$

An experiment reported that OS of H_2CO molecule is smaller for the $^1B_2$ ($n \to 3pa_1$) excitation than for the $^1B_2$ ($n \to 3sa_1$) excitation. However, the order of these OSs is not reflected by recent *ab initio* calculations of the multiconfigurational self-consistent-field (SCF), multireference configuration interaction (CI) singles and doubles, complete active-space SCF, generalized valence bond CI, or equation of motion methods.[41] We confirm as such with the present SAC-CI calculation. This order of OS is reproduced only by LC and AC-BOP functionals.

TABLE IV. Vertical excitation energies and oscillator strengths of C_2H_4 molecule as calculated by TDDFT. Calculated SAC-CI and experimental results are also shown for comparison. An augmented Sadlej pVTZ basis set was employed in all calculations.

State	Transition	LC-BOP	BOP	AC-BOP	LC-PBEOP	PBEOP	LC-BLYP	BLYP	B3LYP	SAC-CI	Expt.
					Valence excitation energies (eV)						
$^3B_{1u}$	$\pi \to \pi^*$	4.18	4.41	4.50	4.19	4.47	4.08	4.32	4.07	4.49	4.36
$^1B_{1u}$	$\pi \to \pi^*$	7.56	7.11	7.66	7.56	7.10	7.52	7.11	7.35	8.05	8.00
					Rydberg excitation energies (eV)						
$^3B_{3u}$	$\pi \to 3s$	7.01	6.14	6.64	7.00	6.07	6.93	6.12	6.49	7.24	6.98
$^1B_{3u}$	$\pi \to 3s$	7.13	6.20	6.76	7.13	6.15	7.04	6.17	6.56	7.36	7.11
$^3B_{1g}$	$\pi \to 3p\sigma$	7.43	6.62	7.22	7.41	6.59	7.32	6.62	7.04	7.96	7.79
$^1B_{1g}$	$\pi \to 3p\sigma$	7.74	6.64	7.29	7.73	6.62	7.67	6.63	7.07	8.00	7.80
$^1B_{2g}$	$\pi \to 3p\sigma$	7.86	6.64	7.35	7.86	6.62	7.79	6.63	7.09	8.09	7.90
^3A_g	$\pi \to 3p\pi$	7.92	6.81	7.48	7.91	6.79	7.95	6.87	7.31	8.20	8.15
^1A_g	$\pi \to 3p\pi$	8.10	6.89	7.64	8.10	6.89	8.11	6.93	7.39	8.38	8.28
$^3B_{3u}$	$\pi \to 3d\sigma$	8.51	6.70	8.03	8.50	6.81	8.49	6.75	7.40	8.84	8.57
$^1B_{3u}$	$\pi \to 3d\sigma$	8.56	7.18	8.06	8.55	7.23	8.53	7.22	7.76	8.87	8.62
$^1B_{3u}$	$\pi \to 3d\delta$	8.76	6.73	8.25	8.75	6.83	8.78	6.77	7.42	9.10	8.90
$^1B_{2u}$	$\pi \to 3d\delta$	8.77	7.26	8.27	8.77	7.31	8.80	7.32	7.85	9.04	9.05
$^1B_{1u}$	$\pi \to 3d\pi$	9.05	7.72	8.57	9.04	7.74	9.10	7.74	8.14	9.37	9.33
					Mean absolute deviations of excitation energies (eV)						
Valence		0.31	0.47	0.24	0.30	0.50	0.38	0.46	0.47	0.09	$\cdots$
Rydberg		0.15	1.41	0.58	0.15	1.40	0.16	1.39	0.92	0.17	$\cdots$
Total		0.17	1.28	0.53	0.17	1.27	0.20	1.26	0.85	0.15	$\cdots$
					Oscillator strengths ($\times 10^{-2}$)						
$^1B_{1u}$	$\pi \to \pi^*$	75.43	12.85	24.41	75.25	14.64	75.45	15.56	34.67	37.31	29
$^1B_{3u}$	$\pi \to 3s$	13.05	3.49	4.77	12.96	4.54	13.23	4.29	6.75	8.07	4
$^1B_{3u}$	$\pi \to 3d\sigma$	0.42	0.06	0.00	0.42	0.15	0.76	0.09	0.29	0.19	$\cdots$
$^1B_{3u}$	$\pi \to 3d\delta$	7.35	2.25	1.92	7.29	1.51	7.77	1.67	1.26	5.37	$\cdots$
$^1B_{2u}$	$\pi \to 3d\delta$	4.26	0.79	1.34	4.25	0.97	4.96	0.94	1.42	2.89	$\cdots$
$^1B_{1u}$	$\pi \to 3d\pi$	6.15	18.45	6.64	6.31	16.51	6.46	15.64	9.41	4.10	$\cdots$

For C_2H_4, the experimental order of OS is attained by all functionals. The OS of the valence $^1B_{1u}$ ($\pi \rightarrow \pi^*$) excitation is underestimated by pure functionals and is significantly overestimated by LC functionals. The failure of LC functionals may be due to the character of molecular orbitals that was erroneously identified by LC functionals. LC functionals also significantly overestimate the OS of the Rydberg $^1B_{3u}$ ($\pi \rightarrow 3s$) excitation. Except for Rydberg $^1B_{1u}$ and $^1B_{3u}$ excitations, there are no other experimental OS values for these excitations. Only LC functionals give the same order of OSs as the SAC-CI results. LC functionals also give the closest OSs to the SAC-CI values.

Finally, the experimental OS of C_6H_6 are known only for the $1\,^1E_{1u}$ ($\pi \rightarrow \pi^*$) state. Five types of OS have been suggested for this state, and except for LC and SAC-CI values, all calculated OSs are half the experimental values. Only LC functionals give OSs close to the largest experimental value. This may indicate that the underestimated OS of $1E_{1u}$ state is attributable to the lack of the long-range exchange interaction between the corresponding π and π^* orbitals. LC functionals give the different order of magnitude for $1\,^1A_{2u}$ and $2\,^1E_{1u}$ states in comparison with the SAC-CI results. However, this order of the present SAC-CI calculation disagrees with the past SAC-CI result.[42] There is a room for further investigation.

Overall, it was found that LC functionals give the most accurate OS of all DFT calculations except for C_2H_4. As is well-known in TDDFT studies, pure functionals (BOP, PBEOP, and BLYP) underestimate OS. AC-BOP and B3LYP somewhat improved the OS estimate of BOP. The experimental order of OS was correctly given by only LC and AC-BOP functionals. No functionals gave the same orders of OSs as the SAC-CI results for all molecules. The LC results have two different orders for the $^1\Pi$ ($\sigma \rightarrow \pi^*$) and $^1\Sigma^+$ ($\sigma \rightarrow 3p\sigma$) excitations of the CO molecule and the $1\,^1A_{2u}$ ($\pi \rightarrow 3p\sigma$) and $2\,^1E_{1u}$ ($\pi \rightarrow 3p\pi$) of the C_6H_6 molecule. The AC-BOP results have three different orders (one for the excitations of CO and two for those of C_2H_4). It is therefore concluded that the LC scheme is one of the most effective to improve OS obtained by a pure functional, provided appropriate molecular orbitals are given in Kohn–Sham calculations.

C. Charge-transfer excitation energy of ethylene–tetrafluoroethylene dimer

Following the study of Dreuw *et al.*,[16] we calculated the lowest charge-transfer (CT) excitation energy of C_2H_4–C_2F_4 dimer by using various functionals while increasing the intermolecular distance (R) as displayed in Fig. 1 and Table VI. The results of the time-dependent HF and high-level *ab initio* SAC-CI calculations are also shown for comparison.

In Fig. 1, calculated lowest CT excitation energies, ω_{CT}, are plotted by setting the excitation energy at 5.0 Å to zero for each method. The figure shows that LC functionals (LC-BOP, LC-PBEOP, and LC-BLYP) give the correct long-range behavior of CT excitation energies in agreement with the behavior of the SAC-CI energy for the long intramolecular distance (R). Calculated ω_{CT} values of LC functionals
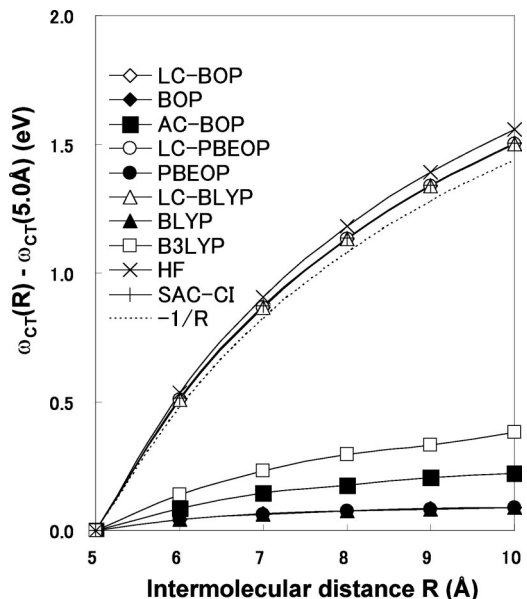

FIG. 1. The lowest charge transfer excitation energy of ethylene–tetrafluoroethylene dimer for the long intermolecular distance calculated by TDDFT employing various types of functionals. For all methods, the excitation energy at 5.0 Å is set to zero. The curve obtained by the time-dependent Hartree–Fock calculations is also shown for comparison.

clearly satisfy the far-nucleus asymptotic relation ($R > 5.0$ Å),[16]

$$\omega_{CT}(R) - \omega_{CT}(5.0 \text{ Å}) \gtrsim -\frac{1}{R} + \frac{1}{5.0 \text{ Å}}. \tag{20}$$

Equation (20) is derived from the relation for the long-range CT excitation energy,

$$\lim_{R \rightarrow \infty} \omega_{CT}(R) = -\frac{1}{R} + IP_D - EA_A, \tag{21}$$

where IP_D is the ionization potential of donor and EA_A is the electron affinity of acceptor. For large R and R_0, ω_{CT}, therefore, satisfies

$$\omega_{CT}(R) - \omega_{CT}(R_0) \approx -\frac{1}{R} + \frac{1}{R_0}. \tag{22}$$

Actually, the left-hand side of Eq. (22) is slightly larger than the right-hand side, because the orbital–orbital interaction decreases the CT excitation energy as the electron-donating and electron-accepting orbitals come close to each other. Since LC functionals reproduce the long-range behavior of the SAC-CI energy in addition to satisfying Eq. (20), it is presumed that these functionals may give a well-balanced electron correlation for such a separated molecule. B3LYP increases the CT excitation energy as about $-0.2/R$ + const., while the mixing rate of the HF exchange integral, c_x in Eq. (15), is 0.2 in this functional. For other functionals including AC-BOP, it is found that the calculated CT excitation energies hardly change for large R. Dreuw *et al.* concluded that the poor long-range CT excitation energy is due to the lack of the exchange interaction between the electron-donating and electron-accepting orbitals.[16] This figure also supports this conclusion. We, therefore, conclude that the LC

TABLE V. Vertical excitation energies and oscillator strengths of C_6H_6 molecule as calculated by TDDFT. Calculated SAC-CI and experimental results are also shown for comparison. An augmented Sadlej pVTZ basis set was employed in all calculations.

State	Transition	LC-BOP	BOP	AC-BOP	LC-PBEOP	PBEOP	LC-BLYP	BLYP	B3LYP	SAC-CI	Expt.
				Valence excitation energies (eV)							
$1\,^3B_{1u}$	$\pi \to \pi^*$	3.73	4.08	4.10	3.76	4.13	3.64	4.01	3.75	4.03	3.94
$1\,^3E_{1u}$	$\pi \to \pi^*$	4.80	4.62	4.65	4.81	4.63	4.76	4.58	4.65	4.81	4.76
$1\,^1B_{2u}$	$\pi \to \pi^*$	5.39	5.16	5.23	5.39	5.16	5.38	5.15	5.34	5.16	4.90
$1\,^3B_{2u}$	$\pi \to \pi^*$	5.03	4.90	4.97	5.03	4.90	4.99	4.87	5.01	5.69	5.60
$1\,^1B_{1u}$	$\pi \to \pi^*$	6.21	5.88	6.00	6.22	5.88	6.20	5.85	6.00	6.37	6.20
$1\,^1E_{1u}$	$\pi \to \pi^*$	7.00	6.80	6.94	7.00	6.78	6.97	6.77	6.96	7.65	6.94
				Rydberg excitation energies (eV)							
$1\,^1E_{1g}$	$\pi \to 3s$	6.70	5.60	5.69	6.70	5.52	6.60	5.53	5.94	6.55	6.33
$1\,^1A_{2u}$	$\pi \to 3p\sigma$	7.17	6.04	6.18	7.16	6.00	7.10	6.01	6.42	7.12	6.93
$1\,^1E_{2u}$	$\pi \to 3p\sigma$	7.32	6.04	6.16	7.31	5.99	7.25	6.00	6.44	7.19	6.95
$2\,^1E_{1u}$	$\pi \to 3p\pi$	7.46	6.28	6.21	7.45	6.26	7.43	6.28	6.67	7.11	7.41
$1\,^1B_{1g}$	$\pi \to 3d\sigma$	7.93	6.49	6.69	7.92	6.51	7.89	6.49	6.97	7.75	7.46
$1\,^1B_{2g}$	$\pi \to 3d\sigma$	7.94	6.48	6.69	7.89	6.50	7.86	6.48	6.96	7.74	7.46
$2\,^1E_{1g}$	$\pi \to 3d\delta$	7.70	6.49	6.69	7.93	6.51	7.90	6.49	6.97	7.61	7.54
$1\,^1E_{2g}$	$\pi \to 3d\pi$	8.06	6.70	6.80	8.05	6.74	8.07	6.73	7.19	7.92	7.81
$2\,^1A_{1g}$	$\pi \to 3d\pi$	8.04	6.72	6.85	8.03	6.76	8.06	6.76	7.21	7.94	7.81
$1\,^1A_{2g}$	$\pi \to 3d\pi$	8.13	6.72	6.81	8.12	6.75	8.14	6.76	7.22	7.96	7.81
				Mean absolute deviations of excitation energies (eV)							
Valence		0.23	0.28	0.24	0.23	0.30	0.24	0.29	0.26	0.23	⋯
Rydberg		0.29	0.99	0.87	0.31	1.00	0.28	1.00	0.55	0.20	⋯
Total		0.27	0.73	0.64	0.28	0.73	0.26	0.73	0.44	0.21	⋯
				Oscillator strengths ($\times 10^{-2}$)							
$1\,^1A_{2u}$	$\pi \to 3p\sigma$	11.36	3.01	2.78	11.28	3.68	12.26	3.48	5.24	4.60	⋯
$1\,^1E_{1u}$	$\pi \to \pi^*$	137.42	49.71	48.59	136.96	48.42	137.70	48.64	58.31	70.39	125,120,88,86,90.0,95.3
$2\,^1E_{1u}$	$\pi \to 3p\pi$	7.71	5.05	2.99	8.22	6.02	7.32	5.88	18.55	13.92	⋯

scheme sufficiently recovers the long-range exchange interaction that is neglected in pure exchange functionals and consequently improves on the poor CT excitation energy estimate of conventional TDDFT.

Table VI summarizes the calculated lowest CT excitation energies. The table shows that LC functionals estimate 1.5–2 times the excitation energies obtained by pure (BOP, PBEOP, and BLYP), AC-BOP and B3LYP functionals even at $R = 5.0$ Å. To assess the calculated CT excitation energies, the CT energy at the limit of $R \to \infty$ (c_0) was evaluated for each method by fitting $\omega_{CT}(R) = c_0 - c_1/R$ into the energy curve for $R = 5.0$–10.0 Å. The c_0 and c_1 values are summarized in Table VI. The table shows that only LC functionals give

correct c_0 values in suit with the experimental value (12.5 eV),[43] which was estimated by Eq. (21) employing the experimental IP of C_2F_4 (10.7 eV)[44] and EA of C_2H_4 (-1.8 eV).[45] Although the HF and SAC-CI methods also provided large excitation energies, the limit energies of these methods are 2 to 3 eV larger than the experimental energy. The validity of LC functionals was supported by the c_1 values that reproduce the theoretical value ($\gtrsim 1$ a.u.). The table also displays the energy difference ($\Delta\epsilon$) between the electron-donating orbital of C_2F_4 and the electron-accepting orbital of C_2H_4. This $\Delta\epsilon$ also indicates the CT excitation energy limit at $R \to \infty$ for each method due to Eq. (21). Since $\Delta\epsilon$ and c_0 values are close to each other except for AC-BOP

TABLE VI. The lowest charge-transfer excitation energy of C_2H_4–C_2F_4 dimer in eV for long intramolecular distances (R) in Å as calculated by TDDFT. Calculated TDHF and SAC-CI results are also shown for comparison. An 6-31G* basis set was employed in all calculations.

R	LC-BOP	BOP	AC-BOP	LC-PBEOP	PBEOP	LC-BLYP	BLYP	B3LYP	HF	SAC-CI	Expt.
5.00	9.48	5.21	5.42	9.44	5.15	9.44	5.18	6.73	12.65	11.49	⋯
6.00	9.98	5.25	5.51	9.95	5.19	9.95	5.22	6.87	13.19	12.00	⋯
7.00	10.34	5.28	5.57	10.31	5.21	10.31	5.24	6.96	13.56	12.36	⋯
8.00	10.61	5.29	5.59	10.58	5.23	10.57	5.25	7.03	13.83	12.63	⋯
9.00	10.82	5.30	5.62	10.78	5.23	10.78	5.26	7.06	14.04	12.83	⋯
10.00	10.98	5.30	5.64	10.95	5.24	10.94	5.27	7.11	14.21	12.99	⋯
∞ $(=c_0)^a$	12.49	5.40	5.87	12.45	5.33	12.45	5.36	7.49	15.78	14.50	12.5[b]
c_1 (a.u.)[c]	1.04	0.06	0.16	1.04	0.06	1.04	0.06	0.26	1.08	1.04	$\gtrsim 1$
$\Delta\epsilon^d$	12.43	5.32	5.43	12.40	5.25	12.43	5.28	7.42	15.67	14.43	12.5[b]

[a]The charge-transfer excitation energy at the limit of $R \to \infty$ in eV, which was estimated by fitting the function, $f = c_0 - c_1/R$, into the excitation energy curve.
[b]This experimental value was estimated by using the vertical ionization potential of C_2F_4 (10.7 eV) and electron affinity of C_2H_4 (-1.8 eV).
[c]The value c_1 in a.u., which was obtained in a.
[d]The energy difference between the electron-donating orbital of C_2F_4 and the electron-accepting orbital of C_2H_4. The SAC-CI value was obtained by the calculation of C_2H_4–C_2F_4 at $R = 1000$ Å.

ones, the calculated $\Delta\epsilon$ values may support the above discussion about the CT excitation energy at $R\to\infty$. It is, therefore, concluded that the LC method corrects the long-range exchange part of pure functionals with maintaining the balance with the short-range part.

V. CONCLUSIONS

We applied the long-range correction (LC) scheme[17] to the time-dependent density functional theory (TDDFT),[1,2] and determined if it could overcome three of the severe problems with TDDFT calculations. The LC scheme modifies an exchange functional by combining the short-range part of exchange functional with the long-range part of the Hartree–Fock exchange integral.

First, the LC-TDDFT scheme was examined by calculating the excitation energies of typical molecules: Nitrogen, carbon monoxide, formaldehyde, ethylene, and benzene molecules. The LC scheme was applied to three types of pure generalized-gradient-approximation (GGA) exchange-correlation functionals including the Becke 1988 exchange +one-parameter progressive correlation (BOP) functional. As the result, we found that TDDFT employing these LC functionals gives accurate Rydberg excitation energies (within 0.5 eV of the measured values), while TDDFT using the BOP functional underestimates these energies by 1 to 2 eV. It should be noted that the accuracies of the calculated valence excitation energies were maintained after the correction. For comparison, the asymptotic correction scheme[14,15] was also applied to the BOP functional (AC-BOP). As a result, it was found that AC-BOP gives equivalent TDDFT excitation energies in comparison with the LC results. We also carried out TDDFT calculations with the hybrid B3LYP functional,[25] and found that the calculated results are inferior to the LC-BOP results for both valence and Rydberg excitation energies.

Next, the oscillator strengths of the above molecules were calculated by TDDFT employing LC functionals. As a result, we found that LC functionals recover the TDDFT oscillator strengths of the same order as the experimental values, while pure GGA functionals give values one or two orders lower for some molecules. Compared with the results of the *ab initio* SAC-CI method,[37] LC functionals gave the same order of calculated oscillator strengths for all molecules, except for two cases. Although AC-BOP also provided more accurate oscillator strengths than those of BOP, the order of the strengths disagreed with the SAC-CI one in three cases. B3LYP gave slightly more accurate oscillator strengths compared with BOP. However, the order differed with the SAC-CI order in many cases.

Finally, we applied the LC functionals to the TDDFT calculation of the charge-transfer (CT) excitation energy of ethylene–tetrafluoroethylene dimer. Dreuw *et al.*[16] suggested that the CT excitation energy of TDDFT should have the correct asymptotic behavior for the long intramolecular distance, Eq. (20). However, they also concluded that this behavior is not given even by using a far-nucleus asymptotic correction scheme. What we should notice is that LC functionals exactly recover the correct asymptotic behavior of the CT excitation energy in TDDFT, unlike AC-BOP. Although

B3LYP partially recovers this behavior, the improvement is in proportion to the mixing rate of the Hartree–Fock exchange integral. It was also found that LC functionals gives the correct CT excitation energy at the long-range limit, while even the SAC-CI method estimates 2 eV larger excitation energy. This may indicate that the LC scheme brings well-balanced short- and long-range exchange effects in exchange functionals.

As mentioned above, the LC scheme may be the first approach to have overcome three problems affecting TDDFT calculations: The underestimations of the Rydberg excitation energies, oscillator strengths, and charge-transfer excitation energies. It is, therefore, presumed that the poor results of TDDFT employing pure functionals may be due to the lack of a long-range orbital–orbital interaction in exchange functionals rather than a poor far-nucleus asymptotic behavior.

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