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# The performance of time-dependent density functional theory based on a noncollinear exchange-correlation potential in the calculations of excitation energies

Fan Wang and Tom Ziegler<sup>a)</sup>

*Department of Chemistry, University of Calgary, Calgary, Alberta T2N1N4, Canada*

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In the present work we have studied the accuracy of excitation energies calculated from spin-flip transitions with a formulation of time-dependent density functional theory based on a noncollinear exchange-correlation potential proposed in a previous study. We compared the doublet-doublet excitation energies from spin-flip transitions and ordinary transitions, calculated the multiplets splitting of some atoms, the singlet-triplet gaps of some diradicals, the energies of excited quartet states with a doublet ground state. In addition, we attempted to calculate transition energies with excited states as reference. We compared the triplet excitation energies and singlet-triplet separations of the excited state from spin-flip and ordinary transitions. As an application, we show that using excited quartet state as reference can help us fully resolve excited states spin multiplets. In total the obtained excitation energies calculated from spin-flip transitions agree quite well with other theoretical results or experimental data. © 2005 American Institute of Physics.

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## I. INTRODUCTION

Time-dependent density functional theory (TDDFT) (Refs. 1–11) is presently one of the most popular methods in theoretical studies of excited states. Ordinary TDDFT cannot deal with spin-flip transitions in which  $S_z$  changes without including some fraction of Hartree–Fock exchange.<sup>12</sup> Recently we have developed a formulation of TDDFT (Ref. 13) based on a noncollinear representation<sup>14–16</sup> of the exchange-correlation (XC) potential. In this noncollinear representation for the XC potential, the spin density is defined as the length of magnetic vector  $\vec{m}: s = |\vec{m}|$  with  $\vec{m} = \sum_i \psi_i^\dagger \vec{\sigma} \psi_i$ , where  $\psi_i$  is molecular orbital,  $\vec{\sigma}$  is the Pauli matrix vector, while it is defined as the difference between spin  $\alpha$  and spin  $\beta$  densities in ordinary representation. The noncollinear XC potential is exactly the same as ordinary XC potential when the molecular orbitals are associated with either spin  $\alpha$  or spin  $\beta$ . The difference between these two schemes lies in that a first-order change in spin  $\beta$  component of a spin  $\alpha$  orbital can result in a first-order change in the spin density and the XC potential in the noncollinear representation, while in ordinary representation for the XC potential, such first-order change can only cause a second-order change in XC potential. The noncollinear TDDFT is in fact a generalization of ordinary TDDFT for systems with molecular orbitals associated with either spin  $\alpha$  or spin  $\beta$ . Besides all the transitions that can be treated in ordinary TDDFT, this noncollinear formulation of TDDFT also includes excitations involving spin flips (SF) with  $\Delta S_z = \pm 1$ . The capability to describe spin-flip transitions by the noncollinear TDDFT formulation makes it possible to resolve more fully the spin multiplets of excited states for systems with an open-shell ground state. In addition, by us-

ing excited states as reference, some double excitations from the ground states can also be reached with the noncollinear TDDFT.

In this investigation we will study the performance of this noncollinear TDDFT in connection with the calculation of excitation energies involving spin flips. We will first compare the excitation energies of doublet-doublet transitions for systems with doublet ground states obtained from ordinary transitions and spin-flip transitions. Second, we will assess the performance of the noncollinear TDDFT method in the calculation of the multiplet splittings of some atoms and the singlet-triplet separations of some diradicals. Third, we will study the properties of the excited quartet states of molecules with doublet ground states. For the last part, we will try to calculate the transition energies with excited states as reference. We will compare the singlet-triplet transition energies and the singlet-triplet splitting of excited states with the closed-shell ground state and the excited triplet states as reference, respectively. Finally, we shall assess the performance of the noncollinear TDDFT for the resolution of excited state spin multiplets with excited states as reference.

## II. THEORY

The basic equation used in TDDFT to calculate the excitation energies reads<sup>2,3</sup>

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

$$A_{ia,jb} = (\varepsilon_a - \varepsilon_i) \delta_{ij} \delta_{ab} + \frac{\partial F_{ia}}{\partial P_{jb}}, \quad B_{ia,bj} = \frac{\partial F_{ia}}{\partial P_{bj}}, \quad (2)$$

where  $\omega$  is the excitation energy, and  $F_{ia}$  and  $P_{jb}$  are the Fock matrix and density matrix elements, respectively. In the

<sup>a)</sup>Electronic mail: ziegler@ucalgary.ca

above equations,  $i, j, \dots$  are indices used for occupied orbitals,  $a, b, \dots$  are indices for empty orbitals, and  $p, q, \dots$  are indices for general orbitals. The elements of  $X, Y$  in Eq. (1) must satisfy<sup>17,18</sup>

$$(X^+ Y^+) \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} X \\ Y \end{pmatrix} = 1. \quad (3)$$

Equation (3) is important in determining the transition energies if the excited states are used as reference. Within the Tamm–Dancoff approximation (TDA),<sup>9</sup> one obtain

$$AX = \omega X. \quad (4)$$

With this approximation, Eq. (3) can be satisfied trivially. If the noncollinear representation for the XC energy functional and XC potential is used to calculate the Fock matrix in Eq. (2) and the molecular orbitals are associated with either spin  $\alpha$  or spin  $\beta$ , we have the following relation for transitions not involving spin flips:<sup>13</sup>

$$\begin{aligned} \frac{\partial F_{pq}}{\partial P_{st}} = & \int \psi_p^+(\vec{r}_1) \psi_q(\vec{r}_1) \psi_t^+(\vec{r}_2) \psi_s(\vec{r}_2) \frac{1}{|\vec{r}_1 - \vec{r}_2|} d\tau_1 d\tau_2 \\ & + \int (\psi_t^+ \psi_s) (\psi_p^+ \psi_q) \frac{1}{4} \left( \frac{\delta^2 E_{XC}}{\delta \rho_\alpha^2} + \frac{\delta^2 E_{XC}}{\delta \rho_\beta^2} + 2 \frac{\delta^2 E_{XC}}{\delta \rho_\alpha \delta \rho_\beta} \right) d\tau \\ & + \int [(\psi_t^+ \sigma_z \psi_s) (\psi_p^+ \psi_q) + (\psi_t^+ \psi_s) (\psi_p^+ \sigma_z \psi_q)] \\ & \times \frac{1}{4} \left( \frac{\delta^2 E_{XC}}{\delta \rho_\alpha^2} - \frac{\delta^2 E_{XC}}{\delta \rho_\beta^2} \right) d\tau + \int (\psi_t^+ \sigma_z \psi_s) (\psi_p^+ \sigma_z \psi_q) \\ & \times \frac{1}{4} \left( \frac{\delta^2 E_{XC}}{\delta \rho_\alpha^2} + \frac{\delta^2 E_{XC}}{\delta \rho_\beta^2} - 2 \frac{\delta^2 E_{XC}}{\delta \rho_\alpha \delta \rho_\beta} \right) d\tau \end{aligned} \quad (5)$$

and

$$\begin{aligned} \frac{\partial F_{pq}}{\partial P_{st}} = & \frac{1}{2} \int [(\psi_p^+ \sigma_x \psi_q) (\psi_t^+ \sigma_x \psi_s) + (\psi_p^+ \sigma_y \psi_q) \\ & \times (\psi_t^+ \sigma_y \psi_s)] \frac{1}{(\rho_\alpha - \rho_\beta)} \left( \frac{\delta E_{XC}}{\delta \rho_\alpha} - \frac{\delta E_{XC}}{\delta \rho_\beta} \right) d\tau \end{aligned} \quad (6)$$

for spin-flip transitions, where  $\rho_\alpha$  and  $\rho_\beta$  are the densities of electrons of spin  $\alpha$  and spin  $\beta$ , respectively,  $E_{XC}$  is the XC energy functional.

It can be seen from Eq. (5) that for transitions not involving spin flips, this noncollinear formulation of TDDFT is exactly the same as that of ordinary TDDFT. As for spin-flip transitions calculated from Eq. (6), it can also be seen that for closed-shell systems, the triplet state excitation energies calculated from spin-flip transition from Eq. (6) are the same as those obtained from ordinary TDDFT according to Eq. (5). Spin-flip transitions can result in some excited states that are also available without resorting to spin flips, for example, the doublet-doublet excitations resulting from singly occupied orbitals to virtual orbitals or from fully occupied orbitals to the singly occupied orbitals out of a doublet ground states. In addition, we can also reach some states that are unattainable without spin flips and with these spin-flip transitions we can resolve more fully the excited state multiplets.

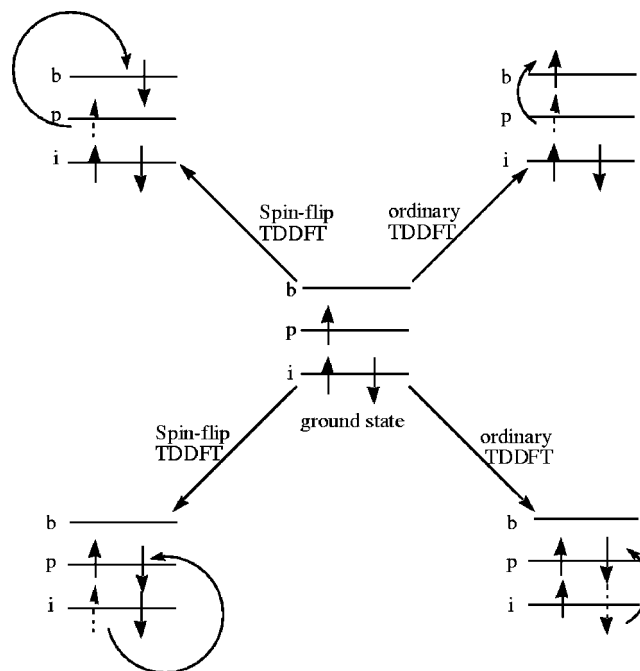


FIG. 1. The doublet-doublet transitions of a system with a ground doublet system from SF-TDDFT and ordinary TDDFT.

We shall in the following study the performance of the non-collinear TDDFT in connection with the type of excitations mentioned above.

### III. RESULTS AND DISCUSSIONS

All the calculations are performed with the Amsterdam density functional program (ADF) (Ref. 19) using the local density functional approximation (LDA) in the form of the Slater–Vosko–Wilk–Nusair (SVWN) functional<sup>20,21</sup> for the XC potential. A TZ2P basis set is employed in all the calculations except for  $H_2O$ ,  $CH_3$  BeH, and BeF, where Rydberg states transitions are involved. In those cases an even-tempered basis set<sup>22,23</sup> with two diffuse basis functions is used.

#### A. Doublet-doublet excitations

For systems with one unpaired electron, the transitions from the singly occupied orbital to completely empty orbital levels or from fully occupied orbitals to the singly occupied orbital level will result in doublet-doublet excitations. Such excitations can be obtained by either spin-flip transitions or ordinary transitions, see Fig. 1. The calculated excitation energies for these two types of transitions with or without TDA for some open-shell molecules are listed in Table I. The related orbital energy difference and experimental data are also displayed. It can be seen from this table that the use of TDA gives rise to a larger deviation from the full calculation for ordinary TDDFT compared to SF-TDDFT. This is a general result that also applies to the calculations discussed later. Related to this observation we note that the excitation energies from SF-TDDFT are closer to the corresponding orbital energy difference than excitation energies from ordinary TDDFT. Furthermore, the excitation energies calculated here by

TABLE I. Doublet-doublet excitation energies from spin-flip transitions or ordinary transitions (unit: eV) (geometry is taken from Ref. 31 and 32).

	State <sup>a</sup>	$\Delta\epsilon$	SF-TDA <sup>b</sup>	SF <sup>c</sup>	TDDFT-TDA <sup>d</sup>	TDDFT <sup>e</sup>	Expt. <sup>f</sup>
BeH	$V^2\Pi$	2.269	2.276	2.258	2.374	2.347	2.48
	$R^2\Pi$	4.680	4.677	4.677	4.667	4.667	6.32
BeF	$V^2\Pi$	3.767	3.765	3.759	4.075	4.032	4.14
	$R^2\Sigma^+$	5.080	5.089	5.089	5.063	5.061	6.16
	$R^2\Sigma^+$	5.190	5.196	5.195	5.177	5.173	6.27
CN	$V^2\pi$	1.457	1.347	1.338	1.450	1.394	1.32
	$V^2\Sigma^+$	2.888	2.807	2.716	3.526	3.239	3.22
CO <sup>+</sup>	$V^2\Pi$	3.309	3.082	3.056	3.218	3.163	3.26
	$V^2\Sigma^+$	4.889	4.738	4.687	5.071	4.947	5.82
N <sub>2</sub> <sup>+</sup>	$V^2\Pi_u$	1.501	1.435	1.386	1.514	1.443	1.35
	$V^2\Sigma_u^+$	3.183	3.081	2.942	4.092	3.688	3.17
CH <sub>3</sub>	$R^2A'_1$	4.889	4.879	4.877	4.839	4.835	5.73
	$R^2A'_2$	5.361	5.358	5.358	5.345	5.343	7.44
CH <sub>2</sub> NO <sub>2</sub>	$V^2B_2$	1.079	1.043	1.032	1.078	1.066	
	$V^2A_1$	1.624	1.600	1.590	1.633	1.616	
	$V^2A_2$	1.959	1.817	1.748	2.259	2.087	
Phenoxy	$V^2B_2$	0.553	0.582	0.566	0.575	0.553	
	$V^2A_2$	1.901	1.843	1.821	2.071	1.983	3.0
	$V^2B_1$	3.309	3.213	3.183	3.534	3.444	3.0
	$V^2A_1$	3.912	3.900	3.895	3.912	3.906	
	$V^2A_2$	3.762	3.740	3.729	4.156	4.032	4.0

<sup>a</sup>R, excited states are principally of Rydberg character; V, excited states are principally of valence character.<sup>b</sup>Using Eq. (6) and the Tamm-Dancoff approximation of Eq. (4).<sup>c</sup>Using Eq. (6).<sup>d</sup>Using Eq. (5) and the Tamm-Dancoff approximation of Eq. (4).<sup>e</sup>Using Eq. (5).<sup>f</sup>References 31 and 32.

SF-TDDFT and ordinary TDDFT agree quite well with each other especially for the lower valence excitations marked with V in Table I. For the higher valence excitations, the calculated energies from SF-TDDFT are a little too low compared with ordinary TDDFT. In total, the excitation energies from ordinary TDDFT agree better with experimental data than the estimates from SF-TDDFT. On the other hand, Rydberg transitions marked with R are underestimated by both methods. They will be reinvestigated in a later study where use is made of XC potentials with the proper long-range asymptotic behavior.<sup>6,24–27</sup>

These results for the valence excitations can be understood in the following way. Within the single-pole approximation (SPA),<sup>28</sup> as well as TDA and neglecting the difference between spin  $\alpha$  and spin  $\beta$  orbitals, the excitation energy from the singly occupied orbital to virtual orbitals using SF-TDDFT is just the orbital energy difference:  $\Delta E^{\text{SF}} = \epsilon_a^\alpha - \epsilon_i^\alpha$ , while the excitation from an ordinary TDDFT can be written as

$$\Delta E^{\text{TDDFT}} = \epsilon_a^\alpha - \epsilon_i^\alpha + [\psi_a \psi_i | f_H + f_{\text{XC}}^{\uparrow\uparrow} | \psi_i \psi_a], \quad (7)$$

where  $\rho_p = |\psi_p|^2$ , and  $[g|h] = \int \int g^*(\vec{r}) f(\vec{r}, \vec{r}') h(\vec{r}') d\vec{r} d\vec{r}'$ ,  $f_H(\vec{r}, \vec{r}') = 1/|\vec{r} - \vec{r}'|$ ,  $f_{\text{XC}}^{\sigma\tau}(\vec{r}, \vec{r}') = \delta(\vec{r} - \vec{r}') \delta^2 E_{\text{XC}}[\rho_\uparrow, \rho_\downarrow] / \delta \rho_\sigma \delta \rho_\tau$  as in Ref. 29. The last two terms on the right-hand

side (rhs) of Eq. (7) are usually positive for the currently used XC functionals and this can explain that the excitation energies from ordinary transitions are usually a little larger than that from spin-flip transitions. Even for the simplest one-electron system, the excitation energies calculated by SF-TDDFT and ordinary TDDFT will differ when use is made of the approximate XC potential. However, if an accurate XC potential is used for single-electron systems the  $\Delta E^{\text{SF}}$  and  $\Delta E^{\text{TDDFT}}$  will be identical and equal to the orbital energy difference. Furthermore, for multielectron systems, the last two terms on the rhs of Eq. (7) should usually be quite small since  $f_H$  and  $f_{\text{XC}}^{\uparrow\uparrow}$  are of similar magnitude but have opposite sign. From this simple argument, we can conclude that the difference between the results from SF-TDDFT and ordinary TDDFT is mainly due to approximations in XC potential. In addition, one can deduce that even with ordinary TDDFT, the doublet-doublet excitation energies will resemble the orbital energy difference, which has been observed before.<sup>30</sup> Usually the error of SPA is smaller for the lowest valencelike excitations and this causes the better agreement between the results from the spin-flip transitions and from ordinary transitions for the lowest valencelike excited state. On the other hand, for Rydberg-like excited states, the transition energies from both methods are similar

TABLE II. The multiplet splitting of the lowest configuration of some atoms (unit: eV).

Atom (ground state)	State	SF-TDA <sup>a</sup>	SF <sup>b</sup>	Expt. <sup>c</sup>
Carbon ( <sup>3</sup> P)	<sup>1</sup> D	1.358	1.318	1.264
	<sup>1</sup> S	3.377	3.397	2.684
Nitrogen ( <sup>4</sup> S)	<sup>2</sup> D	2.417	2.375	2.384
	<sup>2</sup> P	4.025	4.025	3.576
Oxygen ( <sup>3</sup> P)	<sup>1</sup> D	1.933	1.892	1.967
	<sup>1</sup> S	4.767	4.787	4.188
Silicon ( <sup>3</sup> P)	<sup>1</sup> D	0.732	0.699	0.781
	<sup>1</sup> S	1.910	1.926	1.909
Phosphorus ( <sup>4</sup> S)	<sup>2</sup> D	1.253	1.213	1.409
	<sup>2</sup> P	2.172	2.172	2.323
Sulfur ( <sup>3</sup> P)	<sup>1</sup> D	0.970	0.920	1.145
	<sup>1</sup> S	2.524	2.549	2.750

<sup>a</sup>Using Eq. (6) and the Tamm–Dancoff approximation of Eq. (4).<sup>b</sup>Using Eq. (6).<sup>c</sup>Reference 33.

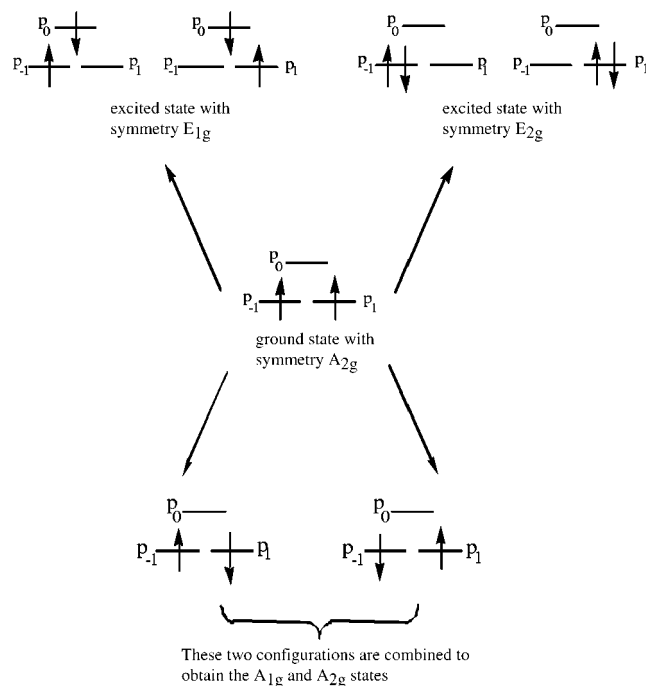
to the orbital energy difference and agree very well with each other.

## B. Multiplet splitting of the lowest energy configuration for some atoms

The multiplet splitting of atoms can only be resolved with SF-TDDFT. The calculated multiplet splitting of C, N, O, Si, P, and S are listed in Table II. For N and P, the ground states are spatially nondegenerate with the term <sup>4</sup>S and it is relatively easy to resolve the multiplets <sup>2</sup>D and <sup>2</sup>P. This is not the case for the other atoms, all of which have two unpaired *p* orbitals. In our calculations, we make use of *D*<sub>7d</sub> symmetry and situate the two unpaired *p* electrons in the two *e*<sub>1,u</sub> orbitals of  $\alpha$  spin for the ground state configuration. This ground state corresponding to the configuration (*e*<sub>1,u</sub>)<sup>2</sup> gives rise to the <sup>3</sup>P state with *M*<sub>S</sub> equal to 1 and *M*<sub>1</sub> equal to zero. The calculated excited states can be assigned according to the irreducible representation of the *D*<sub>7d</sub> group. The *p*→*p* spin-flip transitions will result in states with symmetries *A*<sub>1,g</sub>, *A*<sub>2,g</sub>, *E*<sub>1,g</sub>, *E*<sub>2,g</sub>, respectively, and *M*<sub>S</sub> equal to zero, see Fig. 2. The *A*<sub>2,g</sub> state is just the ground <sup>3</sup>P state with *M*<sub>1</sub> equal to 0, the *A*<sub>1,g</sub> state is a mixture of <sup>1</sup>D and <sup>1</sup>S states with *M*<sub>1</sub> equal to 0, the *E*<sub>1,g</sub> state is a mixture of <sup>3</sup>P and <sup>1</sup>D states with *M*<sub>1</sub> equal to 1. The *E*<sub>2,g</sub> state is a pure <sup>1</sup>D state with *M*<sub>1</sub> equal to 2. With the current implementation of spin-flip TDDFT, we can only calculate directly the <sup>3</sup>P-<sup>1</sup>D splitting of these atoms. As for the <sup>3</sup>P-<sup>1</sup>S splitting, it can be obtained from the excitation energy to the state with *A*<sub>1,g</sub> symmetry in the following way. The leading term of the wave function of the *A*<sub>1,g</sub> state can be written as

$$\Psi_{A_{1,g}} = \frac{1}{\sqrt{2}}(|p_{-1}^{\alpha}p_1^{\beta}| + |p_1^{\alpha}p_{-1}^{\beta}|). \quad (8)$$

This term is thus a combination of leading terms of <sup>1</sup>D and <sup>1</sup>S states with *M*<sub>1</sub> equal to 0 and can be written approximately as

FIG. 2. The spin-flip transitions out of the atoms with the lowest *p*<sup>2</sup> configuration.

$$\Psi_{A_{1,g}} = \sqrt{\frac{1}{3}}\Psi_{1D(M_1=0)^+} \sqrt{\frac{2}{3}}\Psi_{1S}. \quad (9)$$

The excitation energy of the <sup>1</sup>S state can then be obtained from the excitation energy of the <sup>1</sup>D state and the *A*<sub>1,g</sub> state as

$$E_{1S} = (3E_{A_{1,g}} - E_{1D})/2. \quad (10)$$

From the results in Table II it can be seen that the multiplet splitting directly obtained from SF-TDDFT even with the simple LDA XC potential agrees very well with the experimental data, except for the <sup>4</sup>S-<sup>2</sup>P splitting of N. The error for the splittings is always less than 0.2 eV. On the other hand, the <sup>3</sup>P-<sup>1</sup>S splitting energy obtained from Eq. (10) does not agree quite well with experimental for C and O with the error about 0.6 eV, while the error is much smaller for Si and S.

## C. The singlet-triplet gaps of some diradicals

Another application of spin-flip transitions is to calculate the singlet-triplet separations of the diradicals CH<sub>2</sub>, NH<sub>2</sub><sup>+</sup> and their higher homologous SiH<sub>2</sub> and PH<sub>2</sub><sup>+</sup>. Slipchenko and Krylov<sup>34</sup> have already used *ab initio* spin-flip approaches<sup>35,36</sup> to carry out such calculations. In the present work, we calculated the singlet-triplet gaps of these diradicals studied by Krylov *et al.* with the spin-flip TDDFT approach proposed here. In Table III, we listed the adiabatic energy separations of CH<sub>2</sub>, NH<sub>2</sub><sup>+</sup>, SiH<sub>2</sub> and PH<sub>2</sub><sup>+</sup>. The results from the much more complicated *ab initio* approach CASSCF SOCI and from the *ab initio* spin-flip approach SF-OD (Ref. 34) as well as experimental data<sup>34</sup> are also included in the table for comparison. The <sup>3</sup>B<sub>1</sub> state with an electronic configuration (*a*<sub>1</sub>)<sup>1</sup>(*b*<sub>1</sub>)<sup>1</sup> is used as reference to calculate the transitions



TABLE III. The adiabatic singlet-triplet excitation energies of  $\text{CH}_2$ ,  $\text{NH}_2^+$ ,  $\text{SiH}_2$ ,  $\text{PH}_2^+$  (unit: eV) (geometries are taken from Ref. 34).

	State	SF-TDA <sup>a</sup>	SF <sup>b</sup>	CASSCF SOC <sup>c</sup>	SF-OD <sup>c</sup>	Expt. <sup>c</sup>
$\text{CH}_2$ $^3B_1$	$^1A_1$	0.561	0.544	0.411	0.514	0.390
	$^1B_1$	1.351	1.324	1.450	1.564	1.425
	$^1A_1$	2.638	2.638	2.595	2.674	
$\text{NH}_2^+$ $^3B_1$	$^1A_1$	1.349	1.324	1.281	1.305	1.306
	$^1B_1$	1.837	1.798	1.935	1.941	
	$^1A_1$	3.588	3.588	3.308	3.419	
$\text{SiH}_2$ $^1A_1$	$^3B_1$	0.911	0.924	0.871	0.866	0.91
	$^1B_1$	1.757	1.744	1.992	1.994	1.928
	$^1A_1$	3.187	3.199	3.486	3.537	
$\text{PH}_2^+$ $^1A_1$	$^3B_1$	0.836	0.856	0.760	0.761	0.75
	$^1B_1$	1.828	1.809	2.009	2.015	1.92
	$^1A_1$	3.418	3.435	3.686	3.728	

<sup>a</sup>Using Eq. (6) and the Tamm–Dancoff approximation of Eq. (4).<sup>b</sup>Using Eq. (6).<sup>c</sup>Reference 34.

from this  $^3B_1$  state to the  $^1B_1$  also with the configuration  $(a_1)^1(b_1)^1$  and two  $^1A_1$  states with the  $(a_1)^2$  and  $(b_1)^2$  configurations, respectively, see Fig. 3. The ground state of  $\text{SiH}_2$  and  $\text{PH}_2^+$  is in fact of  $^1A_1$  symmetry corresponding to  $(a_1)^2$  configuration and the energies listed in the table for these two molecules are in fact excitation energies from this  $^1A_1$  state that are calculated from the sum of transition energies from the  $^3B_1$  reference state to the ground  $^1A_1$  state, and from the  $^3B_1$  reference state to the other  $^1A_1$  and  $^1B_1$  excited states. The transition from the ground  $^1A_1$  state to the excited  $^1A_1$

state is an excitation from the electronic configuration  $(a_1)^2$  to  $(b_1)^2$ . This transition is actually a double excitation, which means some double excitations can also be reached using SF-TDDFT with carefully selected reference states. From the results listed in this table, it can be seen that the excitation energies for these systems calculated from SF-TDDFT agree very well with experiment data and with other much more complicated and expensive *ab initio* approaches. Except for the highest  $^1A_1$  excitation energies, the spin-flip TDDFT results are always within 0.2 eV of results from *ab initio* approaches and experimental data.

In addition, we have calculated the adiabatic singlet-triplet gaps of some diatomic molecules with a triplet ground state. The calculated singlet-triplet separations and experimental data<sup>21</sup> are listed in Table IV. The ground state of these molecules is of  $^3\Sigma^-$  symmetry with the electronic configuration  $(\pi)^2$ . This electronic configuration can also result in another two states of  $^1\Delta$  and  $^1\Sigma^+$  symmetry, respectively. The transitions from this  $^3\Sigma^-$  ( $M_S=1$ ) state to the  $^1\Delta$  and  $^1\Sigma^+$  states must involve spin flips. These transitions are similar to the transitions demonstrated in Fig. 2 except for the  $p_{\pm 1} \rightarrow p_0$  transition. In this table we also listed the spin  $\alpha$  and spin  $\beta$  orbital energy difference for the  $\pi$  orbitals. From this table, one can see that the excitation energies of the lower  $^1\Delta$  state agree very well with experimental data with an error of less than 0.15 eV, while the error for excitation energies to  $^1\Sigma^+$  is larger. It can also be seen that the excitation energies to the  $^1\Sigma^+$  state closely resemble the orbital energy difference, while the excitation energies to  $^1\Delta$  is about half that value. This observation can be rationalized in the following way. If we neglect the difference in spin  $\alpha$  and spin  $\beta$  orbitals and the coupling of the  $\pi \rightarrow \pi$  transitions with other transitions, the  $A$  matrix will have a  $4 \times 4$  dimension. Considering that  $\pi_x \rightarrow \pi_x$  and  $\pi_y \rightarrow \pi_y$  transitions will not mix with  $\pi_x \rightarrow \pi_y$  and  $\pi_y \rightarrow \pi_x$  excitations, this  $A$  matrix can be block diagonalized to two  $2 \times 2$  matrixes. Writing next the  $\pi_x$  and  $\pi_y$  orbitals in cylindrical coordinate, we have

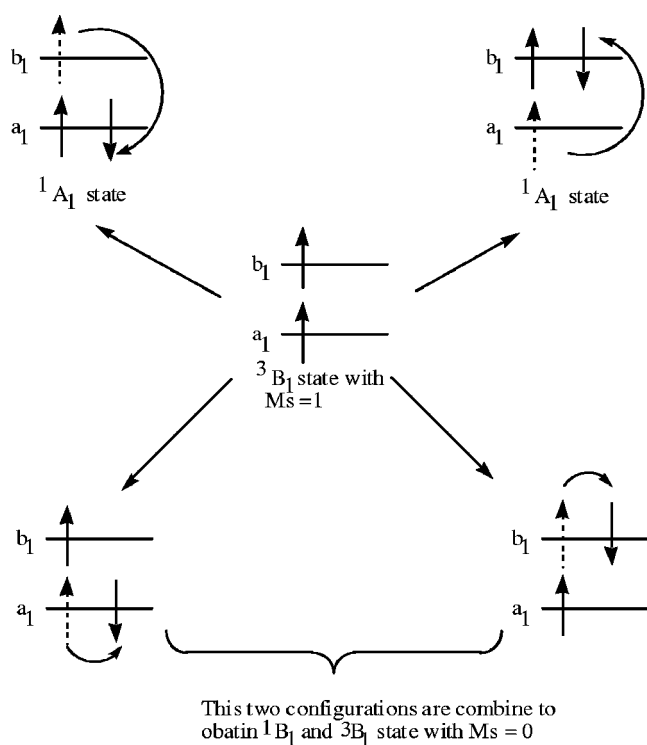


FIG. 3. The spin-flip transitions of some diradicals from triplet reference state.

TABLE IV. The adiabatic singlet-triplet energy gaps of some diatomic diradicals (unit: eV) (geometry and experimental data are taken from Ref. 32).

	$\Delta\epsilon$	$^1\Delta$			$^1\Sigma^+$		
		SF-TDA <sup>a</sup>	SF <sup>b</sup>	Expt.	SF-TDA <sup>a</sup>	SF <sup>b</sup>	Expt.
NH	3.105	1.583	1.542	1.558	3.105	3.105	2.629
NF	2.619	1.348	1.312	1.487	2.603	2.603	2.340
OH <sup>+</sup>	4.248	2.157	2.117	2.190	4.245	4.245	3.602
O <sub>2</sub>	2.059	1.054	1.026	0.980	2.071	2.071	1.636
NO <sup>-</sup>	1.735	0.888	0.862	0.750	1.735	1.735	1.153
PF	1.593	0.774	0.734	0.879	1.594	1.594	1.656
PO <sup>-</sup>	1.098	0.545	0.520	0.554	1.098	1.098	
PH	1.740	0.848	0.808	0.950	1.740	1.740	1.880

<sup>a</sup>Using Eq. (6) and the Tamm–Dancoff approximation of Eq. (4).<sup>b</sup>Using Eq. (6).

$$\psi_{\pi_x} = f(r, z) \cos \theta, \quad \psi_{\pi_y} = f(r, z) \sin \theta. \quad (11)$$

The orbital energy difference between an  $\alpha$  spin  $\pi$  orbital and a  $\beta$  spin  $\pi$  orbital can now be written as

$$\epsilon_{\pi}^{\beta} - \epsilon_{\pi}^{\alpha} = \pi \int (V_{XC}^{\beta} - V_{XC}^{\alpha}) f^2(r, z) r dr dz. \quad (12)$$

The fact that the XC potential should only be a function of  $r$  and  $z$  due to the symmetry has been utilized in Eq. (12). With Eq. (11) and Eq. (12), we obtain the following relations after some derivation:

$$A_{\pi_x \pi_x, \pi_x \pi_x} = A_{\pi_x \pi_x, \pi_y \pi_y} = A_{\pi_y \pi_y, \pi_y \pi_y} = \frac{1}{4}(\epsilon_{\pi}^{\beta} - \epsilon_{\pi}^{\alpha}), \quad (13)$$

$$A_{\pi_x \pi_y, \pi_x \pi_y} = A_{\pi_y \pi_x, \pi_y \pi_x} = \frac{3}{4}(\epsilon_{\pi}^{\beta} - \epsilon_{\pi}^{\alpha}), \quad (14)$$

$$A_{\pi_x \pi_y, \pi_y \pi_x} = \frac{1}{4}(\epsilon_{\pi}^{\beta} - \epsilon_{\pi}^{\alpha}).$$

With Eqs. (13) and (14) SF-TDDFT affords the excitation energies: 0,  $(\epsilon_{\pi}^{\beta} - \epsilon_{\pi}^{\alpha})/2$ ,  $(\epsilon_{\pi}^{\beta} - \epsilon_{\pi}^{\alpha})/2$ , and  $(\epsilon_{\pi}^{\beta} - \epsilon_{\pi}^{\alpha})$  which correspond to the  $^3\Sigma^-$  to  $^3\Sigma^-$  transition, the  $^3\Sigma^-$  to  $^1\Delta$  transition, the  $^3\Sigma^-$  to  $^1\Delta$  transition and the  $^3\Sigma^-$  to  $^1\Sigma^+$  transition, respectively. In fact, one can obtain the same results using a  $\Delta$ SCF DFT approach combined with the method suggested by Ziegler<sup>37</sup> after calculating the energies of the two singlet Slater determinants  $|\pi_x^{\alpha} \pi_x^{\beta}|$  and  $|\pi_x^{\alpha} \pi_y^{\beta}|$ .

#### D. The properties of quartet excited states from spin-flip transitions

The transitions from fully occupied orbitals to virtual orbitals out of a ground doublet state will result in one set of quartet excited states and two sets of doublet excited states. With ordinary TDDFT without spin flips, only two excitation energies can be obtained for this type of transitions, see Fig. 4, and it is already a hard task even to assign the obtained two transitions, let alone fully resolve of the multiplets. In many cases, the two calculated excitation energies are assigned to doublet-doublet transitions,<sup>38</sup> while actually they should be transitions to combinations of all three excited

states. Even with spin flips, we can still obtain only two excitation energies using the ground doublet state as reference. However, the quartet state can be reached from spin-flip transitions. We have studied this type of transitions for CN and SiN. The ground state of these two molecules is  $^2\Sigma^+$  with the electronic configuration  $\pi^2\Sigma^1$ . The lowest unoccupied orbital is the  $\pi^*$  orbital. The spin-flip transition from  $\beta$  spin electron in the  $\pi$  orbital to the  $\pi^*$  orbital with  $\alpha$  spin will result in the quartet states:  $^4\Sigma^+$ ,  $^4\Delta$ , and  $^4\Sigma^-$ . We have calculated the bond length and adiabatic excitation energies of these excited quartet states for SiN and CN. The results and some other theoretical results are listed in Table V. From the results, it can be seen that the adiabatic excitation energies for these excited quartet states obtained from spin-flip TDDFT agree quite well with those obtained from more complicated *ab initio* approaches, while the equilibrium bond lengths are a little too short, likely due to the use of the LDA approximation.

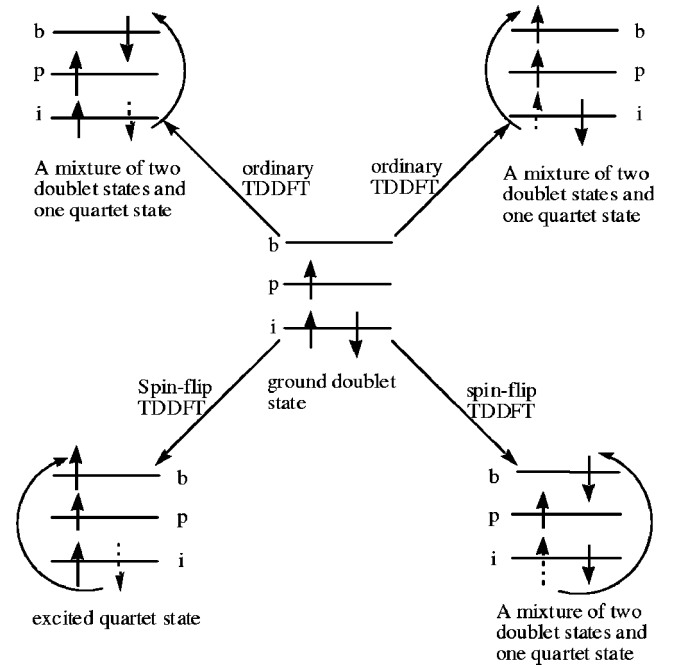


FIG. 4. The transitions from fully occupied orbitals to virtual orbital levels from a ground doublet state using SF-TDDFT and ordinary TDDFT.

TABLE V. The adiabatic excitation energies and equilibrium bond length of the excited quartet states of SiN and CN (the reference data are taken from Ref. 40 with MRCI for CN and from Ref. 39 for SiN with MRDCI).

		Bond length (Å)			Excitation energy (eV)		
	State	SF <sup>a</sup>	SF-TDA <sup>b</sup>	Reference	SF <sup>a</sup>	SF-TDA <sup>b</sup>	Reference
CN <sup>c</sup>	<sup>4</sup> Σ <sup>+</sup>	1.3658	1.3468	1.387	4.909	5.297	4.51
	<sup>4</sup> Δ	1.3491	1.3463	1.390	5.939	6.020	5.77
	<sup>4</sup> Σ <sup>-</sup>	1.3452	1.3452	1.394	6.740	6.740	6.50
SiN <sup>c</sup>	<sup>4</sup> Σ <sup>+</sup>	1.7553	1.7302	1.7566	2.594	2.859	2.752
	<sup>4</sup> Δ	1.7303	1.7267	1.7573	3.229	3.286	3.369
	<sup>4</sup> Σ <sup>-</sup>	1.7218	1.7218	1.7630	3.720	3.720	3.748

<sup>a</sup>Using Eq. (6).<sup>b</sup>Using Eq. (6) and the Tamm–Dancoff approximation of Eq. (4).<sup>c</sup>The ground state is <sup>4</sup>Σ<sup>+</sup>.

### E. The excitation energies for closed-shell systems from spin-flip transitions with triplet state as reference

In most calculations, TDDFT is applied with the ground state as reference. This can be understood since DFT should only be applied to a study of the ground state properties. But it has been argued that DFT may also be used to describe the excited states that are lowest in energy and of another symmetry in space or spin. Using excited states as reference with spin-flip TDDFT will help us resolve the excited states spin multiplets as it will be shown in the next part. In fact, in the above calculations for SiH<sub>2</sub> and PH<sub>2</sub><sup>+</sup>, as well as in our previous study,<sup>13</sup> excited states have already been used as reference. In this part we will study the performance of spin-flip TDDFT with excited states as reference. We have calculated the lowest triplet excitation energies and the singlet-triplet splitting of the same excited configuration with spin-flip

transitions using the lowest triplet state as reference for some molecules with a closed-shell ground state. The results as well as the related energies calculated from ordinary TDDFT using the closed-shell ground state as reference are listed in Table VI. The (SCF results and experimental data are also listed. From these results, one can see that the triplet excitation energies calculated from SF-TDDFT are usually larger than those obtained from ordinary TDDFT, while the results from ΔSCF are usually in between. On the other hand, the singlet-triplet splitting gaps of the excited states from SF-TDDFT are usually smaller than those obtained from ordinary TDDFT while they agree quite well with those obtained from ΔSCF. As far as the experimental data is concerned, it is hard to decide which method is better for triplet excitation energies. However, ordinary TDDFT usually affords better agreement with experiment for the singlet-triplet splitting of the excited states, especially for ethylene, the difference be-

TABLE VI. The singlet-triplet excitation energies and triplet-singlet splitting of the excited state of some closed-shell molecules. (Geometry is taken from Ref. 41 except for H<sub>2</sub>O and naphthalene. The structure of H<sub>2</sub>O is taken from Ref. 9, while the structure of naphthalene is calculated with LDA and TZ2P basis.)

	State	SF-TDA <sup>a</sup>	SF <sup>b</sup>	TDDFT-TDA <sup>c</sup>	TDDFT <sup>d</sup>	ΔSCF	Expt. <sup>e</sup>
CH <sub>2</sub> O	<sup>3</sup> A <sub>2</sub>	3.481	3.492	3.030	3.003	3.252	3.50
	<sup>1</sup> A <sub>2</sub>	0.533	0.482	0.629	0.626	0.487	0.57
C <sub>2</sub> H <sub>4</sub>	<sup>3</sup> B <sub>1u</sub>	4.838	4.881	4.794	4.669	4.783	4.36
	<sup>1</sup> B <sub>1u</sub>	1.777	1.775	3.646	3.104	1.781	3.24
H <sub>2</sub> O	<sup>3</sup> B <sub>1</sub>	8.661	8.668	6.259	6.249	7.413	7.2
	<sup>1</sup> B <sub>1</sub>	0.408	0.366	0.238	0.235	0.363	0.2
Pyridine	<sup>3</sup> B <sub>1</sub>	3.155	3.227	3.122	3.066	3.148	3.0
	<sup>1</sup> B <sub>1</sub>	0.611	0.609	1.207	1.060	0.609	1.15
Naphthalene	<sup>3</sup> B <sub>2u</sub>	4.448	4.458	3.712	3.691	4.114	4.1
	<sup>1</sup> B <sub>2u</sub>	0.459	0.431	0.570	0.543	0.431	0.58

<sup>a</sup>Using Eq. (6) and the Tamm–Dancoff approximation of Eq. (4).<sup>b</sup>Using Eq. (6).<sup>c</sup>Using Eq. (5) and the Tamm–Dancoff approximation of Eq. (4).<sup>d</sup>Using Eq. (5).<sup>e</sup>The experimental data are taken from Ref. 3 except for H<sub>2</sub>O and naphthalene. The experimental data for H<sub>2</sub>O is taken from Ref. 9 and that for naphthalene is taken from Ref. 42.



tween these two approaches amounts to about 1.5 eV, while the experiment data agrees quite well with that from ordinary TDDFT.

The performance of spin-flip TDDFT, ordinary TDDFT, and  $\Delta$ SCF can be understood in the following way. Using TDA, SPA, and neglecting the orbital relaxation, we can write the triplet excitation energies for the three approaches after some derivation as

$$\omega_T^{\text{TDDFT}} = \varepsilon_a^0 - \varepsilon_i^0 + [\psi_a \psi_i | f_{\text{XC}}^{\downarrow\downarrow} + f_{\text{XC}}^{\uparrow\uparrow} | \psi_i \psi_a], \quad (15)$$

$$\omega_T^{\text{SF}} \approx \omega_T^{\text{TDDFT}} + [\Delta\rho | f_H + f_{\text{XC}}^{\uparrow\uparrow} | \Delta\rho], \quad (16)$$

$$\omega_T^{\Delta\text{SCF}} \approx \omega_T^{\text{TDDFT}} + \frac{1}{2}[\Delta\rho | f_H + f_{\text{XC}}^{\uparrow\uparrow} | \Delta\rho], \quad (17)$$

where  $\Delta\rho = |\psi_a|^2 - |\psi_i|^2$ . In the above derivation for the excitation energies of spin-flip TDDFT and  $\Delta$ SCF, the XC energy functional and XC potential of the triplet state is expanded around that of a closed-shell state to the second- and first-order, respectively. Equations (15)–(17) can explain that the triplet state excitation energies from spin-flip TDDFT are usually larger than those from ordinary TDDFT while the excitation energies from  $\Delta$ SCF are usually in between. The difference between spin-flip TDDFT and ordinary TDDFT in the triplet excitation energies are mostly the “charge-transfer term” called by Casida,<sup>29</sup> and Casida also argued that this term should vanish with exact XC functionals and XC potentials. As for the singlet-triplet splitting for the excited states, we have the following relation with the same approximations and expansions:

$$\Delta\omega_{\text{ST}}^{\text{TDDFT}} = 2[\psi_a \psi_i | f_H + f_{\text{XC}}^{\downarrow\downarrow} | \psi_i \psi_a], \quad (18)$$

$$\Delta\omega_{\text{ST}}^{\text{SF}} = \Delta\omega_{\text{ST}}^{\Delta\text{SCF}} = \Delta\omega_{\text{ST}}^{\text{TDDFT}} - 2[\psi_a \psi_i | f_H + f_{\text{XC}}^{\uparrow\uparrow} | \psi_i \psi_a]. \quad (19)$$

With Eq. (19) we can understand that the singlet-triplet splitting of the excited state from spin-flip TDDFT and  $\Delta$ SCF agrees very well with each other while both are smaller than results from ordinary TDDFT. The difference in this splitting between spin-flip TDDFT and ordinary TDDFT are just twice that difference in doublet-doublet excitation energies of these two type transitions in Eq. (7). As the same arguments for the last two terms on rhs of Eq. (7), this difference should generally be small. This is indeed the case in our results except for ethylene. After further study the contributions to the transitions of this excited singlet state, we found some other transitions also contribute substantially to this excited state and SPA will fail for this singlet excitation. This may explain the large difference between these two type transitions.

## F. The resolution of excited states spin multiplets

As has been mentioned above, both ordinary TDDFT and spin-flip TDDFT cannot fully resolve the excited state multiplets resulting from transitions from a fully occupied orbital to virtual orbitals with the doublet ground state as reference. On the other hand, we can possibly do this if we use the excited quartet state as reference. Furthermore, only through spin-flip transitions can we obtain the excitation en-

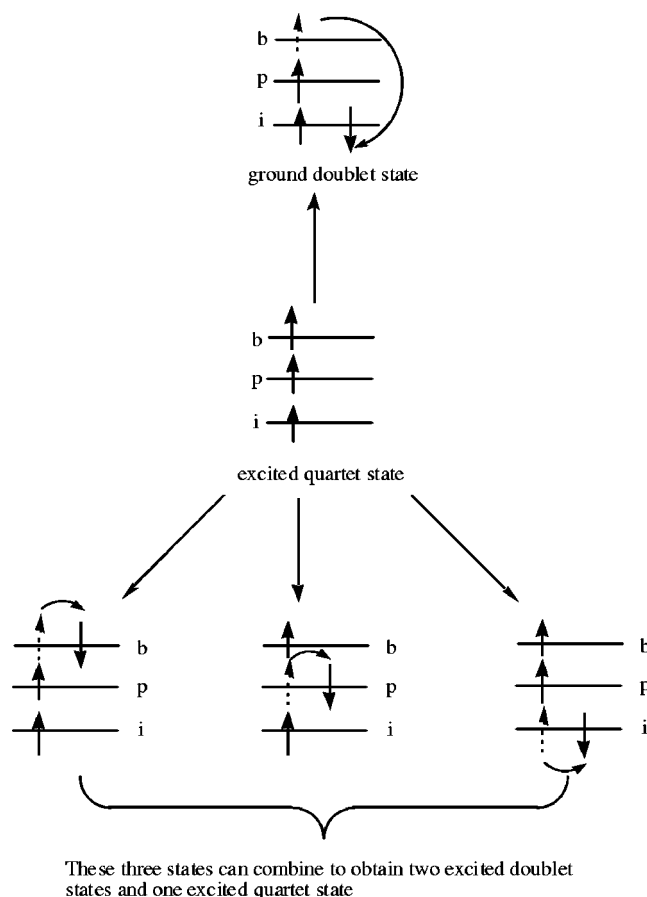


FIG. 5. The resolution of excited state spin multiplets with quartet state as reference using SF-TDDFT.

ergies for all the spin-multiplet states, see Fig. 5. We calculated the adiabatic excitation energies from this type of transitions for CF, CH, and  $\text{NH}^+$  and the calculated results and experimental data are listed in Table VII. The excitations for these molecules are a little different from the excitations plotted in Fig. 5, where a more general case was displayed.

TABLE VII. The adiabatic excitation energies of excited state spin multiplets for some open-shell molecules using quartet state as reference (unit: eV) (geometry and experimental data are taken from Ref. 32).

	State	SF-TDA <sup>a</sup>	SF <sup>b</sup>	Expt. <sup>c</sup>
CF	$4\Sigma^-$	3.341	3.348	2.728
	$2\Delta$	5.685	5.680	6.125
	$2\Sigma^-$	6.740	6.738	
	$2\Sigma^+$	7.515	7.522	5.293
CH	$4\Sigma^-$	0.477	0.490	0.725
	$2\Delta$	2.598	2.567	2.875
	$2\Sigma^-$	2.774	2.733	3.229
	$2\Sigma^+$	3.868	3.880	3.943
$\text{NH}^+$	$4\Sigma^-$	-0.173	-0.155	0.062
	$2\Sigma^-$	2.433	2.376	2.752
	$2\Delta$	2.649	2.630	2.889
	$2\Sigma^+$	4.522	4.539	4.339

<sup>a</sup>Using Eq. (6) and the Tamm–Dancoff approximation of Eq. (4).

<sup>b</sup>Using Eq. (6).

<sup>c</sup>Geometry and experimental data are taken from Ref. 32.

The ground state of these molecules is  $^2\Pi$  with the electronic configuration  $\sigma^2\pi^1$  and the  $\sigma \rightarrow \pi$  transition is in this catalogue. This transition will result in the  $^4\Sigma^-$ ,  $^2\Delta$ ,  $^2\Sigma^-$ , and  $^2\Sigma^+$  states. It is impossible to obtain all these pure states if the ground  $^2\Pi$  state are used as reference with TDDFT. However, if the excited  $^4\Sigma^-$  state is used as reference, we can resolve all these excited states resulting from the configuration  $\sigma^1\pi^2$  with spin flip transitions. One more interesting point is that unlike the  $^2\Pi$  state, the  $^4\Sigma^-$  state is spatially nondegenerate and the spacious symmetry can be kept in the calculations. From the results in this table, one can see that except for the highest excited state of CF, the obtained excitation energies are satisfactory compared with the experimental data with an error around 0.3–0.5 eV. The fact that the ground state of  $\text{NH}^+$  cannot be correctly predicted can be attributed to the small excitation energy of the  $^4\Sigma^-$  state.

#### IV. CONCLUSION

In the present work, the reliability of the newly proposed formulation of TDDFT based on the noncollinear XC potential for the excitation energies involving spin flips was tested. We compared the doublet-doublet excitation energies calculated from spin-flip transitions to those obtained by ordinary TDDFT. Generally the results from these two approaches agree quite well with each other. According to our analysis, the numerical difference obtained between calculations based on SF and ordinary TDDFT can be ascribed to the approximated XC potential used in the calculations. We applied SF-TDDFT to the calculation of the multiplet splitting of some atoms, the singlet-triplet gaps of some diradicals, the properties of some quartet states with doublet state as reference. The results show great promise in calculation for excitation energies with spin flip transitions. Furthermore, we need to calculate the transition energies with excited states as reference to fully resolve the excited states spin-multiplets. Trial calculations on closed-shell molecules with the lowest triplet state as reference demonstrate the reliability of SF-TDDFT and the use of excited states as reference has been used to fully resolve the excited states resulting from transitions from fully occupied orbitals to virtual orbitals. Again, in most cases the calculated excitation energies agree well with experimental results even using the simple LDA XC potential.

#### ACKNOWLEDGMENTS

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