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Valence excitation energies of alkenes, carbonyl compounds, and azabenzenes by time-dependent density functional theory: Linear response of the ground state compared to collinear and noncollinear spin-flip TDDFT with the Tamm-Dancoff approximation

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Time-dependent density functional theory (TDDFT) holds great promise for studying photochemistry because of its affordable cost for large systems and for repeated calculations as required for direct dynamics. The chief obstacle is uncertain accuracy. There have been many validation studies, but there are also many formulations, and there have been few studies where several formulations were applied systematically to the same problems. Another issue, when TDDFT is applied with only a single exchange-correlation functional, is that errors in the functional may mask successes or failures of the formulation. Here, to try to sort out some of the issues, we apply eight formulations of adiabatic TDDFT to the first valence excitations of ten molecules with 18 density functionals of diverse types. The formulations examined are linear response from the ground state (LR-TDDFT), linear response from the ground state with the Tamm-Dancoff approximation (TDDFT-TDA), the original collinear spin-flip approximation with the Tamm-Dancoff (TD) approximation (SF1-TDDFT-TDA), the original noncollinear spin-flip approximation with the TDA approximation (SF1-NC-TDDFT-TDA), combined self-consistent-field (SCF) and collinear spin-flip calculations in the original spin-projected form (SF2-TDDFT-TDA) or non-spin-projected (NSF2-TDDFT-TDA), and combined SCF and noncollinear spin-flip calculations (SF2-NC-TDDFT-TDA and NSF2-NC-TDDFT-TDA). Comparing LR-TDDFT to TDDFT-TDA, we observed that the excitation energy is raised by the TDA; this brings the excitation energies underestimated by full linear response closer to experiment, but sometimes it makes the results worse. For ethylene and butadiene, the excitation energies are underestimated by LR-TDDFT, and the error becomes smaller making the TDA. Neither SF1-TDDFT-TDA nor SF2-TDDFT-TDA provides a lower mean unsigned error than LR-TDDFT or TDDFT-TDA. The comparison between collinear and noncollinear kernels shows that the noncollinear kernel drastically reduces the spin contamination in the systems considered here, and it makes the results more accurate than collinear spin-flip TDDFT for functionals with a low percentage of Hartree-Fock exchange and sometimes for functionals with a higher percentage of Hartree-Fock exchange, but it yields less accurate results than ground-state TDDFT. © 2013 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4798402>]

I. INTRODUCTION

Time-dependent density functional theory¹ (TDDFT) is a potentially transformative methodology for applications to electronic spectroscopy and photochemical dynamics due to the low computational cost of density functional calculations. Conventional TDDFT is based on the linear response (LR) of the ground state to a time-dependent perturbation and may be called LR-TDDFT. The Tamm-Dancoff approximation² (TDA) to TDDFT eliminates the coupling of the occupied–vacant to the vacant–occupied blocks in Casida’s equations,^{1,3} which reduces the instability near a conical intersection. With local exchange-correlation (xc) functionals, such as the local spin density approximation or the generalized gradient approximation (GGA), both LR-TDDFT and TDDFT-TDA suffer from inaccurate treatment of Rydberg excited states compared with valence excited states;^{4,5} this has been explained as arising from systematic errors in the position of the highest

occupied molecular orbital (HOMO) in the ground state when local functionals are employed.⁶

Another problematic issue for LR-TDDFT and the TDDFT-TDA is the description of doubly excited states. The correct description of doubly excited states would require a frequency-dependent xc functional,^{7,8} but most attempts to make TDDFT practical so far have used frequency-independent xc functionals, which is called the adiabatic approximation, and which allows one to use xc functionals that have already been heavily vetted for ground states. So called doubly excited states are known to play a prominent role in polyenes,^{9–12} which are very important in biochemistry and technology, but the nature of these states is now known to be more complicated than is implied by describing them as resulting from double excitations. Molecules for which doubly excited states are a low-energy excitation also have significant contributions from doubly excited configurations in the ground state, so that one should consider such molecules to be

examples of multireference states, where a single Slater determinant is not a good description even in the ground state. It has been suggested that a better description is that in exciting from the ground state to a so called doubly excited state, one switches from a wave function dominated by the Hartree–Fock determinant and one or more double excitations to another (orthogonal) linear combination with a larger weight on the double excitations.⁴

In LR-TDDFT, the reference state is the ground state, obtained by a restricted Kohn–Sham (RKS) calculation. One attempt to make TDDFT more accurate, especially for states with significant double excitation character, is called spin-flip TDDFT (SF-TDDFT). In this method, an unrestricted Kohn–Sham (UKS) spin state with higher multiplicity than the ground-state singlet is taken as a reference; in the cases of interest here this is a singly excited triplet state with $M_S = +1$, where M_S is the spin projection quantum number. One then calculates the “excitation” to both lower- and higher-energy states by spin flips, both with and without orbital excitations; one obtains the singlet ground state and both singly and doubly excited singlet and triplet states (only the $M_S = 0$ components of the latter) as a linear response of the triplet reference state. One advantage of spin-flip TDDFT is that it should be better for treating a system in which the HOMO and the lowest unoccupied molecular orbital are nearly degenerate.

A significant disadvantage of spin-flip TDDFT is that, just like ground-state TDDFT, it tends to generate a number of spurious low-energy states as well as the real low-energy states (this would not occur if one used the unknown, exact, nonadiabatic xc functional), and these spurious states make the state assignments difficult. Actually, it is not clear if one should call these spurious states or spuriously lowered states; we will use the former language for simplicity. Another problem, shared by all unrestricted Kohn–Sham methods,¹³ is that the calculated excited states are not eigenstates of the square \hat{S}^2 of the electron spin operator; rather they correspond to a mixture of the singlets and higher spin states. The restricted open-shell Kohn–Sham (ROKS) method is sometimes used to avoid this problem,¹⁴ but the ROKS equation is *ad hoc* and is often difficult to converge. An apparently better solution for this problem is the spin-adapted SF-TDDFT method sug-

gested by Liu *et al.*,^{15–17} although extra computational cost is required.

Our recent study of the performance of LR-TDDFT for various types of density functionals¹⁸ showed that for most functionals the performance for valence states is superior to that for Rydberg states; including the results by Caricato *et al.*,¹⁹ the average absolute error is 0.38 eV for valence states and 0.98 eV for Rydberg states for 56 density functionals. We also found that the best performing xc functionals are M06-2X and ω B97X-D (M06-2X is also seen to perform well on another database²⁰). We found that the most successful functionals overall have a relatively high percentage (about 40%) of Hartree-Fock exchange. The inclusion of a healthy amount of Hartree-Fock exchange often removes the spurious states.

The purpose of the present study is to explore seven additional formulations of the TDDFT method on some of the same molecules for which we previously studied LR-TDDFT to see if they offer any systematic improvement in accuracy. In particular, we compare results by LR-TDDFT to those by TDDFT-TDA, collinear spin-flip TDDFT-TDA, and noncollinear spin-flip TDDFT-TDA for the first valence excitation energies of alkenes, carbonyls, and azabenzenes. For the latter two methods we test the original spin-flip method, here called SF1, and we also test a scheme²¹ for combining spin-projected spin-flip TDDFT for states not well described by a single Slater determinant with self-consistent-field (SCF) calculations for states that are well described; this is called spin-flip method 2 (SF2). To gain insight we also test SF2 without the spin projection, which is called nonprojected SF2 or NSF2. The SF1 and NSF2 methods do not correct for spin contamination, but SF2 does.

With eight formulations of TDDFT under consideration, the names and even the abbreviations required to distinguish the formulations are rather long. Therefore, we introduce short names for the formulations in Table I, and we will use these in the rest of this article.

Here, we only test frequency-independent functionals. Since the unknown, exact, frequency-dependent xc functional for each case (singlet and triplet) would yield the correct excitation energies, this is, in principle, a test of the xc functionals rather than of the formulations of TDDFT. However, some ways of using TDDFT are less sensitive than others to

TABLE I. Abbreviations for formulations of TDDFT studied in this article.

Method	Long abbreviation	Short abbreviation ^a
Linear response from the ground state	LR-TDDFT	LR
Linear response from the ground state with Tamm-Dancoff approximation	TDDFT-TDA	TDA
Collinear spin-flip method with Tamm-Dancoff approximation ^b	SF1-TDDFT-TDA	SF1
Noncollinear spin-flip method with Tamm-Dancoff approximation ^b	SF1- NC-TDDFT-TDA	NC-SF1
Combined SCF and collinear spin-flip calculations ^c	SF2-C-TDDFT-TDA	SF2
Nonprojected combined SCF and collinear spin-flip calculations ^d	NSF2-C-TDDFT-TDA	NSF2
Combined SCF and noncollinear spin-flip calculations ^c	SF2-NC-TDDFT-TDA	NC-SF2
Nonprojected combined SCF and noncollinear spin-flip calculations ^d	NSF2-NC-TDDFT-TDA	NC-NSF2

^aWhen we use the abbreviation SF, it refers generically to SF1, SF2, and NSF2 or to elements that are the same in all three methods. Similarly, NC-SF refers generically to NC-SF1, NC-SF2, and NC-NSF2 or to elements that are the same in all three methods.

^bIn SF1 methods, the energy of S_0 is based on the $M_S = 0$ state generated by spin-flip excitation from T_1 .

^cIn SF2 methods, the energy of S_0 is based on the $M_S = 0$ RKS SCF ground state.

^dIn nonprojected SF2 methods; no projection procedure is employed in SF2 or NC-SF2.

the inexactness of the xc functionals, and some approximate functionals are more suitable than others for use with a given formulation; and these are additional issues about which the present tests reveal information.

II. THEORETICAL BACKGROUND

Throughout the article, we use the adiabatic approximation, which means that the exchange–correlation potential adjusts instantaneously to any change in the density.¹ A consequence of this approximation is that the density functional is independent of frequency, and we follow the usual procedure of using the approximate density functionals developed for ground-state calculations. To make the methods we employ clear, we first briefly review the key formulas.

First, we consider collinear unrestricted TDDFT. Let i, j denote occupied orbitals and a, b denote unoccupied orbitals, and let σ and τ represent spin components (α or β). In the LR approximation, the excitation energies ω are determined by first carrying out a SCF calculation on the ground state and then solving the LR equations derived by Casida:³

$$\begin{pmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B}^* & \mathbf{A}^* \end{pmatrix} \begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \end{pmatrix} = \omega \begin{pmatrix} \mathbf{1} & \mathbf{0} \\ \mathbf{0} & -\mathbf{1} \end{pmatrix} \begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \end{pmatrix}, \quad (1)$$

where \mathbf{A} is a matrix with elements $A_{a\sigma i\sigma', b\tau j\tau'}$ coupling a one-electron excitation $a\sigma \leftarrow i\sigma'$ to one-electron excitation $b\tau \leftarrow j\tau'$, \mathbf{B} is a matrix with elements coupling the excitation $a\sigma \leftarrow i\sigma'$ to the de-excitation $j\tau' \leftarrow b\tau$, and \mathbf{X} and \mathbf{Y} are vectors of excitation and de-excitation amplitudes, respectively, in particular, $X_{a\sigma i\sigma'}$ and $Y_{b\tau j\tau'}$. The matrix elements of \mathbf{B} are the same as those between the ground and doubly excited states,²² so the effect of nonzero \mathbf{B} is sometimes considered to account for correlation in the ground state.

In the Tamm–Dancoff approximation to LR,² all of the elements of matrix \mathbf{B} are set to zero, and the non-Hermitian eigenvalue equation (1) is reduced to the Hermitian eigenvalue equation:

$$\mathbf{A}\mathbf{X} = \omega\mathbf{X}. \quad (2)$$

The TDA is simpler (although computationally about the same cost as LR), yields a straightforward approximation to the excited-state density matrix, and is more stable for the calculation of potential energy surfaces.¹

The matrix elements of \mathbf{A} and \mathbf{B} are evaluated using the orbitals of a reference SCF state calculated by the UKS method, or—as a special case—the RKS method.

In the usual ground-state LR and TDA approximations, the orbitals come from a ground-state RKS self-consistent field calculation, and only the spin-conserving blocks ($\alpha\alpha$ and $\beta\beta$) of \mathbf{X} and \mathbf{Y} are allowed to be nonzero. Therefore, the spin component is conserved in the orbital excited, and one deals only with $M_S = 0$ states.

In spin-flip TDDFT–TDA, one starts (for the applications considered in the present article) with the $M_S = +1$ component of the lowest-energy triplet state, and only the $\alpha\beta$ and $\beta\alpha$ blocks of \mathbf{X} are considered, so the excitation always involves a change in the spin component. The calculated excitation energies correspond to transitions from a single $M_S = 1$ triplet state (T_1) to a set of states with $M_S = 0$; these final states in-

clude, in principal, the closed-shell ground state S_0 , the lowest excited singlet state S_1 , many other singlet states, and $M_S = 0$ components of triplet states. Due to the approximate nature of the available density functionals and to the adiabatic approximation, these states might be mixed; that is, the calculated final states might be linear combinations of more than one real state. Of special concern is that the calculated states might correspond to linear combinations of singlet and triplet states.

The matrix elements of \mathbf{A} are given in terms of the spin orbitals of the reference function by^{4,23–25}

$$A_{a\sigma i\sigma', b\tau j\tau'} = \delta_{\sigma\tau}\delta_{\sigma'\tau'} \left[\delta_{ij}\delta_{ab}(\varepsilon_{a\sigma} - \varepsilon_{i\sigma'}) + \delta_{\sigma\sigma'}\delta_{\tau\tau'} K_{ai,bj} - \frac{X}{100}(ij|ab) \right], \quad (3)$$

$$K_{ai,bj} = (ai|jb) + \left(1 - \frac{X}{100}\right)(ai|w|jb), \quad (4)$$

where $\varepsilon_{a\sigma}$ is the ground-state molecular orbital energy of orbital a with spin σ , (\dots) is a two-electron integral in the Mulliken notation, and ($\dots|w|\dots$) is a contribution from the exchange–correlation functional; note that the kernel of the integrals ($\dots|w|\dots$) contains the Hessian with respect to the spin densities of the exchange–correlation energy. We see that the $\sigma \neq \sigma'$ and $\tau \neq \tau'$ blocks of \mathbf{A} are nonzero only if the percentage X of Hartree–Fock exchange in the density functional employed is nonzero. Also note that the term involving the Hessian of the exchange–correlation energy does not contribute in the SF theory.

We will let E denote an energy calculated by a Kohn–Sham SCF calculation; $\omega(\text{VIU})$ will denote an energy difference of state V from a reference U as obtained directly from Eqs. (1) or (2), and ΔE will denote an approximation to the excitation energy from S_0 to S_1 .

In the present SF calculations, the reference state is always taken as the lowest triplet state ($\alpha\alpha, M_S = 1$). We estimate the excitation energy in three ways. The first way, called SF1, is the conventional method. In this method the energy difference between the singlet ground state S_0 and the singlet excited state S_1 is obtained as a linear response of the triplet state:

$$\Delta E^{\text{SF1}} = \omega(S_1|T_1) - \omega(S_0|T_1). \quad (5)$$

The second way of using SF–TDDFT, called NSF2 (nonprojected SF2), uses the difference in SCF energies to get the excitation energy of the triplet:

$$\Delta E^{\text{NSF2}} = \omega(S_1|T_1) - [E^{\text{UKS}}(S_0) - E^{\text{RKS}}(T_1)]. \quad (6)$$

In the third method, called SF2 and introduced previously,²¹ one uses Yamaguchi’s formula^{26–30} to correct for spin contamination of the excited singlet state:

$$\Delta E^{\text{SF2}} = \Delta E^{\text{NSF2}} - \left[\omega(S_1|T_1) - \frac{2(\omega(S_1|T_1))}{\langle S^2 \rangle_{T_1} - \langle S^2 \rangle_{S_1}} \right], \quad (7)$$

where $\langle S^2 \rangle$ denotes the expectation value of the spin operator \hat{S}^2 in the UKS reference T_1 state or the spin flip S_1 state. (We know that $\langle S^2 \rangle$ calculated using the Slater determinants

is not the same as its value for the real wave function,¹³ but we use it as an algorithmic tool to correct for spin contamination in the reference state; loosely speaking, this correction is called spin projection.) This correction for spin contamination is less complicated and less well justified than the symmetry-adapted approach of Liu *et al.*^{15–17} but it is simpler, and it has frequently been applied to transition metal systems.^{31–36} Note that if $\langle S^2 \rangle^{T_1}$ is 2 and $\langle S^2 \rangle^{S_1}$ is 0, then Eq. (7) reduces to Eq. (6). Very often though, $\langle S^2 \rangle^{S_1}$ is closer to 1, which means that the final state of the TDDFT calculation is a mixture of singlet and triplet, and Eq. (7) attempts to correct for that.

In noncollinear SF-TDDFT,³⁷ one still employs a collinear Slater determinant for the reference state, that is, every spin function in the reference state is either pure α or pure β , but one employs density functionals whose $(\dots|w|\dots)$ matrix elements (the noncollinear kernels) couple pure spin functions to noncollinear ones, that is, spin functions that are linear combinations of α and β .^{37,38}

III. COMPUTATIONAL DETAILS

The lowest singlet valence excited states are calculated for ten molecules, in particular, two alkenes: ethylene (D_{2h}) and *trans*-1,3-butadiene (C_{2h}), three carbonyls: formaldehyde (C_{2v}), acetaldehyde (C_s), and acetone (C_{2v}), and five azabenzenes: pyridine (C_{2v}), pyrazine (D_{2h}), pyrimidine (C_{2v}), pyrazine (C_{2v}), and symmetric tetrazine (D_{2h}), where the point group of the nuclear coordinates is given in parentheses. All geometries are optimized by MP2/6-311+G**. All excitation energies are calculated using the 6-311(2+,2+)G(d,p) basis set,³⁹ in which the angular momentum quantum numbers and exponential parameters of the additional diffuse subshells are s (H), 0.00108434; sp (C), 0.0131928; sp (O), 0.025451869; sp (N), 0.0192470. This is a well-balanced basis set for the description of either valence excitations or Rydberg excitations.⁴⁰

The reference values of the excitation energy are experimental values taken from the database of Caricato *et al.*¹⁹ We note a recent study⁴¹ that suggests that the correct value for the excitation energy of butadiene is 6.3 eV, not 5.9 eV, which is the experimental value of the peak in the absorption spectrum, but not necessarily the best estimate of the vertical excitation energy. Previously, the literature has used 5.9 eV as the standard, and we retain that value here for consistency with Refs. 18 and 19.

LR, TDA, and collinear spin-flip calculations are performed with the GAMESS⁴² software package and noncollinear spin-flip calculations are performed with the QCHEM⁴³ software package. In these packages Casida's equations are solved by the Davidson algorithm.²² The grid used for the numerical integration of the xc functional has 99 radial shells and 590 angular points per shell. The number of grid points is enough to avoid the numerical instability in noncollinear SF-TDDFT noted in previous work.³⁸

We test 18 density functionals. These are listed and explained in Table II.^{44–63} A key quantity in Table II is X , the percentage of Hartree-Fock exchange. Local density functionals have no Hartree-Fock exchange, and hybrid density functionals have finite X . Table II also lists the type of func-

TABLE II. Density functionals studied in this article.

Functional	Type	X^a	Reference(s)
BLYP	GGA	0	44 and 45
PW91	GGA	0	42
OLYP	GGA	0	43 and 44
revTPSS	Meta-GGA	0	46
B3LYP	Hybrid GGA	20	47 and 48
PBE0	Hybrid GGA	25	49
X3LYP	Hybrid GGA	21.8	50
M06	Hybrid meta-GGA	27	59
M05	Hybrid meta-GGA	28	57
BHHLYP	Hybrid GGA	50	44 and 45
M08-HX	Hybrid meta-GGA	52.23	61
M06-2X	Hybrid meta-GGA	54	59
M05-2X	Hybrid meta-GGA	56	58
M08-SO	Hybrid meta-GGA	56.79	61
CAM-B3LYP	Range-separated hybrid GGA ^b	19–65	52
ω B97X	Range-separated hybrid GGA ^b	15.77–100	53
M11	Range-separated hybrid GGA ^b	42.8–100	54
M06-HF	Hybrid meta-GGA	100	60

^a X is the percentage of Hartree-Fock exchange in the density functional.

^bA range-separated hybrid GGA might also be called a hybrid NGA (hybrid nonseparable gradient approximation).

tional. In a GGA, the density functional depends on electron density and electron density gradient. In the meta-GGAs in Table II, the density functional depends on electron density, electron density gradient, and kinetic energy density. In the range-separated density functionals, the interelectronic separation is divided smoothly into two ranges. In the spectroscopic context, the motivation for range separation is to use a larger percentage of Hartree-Fock exchange at long range in order to partially remedy the self-interaction error of a local density functional at large interelectronic separation and thereby reduce or eliminate the failures of local density functionals for long-range charge transfer excitations.^{4,56,64}

For noncollinear SF-TDDFT-TDA, we examined a smaller number of density functionals, in particular, BLYP, B3LYP, PBE0, ω B97X, M06, M06-2X, and M06-HF.

IV. RESULTS AND DISCUSSION

IV.A. Assignments

The excitations we study in this article are the lowest valence excitation of each of the ten organic molecules mentioned above. The assignments and state symmetries are as follows: B_{1u} ($\pi \rightarrow \pi^*$) for ethylene, B_u ($\pi \rightarrow \pi^*$) for *trans*-1,3-butadiene, A_2 ($n \rightarrow \pi^*$) for formaldehyde, A'' ($n \rightarrow \pi^*$) for acetaldehyde, $1A_2$ ($n \rightarrow \pi^*$) for acetone, B_1 ($n \rightarrow \pi^*$) for pyridine, $1B_{3u}$ ($n \rightarrow \pi^*$) for pyrazine, B_1 ($n \rightarrow \pi^*$) for pyrimidine, B_1 ($n \rightarrow \pi^*$) for pyridazine, and B_{3u} ($n \rightarrow \pi^*$) for s-tetrazine.

In the previous assessment¹⁸ of density functionals for LR calculations, we observed spurious low-energy states (or spuriously lowered real charge transfer states), especially for the local density functionals, and following Caricato *et al.*'s study,¹⁹ we checked the orbital shape for the valence states.

We found that making assignments based on orbital shape reduced the deviation from experiment, and we therefore chose to use this procedure for LR and TDA calculations in the present study as well. For the LR and TDA calculations, we do not find any spurious states for the first valence excitation for any of the molecules and density functionals we examined in this study; therefore, the lowest excitation energy corresponding to the irreducible representation of interest is selected for all excited states.

In SF-TDDFT (for the case that the reference state is a triplet, $|\alpha\alpha\rangle$), the states produced in the response include both singlets, $\frac{1}{\sqrt{2}}(|\alpha\beta\rangle - |\beta\alpha\rangle)$, and triplets, $\frac{1}{\sqrt{2}}(|\alpha\beta\rangle + |\beta\alpha\rangle)$, as well as mixed singlet-triplets, $|\alpha\beta\rangle$ and $|\beta\alpha\rangle$, where $M_S = 0$ for all states. We will simply consider any state with $\langle S^2 \rangle < 1$ to be an approximation to a singlet and any state with $\langle S^2 \rangle > 1$ to be an approximation to a triplet. Only the states with $\langle S^2 \rangle < 1$ should be considered in making assignments for the lowest excited singlet state. We next summarize the procedures used to assign the final states for spin-flip calculations by a collinear kernel.

The lowest B_{1u} state of ethylene has high spin contamination; $\langle S^2 \rangle$ is ~ 2.0 ; therefore, we regard this as a triplet, and the lowest singlet state is taken for all of the density functionals except for M11 and M06-HF. For these two functionals, $\langle S^2 \rangle$ of the lowest singlet state ($\langle S^2 \rangle < 1$) is more than twice as high as that of the next lowest singlet state, and the second lowest singlet state is chosen.

For most of the density functionals, $\langle S^2 \rangle$ is ~ 2.0 for the lowest spin-flip B_u state of butadiene; and the second as well as the third lowest spin-flip B_u states, although both singlets, are both characterized mainly as electron transitions from the second highest occupied α -orbital to the lowest unoccupied β -orbital and from highest occupied α -orbital to the third lowest unoccupied β -orbital or to an energetically higher β -orbital. Except for M08-HX, M08-SO, M11, and M06-HF, the lowest singlet B_u state of butadiene is chosen. For M08-HX, M08-SO, M11, and M06-HF, the second lowest singlet state is chosen because it has smaller spin contamination than the first one; $\langle S^2 \rangle$ is 0.49, 0.54, 0.36, and 0.50 for the second lowest state against 0.70, 0.64, 0.94, 0.91 for the lowest state. As a consequence, the error of the S_0 - S_1 excitation energy estimated by the conventional way (SF1) is lower for M08-HX and M11, but is higher for M08-SO and M06-HF compared with the choice of the lowest singlet state.

For spin-flip calculations on all carbonyl compounds (formaldehyde, acetaldehyde, and acetone), the lowest singlet state shows the minimum $\langle S^2 \rangle$ value for the irreducible representation of interest (A_2 for formaldehyde, A'' for acetaldehyde, and A_2 for acetone) for all of the density functionals. The lowest state of these irreducible representations is triplet for all cases. The electronic transition from the reference triplet state to the lowest singlet state of each irreducible representation is strongly characterized by the spin-flip electron transition within the lowest singly occupied molecular orbital for density functionals with 50% or lower Hartree-Fock exchange (B3LYP, X3LYP, PBE0, M06, M05, and BHLYP); on the other hand, the contributions of the other orbitals increase for the density functionals with higher percentages of Hartree-Fock exchange.

For spin-flip calculations on all azabenzenes, the lowest calculated singlet state is assigned as the first singlet excited state; in every case there is a triplet below this.

IV.B. Criteria for success

In our previous article, we classified density functionals with mean unsigned errors (MUEs) of 0.30 eV or less as successful and those with MUEs in the range 0.31–0.36 eV as moderately successful. To make it easier to spot trends in tables, in the present article we place density functionals and their MUEs in bold font if they correspond to a MUE of 0.36 eV or smaller for that table.

IV.C. LR and TDA

Table III shows the first valence excitation energy calculated by LR, and Table IV shows the results for TDA. For the ethylene molecule, all of the density functionals give an excitation energy lower than the experimental one, 7.65 eV, and TDA gives a larger value than LR by ~ 0.90 eV except for M05-2X. This trend is observed for all density functionals and molecules except for *s*-tetrazine. As a consequence, TDA makes some energetic improvement for molecules for which the excited state energy is underestimated LR; however, it makes the error larger in other cases. The MUEs, therefore, depend on the composition of the test set. Nevertheless, the test set used here is representative of many applications in organic and biological chemistry, and we believe that the MUE is useful for organizing the discussion. Tables III and IV show that most of the density functionals studied here are successful with LR and TDA.

IV.D. Collinear SF-TDA: Comparisons of SF1, SF2, and NSF2

Table V shows the excitation energy evaluated by collinear SF-TDDFT, where the excitation energies are calculated using SF1 and SF2 as shown in Eqs. (5) and (7). Fairly high spin contaminations ($\langle S^2 \rangle > 0.4$) are observed for every density functional at least for one molecule except for M05-2X and M06-2X.

We first compare the results given by Eqs. (5) and (7). The MUE tends to be large when the spin-contamination is large, and we found that SF2 showed a larger MUE for all density functionals except M05-2X. For several density functionals, the results with SF2 are terrible. Figures 1(a)–1(c) plot the absolute error of excitation energy by SF1, SF2, and NSF2 vs. $\langle S^2 \rangle$ value. The error of excitation energy by SF1 (Fig. 1) seems to have no relationship with the expectation value of $\langle S^2 \rangle$; on the other hand, the error by SF2 is clearly larger for large $\langle S^2 \rangle$. We conclude from the table that SF2 should not be applied when there is a large degree of spin-contamination.

One can also see in the tables that, except for M06-2X, SF1 is less accurate than LR.

One of the unexpected results is the fairly large MUE of the ω B97X functional (0.60 eV and 1.51 eV for SF1 and SF2, against 0.27 eV for TDA), because this functional was one

TABLE III. The lowest excitation energies (in eV) of valence states calculated by LR.

Functional	X^a	Ethylene	Butadiene	HCHO	CH ₃ CHO	Acetone	Pyridine	Pyrazine	Pyrimidine	Pyridazine	<i>s</i> -Tetrazine	MUE
		1B _{1u} $\pi \rightarrow \pi^*$	1B _u $\pi \rightarrow \pi^*$	1A ₂ $n \rightarrow \pi^*$	A'' $n \rightarrow \pi^*$	1A ₂ $n \rightarrow \pi^*$	B ₁ $n \rightarrow \pi^*$	B _{3u} $n \rightarrow \pi^*$	B ₁ $n \rightarrow \pi^*$	B ₁ $n \rightarrow \pi^*$	B _{3u} $n \rightarrow \pi^*$	
BLYP	0	7.03	5.01	3.83	4.16	4.22	4.40	3.61	3.83	3.17	1.90	0.32
OLYP	0	6.96	5.25	3.86	4.20	4.24	4.44	3.63	3.85	3.22	1.91	0.28
PW91	0	7.20	5.36	3.81	4.14	4.22	4.37	3.57	3.80	3.14	1.85	0.29
revTPSS	0	7.34	5.52	4.06	4.31	4.39	4.58	3.75	4.00	3.35	2.02	0.15
B3LYP	20	7.31	4.94	3.92	4.26	4.38	4.81	3.97	4.29	3.59	2.26	0.23
X3LYP	21.8	7.31	5.54	3.92	4.26	4.39	4.84	4.00	4.32	3.62	2.29	0.18
PBE0	25	7.47	5.65	3.92	4.27	4.41	4.88	4.01	4.35	3.66	2.29	0.16
M06	27	6.94	5.37	3.87	4.23	4.35	4.75	3.88	4.23	3.48	2.08	0.24
M05	28	7.16	5.44	3.89	4.26	4.36	4.73	3.80	4.16	3.41	1.90	0.22
BHLYP	50	7.44	5.77	4.07	4.43	4.61	5.32	4.41	4.89	4.10	2.73	0.41
M08-HX	52.23	7.32	5.64	3.61	4.01	4.21	4.94	4.08	4.50	3.79	2.47	0.31
M06-2X	54	7.51	5.79	3.61	3.99	4.13	4.92	4.03	4.46	3.71	2.33	0.26
M05-2X	56	7.59	5.83	3.62	4.01	4.15	4.99	4.07	3.31	3.74	2.33	0.25
M08-SO	56.79	7.23	5.61	3.55	3.95	4.08	4.87	3.99	4.45	3.64	2.28	0.30
CAM-B3LYP	19–65	7.46	5.74	3.91	4.27	4.43	5.08	4.20	4.57	3.84	2.48	0.25
ω B97X	15.77–100	7.60	5.90	3.95	4.29	4.47	5.20	4.28	4.68	3.95	2.55	0.27
M11	42.8–100	7.33	5.71	3.54	3.93	4.07	4.96	4.07	4.51	3.76	2.40	0.33
M06-HF	100	7.42	5.86	2.95	3.34	3.40	4.81	3.95	4.53	3.64	2.38	0.45
		7.65	5.91	4.00	4.28	4.43	4.59	3.83	3.85	3.60	2.25	

^aX is the percentage of Hartree-Fock exchange in the density functional.

of the best functionals in our previous LR study for the excitation energy for a database that includes both valence and Rydberg states. This unexpectedly poor behavior of ω B97X with SF1 was also observed in the study by Bernard *et al.*¹⁴ Another unexpected result is seen for the M11 functional; the SF2 calculation with this functional shows a fairly large deviation from experiment, even though M11 showed good per-

formance, comparable to that of M08-SO, with the LR and SF1 methods.

In Table S1 in supplementary material,⁶⁵ we show the singlet (S_0)-singlet (S_1) excitation energies calculated based on NSF2. The NSF2 method usually has lower MUEs than SF2; however, the error is larger than for SF1. The latter is an unexpected result, because the error of the excitation

TABLE IV. The lowest excitation energies (in eV) of valence states calculated by TDA.

Functional	X^a	Ethylene	Butadiene	HCHO	CH ₃ CHO	Acetone	Pyridine	Pyrazine	Pyrimidine	Pyridazine	<i>s</i> -Tetrazine	MUE
		1B _{1u} $\pi \rightarrow \pi^*$	1B _u $\pi \rightarrow \pi^*$	1A ₂ $n \rightarrow \pi^*$	A'' $n \rightarrow \pi^*$	1A ₂ $n \rightarrow \pi^*$	B ₁ $n \rightarrow \pi^*$	B _{3u} $n \rightarrow \pi^*$	B ₁ $n \rightarrow \pi^*$	B ₁ $n \rightarrow \pi^*$	B _{3u} $n \rightarrow \pi^*$	
BLYP	0	7.15	5.14	3.84	4.17	4.23	4.44	3.66	3.86	3.23	1.97	0.27
OLYP	0	7.08	5.43	3.87	4.21	4.26	4.48	3.67	3.88	3.28	1.98	0.23
PW91	0	7.41	5.67	3.83	4.16	4.24	4.42	3.62	3.82	3.20	1.92	0.21
revTPSS	0	7.78	6.08	4.13	4.49	4.66	5.40	4.50	4.95	4.21	2.83	0.46
B3LYP	20	7.56	5.16	3.94	4.28	4.40	4.86	4.02	4.32	3.66	2.34	0.20
X3LYP	21.8	7.78	6.00	3.95	4.29	4.43	4.94	4.07	4.39	3.74	2.38	0.17
PBE0	25	7.59	5.84	3.94	4.28	4.41	4.89	4.05	4.35	3.69	2.37	0.14
M06	27	7.84	6.07	3.93	4.29	4.46	5.14	4.27	4.62	3.93	2.57	0.29
M05	28	7.60	5.90	3.95	4.29	4.47	5.20	4.28	4.68	3.95	2.55	0.27
BHLYP	50	7.50	5.85	4.07	4.32	4.40	4.61	3.79	4.02	3.40	2.07	0.10
M08-HX	52.23	7.53	5.78	3.94	4.31	4.41	4.81	3.88	4.21	3.52	2.04	0.13
M06-2X	54	8.06	6.24	3.73	4.10	4.25	5.11	4.21	3.31	3.90	2.52	0.34
M05-2X	56	7.15	5.58	3.90	4.26	4.38	4.82	3.95	4.27	3.57	2.19	0.19
M08-SO	56.79	7.89	6.12	3.69	4.07	4.21	5.02	4.15	4.54	3.85	2.50	0.31
CAM-B3LYP	19–65	7.85	6.17	3.27	3.64	3.70	5.10	4.26	4.79	4.00	2.79	0.54
ω B97X	15.77–100	7.64	5.87	3.69	4.08	4.29	5.04	4.19	4.57	3.92	2.61	0.29
M11	42.8–100	7.56	5.87	3.65	4.04	4.17	4.99	4.12	4.54	3.79	2.46	0.28
M06-HF	100	7.61	5.89	3.63	4.01	4.14	5.07	4.19	4.59	3.91	2.58	0.32
		7.65	5.91	4.00	4.28	4.43	4.59	3.83	3.85	3.60	2.25	

^aX is percentage of Hartree-Fock exchange in the density functional.

TABLE V. The lowest excitation energies (in eV) of valence states calculated by collinear SF1 and SF2.

Functional	X^a		Ethylene	Butadiene	HCHO	CH ₃ CHO	Acetone	Pyridine	Pyrazine	Pyrimidine	Pyridazine	<i>s</i> -Tetrazine	MUE
			1B _{1u}	1B _u	1A ₂	A''	1A ₂	B ₁	B _{3u}	B ₁	B ₁	B _{3u}	
			$\pi \rightarrow \pi^*$	$\pi \rightarrow \pi^*$	$n \rightarrow \pi^*$	$n \rightarrow \pi^*$	$n \rightarrow \pi^*$	$n \rightarrow \pi^*$	$n \rightarrow \pi^*$	$n \rightarrow \pi^*$	$n \rightarrow \pi^*$	$n \rightarrow \pi^*$	
B3LYP	20	SF1	6.41	4.72	4.83	5.13	5.25	5.73	4.14	4.84	4.18	2.47	0.82
		SF2	7.42	5.32	6.31	6.39	6.42	7.14	4.48	5.40	5.07	2.92	1.41
		$\langle S^2 \rangle$	0.15	0.08	0.79	0.74	0.73	0.86	0.16	0.57	0.66	0.28	
X3LYP	21.8	SF1	6.49	4.78	4.80	5.10	5.22	5.71	4.17	4.84	4.17	2.49	0.80
		SF2	7.41	5.36	6.21	6.32	6.35	7.05	4.49	5.37	5.00	2.93	1.37
		$\langle S^2 \rangle$	0.14	0.09	0.78	0.73	0.72	0.85	0.14	0.55	0.62	0.27	
PBE0	25	SF1	6.68	4.97	4.72	5.06	5.20	5.70	4.19	4.82	4.16	2.52	0.75
		SF2	7.88	5.65	6.08	6.26	6.37	7.34	4.48	5.25	4.96	2.98	1.34
		$\langle S^2 \rangle$	0.15	0.10	0.70	0.67	0.68	0.85	0.07	0.37	0.57	0.28	
M06	27	SF1	6.45	4.85	4.65	4.95	5.05	5.32	4.03	4.56	3.84	2.37	0.62
		SF2	7.94	5.43	5.45	5.58	5.63	6.57	4.10	4.64	3.98	2.57	0.85
		$\langle S^2 \rangle$	0.39	0.21	0.75	0.71	0.66	0.81	0.02	0.05	0.22	0.40	
M05	28	SF1	6.80	4.95	4.66	4.98	5.05	5.26	4.01	4.66	3.83	2.27	0.57
		SF2	7.02	5.41	5.43	5.53	5.56	5.89	4.00	5.01	3.87	2.34	0.79
		$\langle S^2 \rangle$	0.07	0.10	0.69	0.61	0.56	0.62	0.03	0.60	0.11	0.33	
BHHLYP	50	SF1	7.56	5.79	4.12	4.44	4.58	5.20	4.54	4.81	4.07	2.85	0.40
		SF2	8.25	6.52	5.02	5.28	5.40	5.79	4.86	5.27	4.51	3.37	0.99
		$\langle S^2 \rangle$	0.26	0.33	0.57	0.54	0.52	0.35	0.06	0.15	0.16	0.26	
M08-HX	52.23	SF1	8.09	6.25	3.91	4.30	4.40	4.97	4.36	4.71	3.96	2.73	0.35
		SF2	9.24	7.07	3.54	3.92	4.10	4.86	4.15	4.42	3.62	2.63	0.55
		$\langle S^2 \rangle$	0.52	0.49	0.02	0.06	0.06	0.15	0.06	0.06	0.07	0.10	
M06-2X	54	SF1	7.63	5.80	3.87	4.25	4.34	4.84	4.34	4.64	3.93	2.64	0.26
		SF2	7.54	6.00	3.38	3.71	3.88	4.84	4.05	4.30	3.52	2.40	0.31
		$\langle S^2 \rangle$	0.11	0.28	0.06	0.02	0.02	0.20	0.04	0.06	0.11	0.07	
M05-2X	56	SF1	8.03	6.08	3.90	4.29	4.39	5.09	4.45	4.78	4.02	2.70	0.36
		SF2	7.27	5.92	3.46	3.82	3.99	4.74	4.12	4.42	3.57	2.45	0.31
		$\langle S^2 \rangle$	0.04	0.13	0.04	0.02	0.02	0.13	0.05	0.12	0.10	0.11	
M08-SO	56.79	SF1	7.19	6.41	3.87	4.26	4.34	4.95	4.29	4.54	3.84	2.58	0.33
		SF2	7.79	7.27	3.04	3.34	3.49	4.45	3.94	4.17	3.31	2.28	0.52
		$\langle S^2 \rangle$	0.52	0.54	0.22	0.30	0.33	0.40	0.04	0.12	0.18	0.07	
CAM-B3LYP	19–65	SF1	7.39	5.66	4.15	4.53	4.71	5.10	4.30	4.69	3.87	2.58	0.36
		SF2	8.60	6.97	4.84	5.33	5.58	5.95	5.13	5.85	4.65	3.50	1.20
		$\langle S^2 \rangle$	0.18	0.23	0.30	0.41	0.48	0.19	0.09	0.42	0.07	0.18	
ω B97X	15.77–100	SF1	9.35	7.23	4.29	4.56	4.71	5.50	4.16	4.36	3.93	2.34	0.60
		SF2	7.42	6.51	0.41	0.74	0.95	3.79	3.35	3.37	2.54	1.45	1.51
		$\langle S^2 \rangle$	0.04	0.19	0.82	0.84	0.86	0.91	0.14	0.83	0.49	0.12	
M11	42.8–100	SF1	8.13	6.31	3.85	4.26	4.39	4.89	4.37	4.69	3.81	2.64	0.34
		SF2	10.55	8.96	5.69	6.27	6.64	6.83	6.03	6.88	5.51	4.37	2.33
		$\langle S^2 \rangle$	0.32	0.36	0.37	0.48	0.57	0.24	0.06	0.43	0.12	0.07	
M06-HF	100	SF1	9.64	7.90	3.17	3.40	3.20	4.78	4.62	4.46	4.08	3.11	0.98
		SF2	8.06	7.08	-0.30	-0.12	-0.18	2.62	3.50	3.10	2.32	2.14	1.93
		$\langle S^2 \rangle$	0.38	0.50	0.74	0.72	0.70	0.74	0.10	0.28	0.35	0.35	
			7.65	5.91	4.00	4.28	4.43	4.59	3.83	3.85	3.60	2.25	

^aX is percentage of Hartree-Fock exchange in the density functional.

energy is expected to be reduced by the more accurate descriptions of ground states obtained by RKS than those by SF-TDDFT.

Table V does not show results for BLYP, OLYP, and PW91 because the local functionals give such high spin contamination with collinear spin-flip TDDFT that state assignments of singlets are ambiguous. Such a failure of local density functionals is disappointing, because local density functionals are much less expensive than nonlocal ones for large systems, and this motivates the examination of the noncollinear methods.

IV.E. Collinear SF vs. noncollinear SF

Table VI gives the excitation energies by NC-SF1 for several density functionals. The noncollinear excitation energies obtained with PBE0, B3LYP, M06, M06-2X, ω B97X, and M06-HF can be compared with the collinear ones for the same density functionals in Table V.

The most remarkable difference between the collinear and noncollinear treatments is that the degree of spin-contamination is drastically reduced by applying the noncollinear kernel; the spin expectation value of squared spin

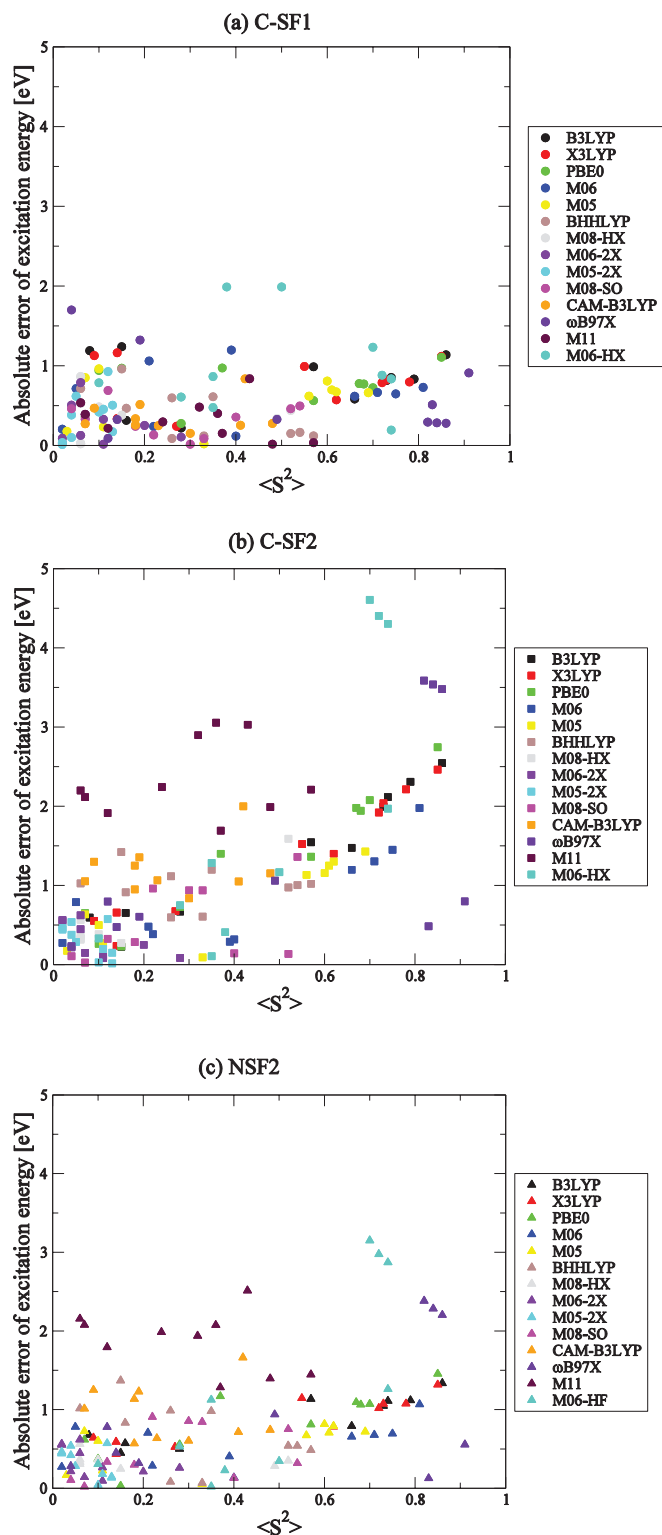


FIG. 1. Absolute errors of electronic excitation energy (in eV) calculated by (a) SF1, (b) SF2, and (c) NSF2 plotted vs. $\langle S^2 \rangle$.

operator of NC-SF2 is under 0.4 except for M06-HF which includes 100% Hartree-Fock exchange. The comparison of MUEs between SF and NC-SF shows that the MUE is reduced by applying the noncollinear kernel for the density functionals with a low percentage of Hartree-Fock exchange; 0.55, 0.68, and 0.43 eV for B3LYP, PBE0, and M06 with the noncollinear kernel against 0.82, 0.75, and 0.62 eV with the collinear ker-

nel, on the other hand the error becomes large for the density functionals with high percentage of Hartree-Fock exchange; 0.26, 0.60, and 0.98 eV for M06-2X, ω B97X, and M06-HF with collinear kernel against 0.88, 0.66, and 1.61 eV with non-collinear kernel.

Overall, the calculated error by NC-SF2 is comparable to that obtained with NC-SF1 for most cases, and the energy difference between the predictions of NC-SF1 and NC-SF2 is rather small compared with the case of collinear xc kernel for the systems with low spin contamination. The SF1 and SF2 noncollinear excitation energies are very different for M06-HF for alkenes, which have large $\langle S^2 \rangle$.

Table S2 in supplementary material⁶⁵ shows results for NC-NSF2. Comparison of Table VI and Table S2 shows that the excitation energies calculated NC-SF2 and NC-NSF2 are very similar.

Tables V and VI show that when $\langle S^2 \rangle$ is small, as for M05-2X and M06-2X, SF1 and SF2 show similar errors; on the other hand, when $\langle S^2 \rangle$ is larger than 0.4, SF2 has a significantly larger error. This trend is especially strong in the noncollinear case. This tendency suggests that, without special justification, one should avoid applying SF2 for systems with $\langle S^2 \rangle > 0.4$.

Another notable conclusion from Table VI is that there is less difference among the different kinds of functionals, as long as $\langle S^2 \rangle$ is small. However, none of the functionals tested give an error below 0.43 eV with NC-SF1 or below 0.41 eV with NC-SF2.

IV.F. Energy differences of the singlets from the triplets

The SF1 formula has two components: the energy differences of S_0-T_1 and T_1-S_1 as shown in Eq. (5). To ascertain which of the energy components provide the larger contributions to the errors in SF1, we show these energy components in Tables VII and VIII.

Table VII lists the S_0-T_1 energy difference. The SF2 rows give the energy differences between S_0 and T_1 which are obtained by solving the RKS and UKS equations, respectively, and the SF1 rows give the energy difference between the singlet spin state obtained by a SF-TDDFT calculation and the triplet spin state obtained by solving UKS; $\omega(S_0|T_1)$. The reference used to compute the MUEs is the energy difference between ground singlet and triplet state as calculated in the present work by CCSD(T) with the 6-311(2+,2+)G** basis set.

One can see in Table VII that the SF-TDDFT excitation energies show larger MUEs (often more than twice as large) than are obtained by RKS and UKS. The energy gap between T_1 and S_0 state is best estimated by SF2 calculations of density functionals with a high percentage of Hartree-Fock exchange and one of the range-separated density functionals: M08-HX, M06-2X, M05-2X, M08-SO, ω B97X, and M06-HF. On the other hand, the energy gap is underestimated for density functionals with a low percentage of Hartree-Fock exchange.

Although Table VII shows that the ground state obtained by SF-TDDFT does not have a significant spin contamination

TABLE VI. The lowest excitation energies (in eV) of valence states calculated by NC-SF1 and NC-SF2.

Functional	X^a		Ethylene	Butadiene	HCHO	CH ₃ CHO	Acetone	Pyridine	Pyrazine	Pyrimidine	Pyridazine	<i>s</i> -Tetrazine	MUE
			1B _{1u} $\pi \rightarrow \pi^*$	1B _u $\pi \rightarrow \pi^*$	1A ₂ $n \rightarrow \pi^*$	A'' $n \rightarrow \pi^*$	1A ₂ $n \rightarrow \pi^*$	B ₁ $n \rightarrow \pi^*$	B _{3u} $n \rightarrow \pi^*$	B ₁ $n \rightarrow \pi^*$	B ₁ $n \rightarrow \pi^*$	B _{3u} $n \rightarrow \pi^*$	
BLYP	0	NC-SF1	6.27	4.35	4.26	4.60	4.70	4.97	3.67	4.26	3.72	1.96	0.52
		NC-SF2	6.73	4.58	4.29	4.59	4.67	4.93	3.73	4.18	3.61	2.04	0.41
		$\langle S^2 \rangle^b$	0.08	0.03	0.03	0.01	0.01	0.09	0.01	0.02	0.05	0.03	
B3LYP	20	NC-SF1	6.89	5.03	4.09	4.43	4.56	6.51	4.01	4.91	3.83	2.31	0.55
		NC-SF2	7.29	5.24	4.20	4.52	4.63	6.73	4.10	4.91	3.85	2.44	0.56
		$\langle S^2 \rangle$	0.12	0.08	0.04	0.03	0.03	0.06	0.02	0.04	0.05	0.07	
PBE0	25	NC-SF1	7.28	5.37	3.84	4.20	4.36	6.82	4.01	6.68	3.79	2.36	0.68
		NC-SF2	7.73	5.55	3.95	4.31	4.46	7.03	4.09	6.84	3.81	2.46	0.67
		$\langle S^2 \rangle$	0.20	0.11	0.02	0.02	0.02	0.09	0.05	0.07	0.05	0.07	
M06	27	NC-SF1	7.43	5.05	4.04	4.51	4.57	4.76	5.13	4.85	3.94	2.26	0.43
		NC-SF2	8.25	5.57	4.00	4.44	4.50	5.13	5.14	4.86	3.91	2.27	0.44
		$\langle S^2 \rangle$	0.33	0.37	0.06	0.03	0.03	0.28	0.07	0.19	0.18	0.11	
M06-2X	54	NC-SF1	7.09	5.41	4.60	4.89	5.01	7.00	4.43	5.63	4.22	2.74	0.88
		NC-SF2	8.28	6.23	4.46	4.55	4.72	7.53	4.32	5.50	4.01	2.74	0.80
		$\langle S^2 \rangle$	0.40	0.33	0.48	0.35	0.11	0.17	0.05	0.37	0.09	0.20	
ω B97X	15.77–100	NC-SF1	7.54	7.83	4.06	4.37	4.50	5.01	4.36	6.68	3.77	2.60	0.66
		NC-SF2	7.79	7.93	4.15	4.44	4.57	5.38	4.50	6.69	3.98	2.78	0.78
		$\langle S^2 \rangle$	0.09	0.26	0.02	0.02	0.04	0.18	0.04	0.05	0.06	0.09	
M06-HF	100	NC-SF1	6.57	5.16	5.76	5.73	5.73	5.58	6.06	8.07	4.74	3.42	1.61
		NC-SF2	8.37	7.02	4.85	4.74	4.87	5.60	6.41	7.51	4.49	3.24	1.27
		$\langle S^2 \rangle$	0.51	0.72	0.27	0.05	0.49	0.59	0.17	0.18	0.70	0.12	
			7.65	5.91	4.00	4.28	4.43	4.59	3.83	3.85	3.60	2.25	

^a X is the percentage of Hartree-Fock exchange in the density functional.

^b $\langle S^2 \rangle$ is given for the S_0 state obtained by spin-flip TDDFT.

problem, the deviation of the excitation energy from the reference is fairly large. This indicates the large error observed in S_0 - S_1 energy is not only due to the spin-mixing problem but it also seems to reflect inaccuracy in the xc functional. A related finding was reported in the previous study,³⁸ in which the authors compared the performance of SF1-TDDFT with SF-EOM-CCSD⁶⁶ method and found that the larger error of SF1-TDDFT is due to the xc functional rather than the spin-flip approach *per se*.

Table VIII gives the S_1 - T_1 energy difference; $\omega(S_1|T_1)$, where the reference value used to compute MUEs is determined by using the T_1 - S_0 energy gap and the S_0 - S_1 excitation energy from experiment:

$$(E^{S_1} - E^{T_1})_{\text{ref.}} = (\Delta E^{S_1-S_0})_{\text{exp}} - (E^{T_1} - E^{S_0})_{\text{CCSD(T)}}. \quad (8)$$

(We used the same basis set for the coupled cluster calculations.) A negative value in Table VIII indicates that the triplet is incorrectly predicted to lie above the singlet. This incorrect prediction occurs for four molecules with M06-2X, five with M08-SO, and eight with ω B97X and M06-HF.

One can see that most of the errors in Table VIII are larger than those that we saw for the T_1 - S_0 energy difference in Table VII; in particular, nine of the 14 density functionals give a greater mean unsigned error for S_1 - T_1 than for T_1 - S_0 . Thus, the error of the S_0 - S_1 excitation energy is predominantly due to the error of the T_1 - S_1 excitation energy for most density functionals.

In previous work on triplet states, it was already discussed that hybrid functionals with similar values of X may give quite different errors,⁶⁷ and this was later discussed in terms of triplet instability in the ground state.^{68,69}

IV.G. Effect of percentage of Hartree-Fock exchange in functional

The role of Hartree-Fock exchange is especially important for improving the description of two electrons that are widely separated (e.g., in delocalized interactions, Rydberg states, long-range charge transfer, and diradicals obtained by partial bond dissociation); however, inclusion of Hartree-Fock exchange introduces static correlation error. It seems to be a consequence of compromising these two demands, one for high X and one for low X , that the density functionals with best performance have about 40% Hartree-Fock exchange when one considers both valence states and Rydberg states.¹⁸ However, when one considers only valence states in LR calculations, the best functionals are those with 20%–30% Hartree-Fock exchange,⁵ and even the local density functionals can compete reasonably well with the hybrid ones^{18,70} (the errors of the local density functionals are unacceptable for the Rydberg states but not necessarily for the valence states). One can see from Table III, which contains only valence states, that no remarkable difference is observed between the type of density functional and the percentage of Hartree-Fock exchange for LR and TDA calculations.

TABLE VII. Singlet (S_0)-triplet (T_1) state excitation energies (in eV) based on collinear calculations: $\omega(S_0|T_1)$ (as used in SF1) and $[E^{\text{RKS}}(T_1) - E^{\text{UKS}}(S_0)]$ (as used in SF2).

Functional	X^a		Ethylene	Butadiene	HCHO	CH ₃ CHO	Acetone	Pyridine	Pyrazine	Pyrimidine	Pyridazine	s-Tetrazine	MUE
B3LYP	20	SF2	4.35	3.18	3.28	3.66	3.82	4.27	3.35	3.90	2.95	1.61	0.30
		SF1	3.56	2.66	2.99	3.40	3.59	4.07	3.10	3.75	2.74	1.32	0.62
		$\langle S^2 \rangle$	0.01	0.04	0.02	0.02	0.02	0.04	0.02	0.03	0.03	0.03	0.03
X3LYP	21.8	SF2	4.35	3.18	3.27	3.66	3.82	4.28	3.38	3.93	2.96	1.63	0.29
		SF1	3.62	2.70	3.00	3.41	3.59	4.08	3.13	3.77	2.75	1.35	0.60
		$\langle S^2 \rangle$	0.01	0.04	0.02	0.02	0.02	0.04	0.02	0.03	0.03	0.03	0.03
PBE0	25	SF2	4.21	3.11	3.19	3.59	3.77	4.21	3.37	3.91	2.94	1.61	0.35
		SF1	3.27	2.54	2.84	3.27	3.48	3.86	3.11	3.71	2.69	1.33	0.73
		$\langle S^2 \rangle$	0.01	0.05	0.03	0.03	0.03	0.05	0.02	0.04	0.03	0.04	0.04
M06	27	SF2	4.30	3.16	3.43	3.80	3.97	4.25	3.43	3.94	2.99	1.57	0.26
		SF1	3.51	2.81	3.38	3.79	3.93	3.91	3.36	3.88	2.95	1.56	0.43
		$\langle S^2 \rangle$	0.03	0.04	0.02	0.02	0.02	0.05	0.02	0.04	0.02	0.03	0.03
M05	28	SF2	4.17	2.98	3.37	3.74	3.88	4.15	3.29	3.82	2.88	1.37	0.38
		SF1	4.04	2.62	3.31	3.73	3.83	4.04	3.30	3.81	2.89	1.44	0.44
		$\langle S^2 \rangle$	0.02	0.04	0.03	0.03	0.03	0.06	0.02	0.04	0.03	0.04	0.04
BHLYP	50	SF2	4.11	3.12	3.13	3.51	3.69	4.26	3.76	4.26	3.09	1.97	0.26
		SF1	3.94	2.93	2.76	3.14	3.31	3.89	3.46	3.85	2.73	1.58	0.58
		$\langle S^2 \rangle$	0.02	0.08	0.07	0.07	0.07	0.13	0.05	0.09	0.06	0.08	0.08
M08-HX	52.23	SF2	4.41	3.39	3.46	3.85	4.05	4.46	3.72	4.34	3.19	2.11	0.10
		SF1	4.49	3.44	3.84	4.24	4.35	4.59	3.94	4.64	3.54	2.23	0.19
		$\langle S^2 \rangle$	0.02	0.08	0.05	0.05	0.05	0.06	0.03	0.04	0.04	0.04	0.04
M06-2X	54	SF2	4.47	3.44	3.48	3.85	4.02	4.44	3.72	4.34	3.17	2.01	0.09
		SF1	4.72	3.59	3.98	4.38	4.48	4.48	4.01	4.68	3.59	2.26	0.30
		$\langle S^2 \rangle$	0.02	0.08	0.04	0.04	0.04	0.07	0.03	0.04	0.04	0.04	0.04
M05-2X	56	SF2	4.43	3.33	3.41	3.79	3.96	4.44	3.72	4.34	3.13	1.97	0.11
		SF1	5.24	3.65	3.85	4.26	4.37	4.81	4.06	4.70	3.59	2.24	0.34
		$\langle S^2 \rangle$	0.01	0.06	0.06	0.06	0.06	0.08	0.03	0.05	0.04	0.05	0.05
M08-SO	56.79	SF2	4.34	3.35	3.54	3.90	4.07	4.51	3.76	4.36	3.14	2.04	0.08
		SF1	4.63	3.53	4.31	4.74	4.83	5.00	4.11	4.72	3.68	2.35	0.45
		$\langle S^2 \rangle$	0.02	0.07	0.05	0.05	0.05	0.07	0.03	0.05	0.04	0.04	0.04
CAM-B3LYP	19–65	SF2	4.30	3.22	3.26	3.66	3.85	4.30	3.60	4.13	3.00	1.82	0.22
		SF1	3.47	2.34	2.81	3.20	3.38	3.59	2.82	3.31	2.27	1.02	0.92
		$\langle S^2 \rangle$	0.01	0.06	0.05	0.05	0.05	0.09	0.03	0.06	0.04	0.05	0.05
ωB97X	15.77–100	SF2	4.37	3.30	3.36	3.74	3.93	4.35	3.73	4.27	3.07	1.93	0.14
		SF1	6.35	4.30	6.04	6.31	6.42	5.82	4.51	4.91	4.33	2.80	1.44
		$\langle S^2 \rangle$	0.02	0.08	0.17	0.17	0.18	0.21	0.04	0.12	0.09	0.07	0.07
M11	42.8–100	SF2	4.47	3.38	3.45	3.79	3.95	4.34	3.75	4.31	3.09	2.03	0.12
		SF1	3.01	1.71	2.01	2.38	2.47	2.66	2.13	2.63	1.51	0.34	1.66
		$\langle S^2 \rangle$	0.01	0.06	0.07	0.07	0.07	0.10	0.03	0.06	0.04	0.04	0.04
M06-HF	100	SF2	4.63	3.73	3.63	3.91	4.03	4.61	4.20	4.88	3.35	2.71	0.26
		SF1	6.84	5.38	5.67	6.00	5.95	6.07	5.29	6.02	4.95	3.59	1.84
		$\langle S^2 \rangle$	0.04	0.11	0.14	0.13	0.13	0.17	0.06	0.09	0.10	0.08	0.08
		ref.	4.47	3.34	3.63	3.98	4.14	4.60	3.73	4.25	3.29	1.97	

^aX is percentage of Hartree-Fock exchange in the density functional.

On the other hand, SF1 shows a trend; a small MUE is seen for density functionals with 50%–60% Hartree-Fock exchange; this includes BHLYP, M08-HX, M06-2X, M05-2X, and M08-SO; in addition, the range-separated density functionals also show low MUEs. The same trend has been reported for the electronic excitations in diradicals²⁵ and for conical interaction of the ethylene molecule.⁷¹

However, this trend becomes unclear for SF2, for example, BHLYP (50% of Hartree-Fock exchange) has large error. The most disappointing thing for the use of SF2 is that the error is enhanced 3–7 times compared with SF1 for range separated density functionals which generally corrects the de-

scription of the charge transfer excited state: CAM-B3LYP, ω B97X, and M11. Thus, SF1 seems more reasonable to evaluate the nature of density functionals.

IV.H. Additional remarks on polyenes

Polyenes are especially challenging for electronic structure theory because doubly excited configurations are important even for some low-energy states. This is an especially serious problem for LR and TDA since ground-state TDDFT with the adiabatic approximation formally includes only single excitations. Although nonadiabatic approaches can be

TABLE VIII. Energy difference $\omega(S_1|T_1)$ (in eV) between T_1 and S_1 states based on collinear NSF2 calculations.^a

Functional	X ^a	Ethylene	Butadiene	Formaldehyde	Acetaldehyde	Acetone	Pyridine	Pyrazine	Pyrimidine	Pyridazine	s-Tetrazine	MUE
B3LYP	20	2.85	2.06	1.84	1.73	1.65	1.66	1.05	1.08	1.44	1.15	1.12
X3LYP	21.8	2.86	2.09	1.80	1.70	1.62	1.63	1.04	1.07	1.42	1.14	1.10
PBE0	25	3.41	2.42	1.88	1.78	1.72	1.83	1.08	1.11	1.47	1.19	1.12
M06	27	2.94	2.04	1.27	1.16	1.12	1.41	0.67	0.69	0.89	0.81	0.75
M05	28	2.75	2.33	1.35	1.25	1.22	1.23	0.71	0.85	0.95	0.83	0.78
BHHLYP	50	3.62	2.86	1.36	1.31	1.28	1.31	1.08	0.96	1.34	1.27	0.94
M08-HX	52.23	3.60	2.80	0.07	0.06	0.05	0.38	0.41	0.08	0.42	0.50	0.29
M06-2X	54	2.92	2.21	-0.10	-0.13	-0.14	0.36	0.32	-0.04	0.34	0.38	0.30
M05-2X	56	2.80	2.43	0.05	0.03	0.02	0.28	0.39	0.08	0.43	0.46	0.27
M08-SO	56.79	2.56	2.87	-0.45	-0.47	-0.49	-0.06	0.18	-0.18	0.16	0.23	0.38
CAM-B3LYP	19–65	3.92	3.32	1.34	1.33	1.32	1.52	1.48	1.38	1.61	1.56	1.18
ω B97X	15.77–100	3.00	2.93	-1.74	-1.75	-1.71	-0.31	-0.35	-0.55	-0.41	-0.46	0.91
M11	42.8–100	5.12	4.61	1.84	1.89	1.92	2.23	2.24	2.05	2.31	2.30	1.95
M06-HF	100	2.79	2.52	-2.50	-2.61	-2.75	-1.28	-0.68	-1.56	-0.87	-0.48	1.44
		3.18	2.57	0.37	0.30	0.29	0.01	0.10	0.40	0.31	0.28	

^aX is the percentage of Hartree-Fock exchange in the density functional.

used,^{7,8} SF-TDDFT has been proposed as a way to treat this problem within the adiabatic framework, and it has been reported that TDA improves the excitation energies that have double excitation character due to error cancelation.¹¹ However, it is the $2A_g$ state of butadiene that has significant double excitation character, not the $1B_u$ state studied here; therefore, the error on the lowest valence excitation energy of butadiene is not relevant to this debate.

Nevertheless, it is interesting to make a special comparison of LR and TDA for ethylene and butadiene. We did observe some energetic improvement in LR over TDA in unsaturated compounds as a result of a systematic increase of the excitation energy; the MUE of LR calculations on ethylene for 18 density functionals is 0.34 eV and the MUE by TDA is 0.21 eV; the MUE of *trans*-butadiene by LR is 0.36 eV and the MUE by TDA is 0.23 eV. The $1B_{1u}$ state of ethylene and the $1B_u$ state of butadiene have partial Rydberg character, so we expect TDDFT to underestimate these excitation energies. We note though that the increase in excitation energy by LR is seen for most of the molecules, not just these, so it is not clear if the improvement is just fortuitous.

Double excitations are formally included in the SF-TDDFT method, and yet examination of the excitation amplitudes shows that, consistent with the above discussion, they are present to only a small extent in the spin flip S_1 states, and the excitation energy estimated by SF-TDDFT is quantitatively less accurate than that obtained with LR and TDA; the MUE on ethylene for 18 density functionals by LR is 0.34 eV and that for 14 density functionals by SF1 is 0.80 eV; for *trans*-butadiene, it is 0.36 eV by LR and 0.75 eV by SF1, and SF2 shows larger errors than SF1. The error of the spin-flip method is somewhat reduced for several functionals by using a noncollinear kernel instead of collinear kernel for both molecules, as already discussed.

V. CONCLUSIONS

This article tests eight different formulations of TDDFT on the same test set. We compared the performance of several

types of TDDFT methods, including considerations of spin contamination, for the lowest valence state singlet excitation energies of ten organic molecules. We can draw several conclusions.

First, we consider using the ground state as the reference state. The Tamm-Dancoff approximation increases the excitation energy as compared to full linear response, but the average absolute error is not significantly different from the full linear response formulation. The latter conclusion agrees with previous experience suggesting that the TDA is a safe way to simplify the original TDDFT formulation and it provides a comparison framework for testing spin-flip TDDFT.

None of the collinear spin-flip methods (SF1, SF2, and NSF2—acronyms are summarized in Table I) shows quantitatively better average performance for the first excitation energies than those calculated by the ground-state linear response (see Fig. 1). The most successful functionals for collinear SF1 calculations are those that include 50%–60% Hartree-Fock exchange (see Fig. 1). However, noncollinear SF1-TDDFT has a smaller dependency on the percentage of Hartree-Fock exchange than does collinear SF1. Just as for the collinear spin-flip methods, though, none of the noncollinear spin-flip methods improves the accuracy compared to the ground-state TDDFT.

Yamaguchi's equation, introduced in SF2 methods to approximately correct the excitation energies for spin contamination, tends to give large errors except for the M06-2X and M05-2X functionals, especially for systems that have large spin contamination in the spin-flipped states (see Fig. 2). One can also see from Fig. 2 that the NSF2 method shows intermediate accuracy between SF1 and SF2.

The most successful spin-flip methods, ranked by their MUE for the ten valence excitation energies, are all collinear; those with mean MUEs of 0.36 eV or less are SF1/M06-2X (0.26 eV), SF2/M06-2X (0.31 eV), SF2/M05-2X (0.31 eV), NSF2/M05-2X (0.32 eV), NSF1/M08-HX (0.33 eV), NSF2/M08-HX (0.33 eV), SF1/M11 (0.34 eV), NSF2/M06-2X (0.34 eV), SF1/M08-HX (0.35 eV), SF1/M06-2X (0.36 eV), SF1/M05-2X (0.36 eV), and SF1/CAM-B3LYP

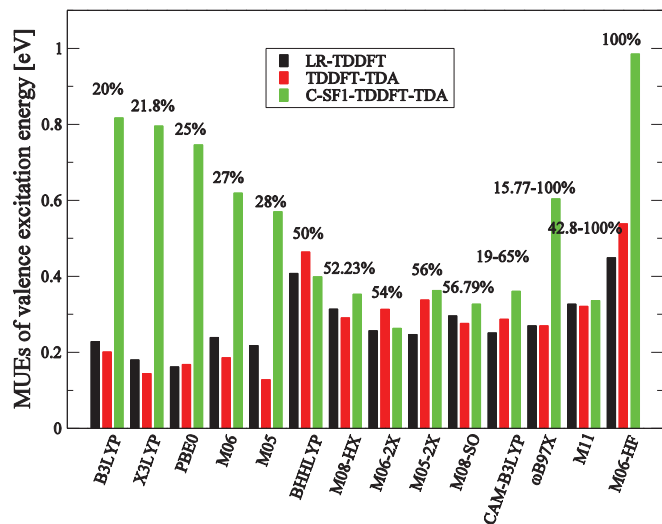


FIG. 2. Comparison of MUEs of valence excitation energy for LR-TDDFT, TDDFT-TDA, and SF1-TDDFT-TDA. Percentage of Hartree-Fock exchange of each density functional is filled in the figure.

(0.36 eV). The best methods with a ground-state reference are much better: TDA/BHHLYP (0.10 eV), TDA/M08-HX (0.13 eV), TDA/PBE0 (0.14 eV), and LR/revTPSS (0.15 eV).

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