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# A Simplified Spin-Flip Time-Dependent Density Functional Theory Approach for the Electronic Excitation Spectra of Very Large **Diradicals**

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Supporting Information

ABSTRACT: Experimentalists working with diradicals are often facing the question of what kind of species among singlet or triplet diradicals or closed-shell molecules are observed. To treat large diradicals with a high density of electronic states, we propose a simplified version of the spinflip time-dependent density functional theory (SF-TD-DFT) method for a fast computation of their state energies and absorption spectra with an accuracy similar to the nonsimplified scheme. An ultrafast tight-binding variant called SFsTD-DFT-xTB is also developed to treat even larger systems. For a benchmark set of nine diradicals, good agreement



between simplified and conventional SF excitation energies for standard functionals is found. This shows that the proposed parameterization is robust for a wide range of Fock exchange mixing values. With the asymptotically correct response integrals used in SF-sTD-DFT and a correction factor of  $\sqrt{2}$  for the transition moments, the SF-sTD-DFT/B5050LYP/cc-pVDZ method even outperforms the nonsimplified scheme at drastically reduced computational effort when comparing to the experimental absorption spectra for this set of diradicals. To showcase the actual performance of the method, absorption spectra of two  $\mu$ -hydroxo-bridged dimers of corrole tape Ga(III) complex derivatives were computed and compared to the experiment, providing good qualitative agreement. Finally, a comparison with the high-spin triplet spectrum of a perylene bisimide biradical and the one determined at the SF-sTD-DFT level showed that at room temperature, mostly triplet diradicals are present in solution.

#### 1. INTRODUCTION

A molecule with two nearly degenerated singly occupied molecular orbitals (SOMOs) is called a diradical<sup>1</sup> and can either be in a singlet or triplet spin state. Although the synthesis of large stable open-shell diradicals is a challenging task, the identification of the open-shell nature of the compound could be difficult, requiring extra experiments such as electron spin resonance (ESR) or superconducting quantum interference device (SQUID) measurements.<sup>2</sup> Quantum chemical calculations are usually needed to further identify the character of the species. Often unrestricted mean-field electronic structure methods are used to characterize the open-shell nature of the system. For the low-spin case, these methods are not adequate because of the near-degeneracy of the SOMOs, leading often to a large amount of spin contamination in the wave function. A singlet diradical should be described by a multiconfigurational wave function with strong contributions from (restricted) doubly excited determinants. In the unrestricted scheme, singlet and triplet configurations are mixed leading to excited states that could be contaminated by higher multiplets. Neese<sup>3</sup> showed that unrestricted solutions provide poor spin densities. Despite these drawbacks, to compute singlet-triplet and quartet-doublet energy gaps of large systems, unrestricted methods are still widely used. Krylov $^{4-7}$  proposed the efficient spin-flip (SF) method to treat such systems. It starts with a single determinant treatment of high-spin ( $\alpha \alpha$ ) triplet state, which is normally well behaved. The target open-shell singlet state is then obtained by spin-flipping excitations ( $\Delta S_z = -1$ ) from this reference triplet state.

Figure 1 schematically represents this procedure for a fourorbital/four-electron model. The type I set of determinants represent configurations generated by a single flip-down within open-shell orbitals and forms a spin-complete ensemble. Type II are closed-shell to open-shell, type III are open-shell to virtual, and type IV are closed-shell to virtual excitations. These last three sets are not complete, that is, they do not form a spin-pure  $m_{\rm s} = 0$  set of configurations. They miss their spin-counterparts (represented in light gray). These missing configurations can

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Figure 1. SF target determinants (in dark gray) generated from a high-spin triplet state for a four-orbital/four-electron system. In white gray are represented some of the missing spin-counterparts.



5. Bisan<br/>thene derivative 1 $\,$  6. Bisan<br/>thene derivative 2 $\,$  7. Bisan<br/>thene derivative 3 $\,$ 



9. Superoctazethrene derivative (SOZ-CI)

# Figure 2. Nine diradical systems.<sup>24–27</sup>

lead to a spin-contaminated solution if the target state involves others than type I configurations. However, for most low-lying SF states, their contribution is small resulting in typically small spin contamination. Several ways were proposed to circumvent

this, such as spin-adapted (SA-) SF time-dependent density functional theory (SF-TD-DFT)<sup>8</sup> and mixed-reference SF-TD-DFT<sup>9</sup> methods, but these are out of the scope of the present investigation.

In its original (collinear) formulation, the SF-TD-DFT<sup>10</sup> method was only available for hybrid exchange-correlation functionals because SF states are only coupled by the Hartree-Fock exchange operator. This formalism was extended to semilocal functionals and reformulated by using a noncollinear exchange–correlation kernel.<sup>11–13</sup> The SF-TD-DFT method describes excitation energies 10-17 with a similar accuracy that is usually achieved by highly correlated methods. Although SF-TD-DFT can be applied routinely to systems with about a hundred atoms, however, larger diradicals with high densities of electronic states or involving flexible molecular units are still out of the scope. Note that for applications involving large molecular magnets, it is particularly important to provide good singlettriplet energy gaps that are directly linked to their exchangecoupling constants. Orms and Krylov<sup>18</sup> showed that for such applications on binuclear copper molecular magnets, the SF-TD-DFT method with PBE50 and B5050LYP exchangecorrelation functionals perform as well as the equation-ofmotion SF coupled-cluster method with single and double substitutions (EOM-SF-CCSD).

Here, we propose a SF version of the simplified timedependent density functional theory (sTD-DFT) method proposed by Grimme and co-workers.<sup>19–21</sup> This method was designed to treat very large systems on the order of a thousand atoms routinely. The key of this approach is to approximate the time-dependent part of the treatment by short-range damped Coulomb interactions of transition density monopoles to evaluate two-electron integrals. To treat larger systems more efficiently, a tight-binding-based version (sTD-DFT-xTB)<sup>21</sup> was developed. Recently, two of us successfully extended the capability of the sTD-DFT method for the computation of the first hyperpolarizability<sup>22</sup> and excited-state absorption spectra.<sup>23</sup>

Figure 2 presents the nine diradical systems chosen to benchmark the SF-sTD-DFT method. We carefully selected those systems to be still able to run full SF-TD-DFT calculations on them which is taken in addition to experimental spectra as a reference. Except for para-quinodimethane (PQM) which is quite unstable, experimental absorption spectra are available for all of these compounds.<sup>24-27</sup> The di-p-quinodimethane (di-PQM) and tri-p-quinodimethane (tri-PQM) derivatives<sup>24</sup> are composed of several PQM units connected together and yielding planar  $\pi$ -conjugated systems. The cyano groups in these derivatives tend to stabilize diradicals against molecular oxygen, whereas the 4-octylphenyl and phenyl groups increase the solubility and stabilize the two diradicals probably kinetically. Teranthene derivative<sup>25</sup> and the three mesosubstituted bisanthenes<sup>26</sup> are singlet diradical polycyclic aromatic hydrocarbons that are related to nanographenes. To prevent the oxidative addition of singlet oxygen, all of them are substituted at the mesoposition by bulky groups, which increases the solubility. Trifluoromethylphenyl and triisopropylsilylethynyl electron-withdrawing groups are supposed to stabilize the bisanthene core. Another type of graphene-like molecules is Zshaped zethrenes: octazethrene (OZ-TIPS) and superoctazethrene (SOZ-CI) derivatives.<sup>27</sup> For the nine diradicals composing our benchmark set, we first compare SF-sTD-DFT singlettriplet gaps to the respective SF-TD-DFT ones. Second, SF-TD-DFT, SF-sTD-DFT, and SF-sTD-DFT-xTB absorption spectra are compared to experimental ones. Figure 3 presents eight smaller diradical systems taken from ref 13: trimethyl-methane, o-benzyne, *m*-benzyne, *p*-benzyne,  $\alpha$ ,2-didehydrotoluene,  $\alpha$ ,3didehydrotoluene,  $\alpha$ ,4-didehydrotoluene, and *m*-xylylene. To further assess the performance of the SF-sTD-DFT method, we



compare total ground state energies for this second set of smaller diradicals to ones determined at the EOM-SF-CCSD(dT) level.<sup>13</sup> To show the capability of SF-sTD-DFT and SF-sTD-DFT-xTB methods to reproduce experimental absorption of large diradicals, we study two stable face-to-face singlet diradicaloids: triply-linked corrole dimer gallium(III) complexes with two  $\mu$ -hydroxo-bridges<sup>28</sup> (Figure 4). Finally, a perylene bisimide derivative (PBI) diradical<sup>29</sup> is the last challenging system investigated here. Note that molecular magnets containing transition metals similar to those studied by Orms and Krylov<sup>18</sup> are out of the scope of this method because the monopole approximation in the sTD methods is expected to be very inaccurate for local transitions involving d-orbitals.

This paper is organized as follows: Section 2.1 presents the SF-sTD-DFT formalism, Computational Details are provided in Section 2.2, Section 3 presents the results, and conclusions are given in Section 4.

#### 2. METHODS

**2.1. Theory.** The SF-sTD-DFT level of theory starts from a high-spin reference state from which SF states are constructed. If the first SF state is the open-shell singlet ground state, it should suffer less from spin contamination as if it was determined by a regular unrestricted DFT calculation. To determine the absorption spectrum, the first SF state to higher SF state transition dipole moments needs to be calculated. Recently, we showed that the state-to-state transition dipole moment is easily derived from the double residue of the sTD-DFT quadratic-response function.<sup>22,23</sup> In this section, we applied the sTD-DFT approximations<sup>19–23</sup> to the SF-TD-DFT formalism and expressed the SF state to SF state transition dipole moment. In the following, *p*,*q*,*r*,*s* indices refer to general molecular orbitals, *i*,*j*,*k*,*l* to occupied and *a*,*b*,*c*,*d* to unoccupied molecular orbitals.

In the density-based linear-response TD-DFT formalism,  $^{30-36}$  when the external perturbation is switched off, the TD-DFT equation reads

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

allowing one to compute excited-state energies  $(\omega_n)$  and their eigenvectors  $(\mathbf{X}_n \text{ and } \mathbf{Y}_n)$ , where

$$A_{ia,jb} = \delta_{ij}\delta_{ab}(\epsilon_a - \epsilon_i) + 2(ialjb) - a_x(ijlab) + (1 - a_x)(ialf_{\rm XC}|jb)$$
(2)

and



Figure 4. Two  $\mu$ -hydroxo-bridged dimers of corrole tape Ga(III) complex derivatives.<sup>28</sup>

$$B_{ia,jb} = 2(ialbj) - a_x(iblaj) + (1 - a_x)(ialf_{XC}|bj)$$
(3)  $y_{\alpha \to \beta} = a_x + 0.3$ 

considering a global hybrid density functional in the singlet restricted case.  $a_x$  is the amount of Fock exchange,  $\epsilon_p$  is the energy of the p orbital, (ialjb), (ialbj), and (iblaj) are exchange type integrals in the Mulliken notation, (ijlab) is a Coulomb-type integral, and  $(ialf_{\rm XC}|jb)$  and  $(ialf_{\rm XC}|bj)$  are the responses of the exchange–correlation functional. Because the SF treatment generally starts from a higher lying (high-spin) reference state, in its original formulation, SF-TD-DFT is performed in the Tamm–Dancoff approximation to TD-DFT<sup>31</sup> to avoid the occurrence of complex excitation energies. In this formalism, only single excitations from the  $\alpha$  space to the  $\beta$  space are considered. For collinear functionals, exclusively, the  $(i_{aja}|a_{\beta}b_{\beta})$  two-electron integrals remain and the SF-TD-DFT eigenvalue equation becomes

$$\mathbf{A}^{\alpha \to \beta} \mathbf{X}^{\mathbf{SF}} = \omega \mathbf{X}^{\mathbf{SF}} \tag{4}$$

where

$$A_{i_{a}a_{\beta},j_{a}}^{\alpha\to\beta} = \delta_{i_{a}j_{a}}\delta_{a_{\beta}b_{\beta}}(\epsilon_{a_{\beta}} - \epsilon_{i_{\alpha}}) - a_{x}(i_{a}j_{\alpha}|a_{\beta}b_{\beta})$$
(5)

In the sTD-DFT framework, both **A** and **B** matrices in eq 1 are simplified by neglecting the response of the exchange– correlation functional. This limits our SF-sTD-DFT approach to the collinear case. Two-electron integrals are approximated by short-range damped Coulomb interactions of transition density monopoles

$$(pq|rs)' = \sum_{A}^{N} \sum_{B}^{N} q_{pq}^{A} q_{rs}^{B} \Gamma_{AB}$$
(6)

where  $q_{pq}^A$  are transition charge densities centered on atom A determined by a Löwdin population analysis.  $\Gamma_{AB}$  is the Mataga–Nishimoto–Ohno–Klopman<sup>37–39</sup> damped Coulomb operator. With respect to the original sTD-DFT formulation,<sup>19</sup> considering  $\alpha \rightarrow \beta$  single excitations, the damped Coulomb operator has been adjusted and reparameterized

$$\Gamma_{AB}^{\alpha \to \beta} = \left(\frac{1}{\left(R_{AB}\right)^{y_{\alpha \to \beta}} + \left(1.4 \times a_x \eta\right)^{-y_{\alpha \to \beta}}}\right)^{1/y_{\alpha \to \beta}}$$
(7)

 $y_{\alpha \to \beta} = a_x + 0.3 \tag{8}$ 

The chemical hardness values used are tabulated for all elements.<sup>40</sup> Note that an empirical parameter of 1.4 in eq 7 multiplies the amount of exact exchange in the denominator to best reproduce SF-TD-DFT excitation energies in our benchmark set. In the SF-sTD-DFT formalism,  $A^{\alpha \to \beta}$  matrix elements are expressed as

$$A_{i_{\alpha}a_{\beta}j_{\alpha}b_{\beta}}^{\prime\alpha\rightarrow\beta} = \delta_{i_{\alpha}j_{\alpha}}\delta_{a_{\beta}b_{\beta}}(\epsilon_{a_{\beta}} - \epsilon_{i_{\alpha}}) - (i_{\alpha}j_{\alpha}|a_{\beta}b_{\beta})_{\alpha\rightarrow\beta}^{\prime}$$
(9)

In addition to these two approximations, the single configuration space is truncated based on an energy cutoff parameter.<sup>19</sup> From the sTD-DFT state-to-state transition dipole moment expression,<sup>23</sup> its SF analogue reads

$$\langle m|\mu_{\xi} - \langle 0|\mu_{\xi}|0\rangle|n\rangle_{\rm SF} = \frac{\sqrt{2}}{2} \left\{ \sum_{a_{\beta}i_{\alpha}j_{\alpha}} [X_{i_{\alpha}a_{\beta}}^{n}\mu_{i_{\alpha}j_{\alpha},\xi}X_{j_{\alpha}a_{\beta}}^{m}] - \sum_{a_{\beta}b_{\beta}i_{\alpha}} [X_{i_{\alpha}a_{\beta}}^{n}\mu_{a_{\beta}b_{\beta},\xi}X_{b_{\beta}i_{\alpha}}^{m}] \right\}$$
(10)

Note that the prefactor 1/2 results from the unrestricted expression of the quadratic response function and we multiply it by  $\sqrt{2}$  to partially correct for the missing excitations in the  $\alpha$ space, like it is done in the restricted model. Although this prefactor double-counts the four unique type I excitations (Figure 1), it corrects for missing types II, III, and IV ones and strongly improves the description of the computed transition moments (see the Appendix in the Supporting Information for more information). Expression 10 is the trace of the product between the dipole moment matrix and the one-electron transition density matrix (1-TDM) between two SF states. Thus, all excitations from a SF state to another can be decomposed in two blocks: occupied-occupied  $\alpha$ -spin and unoccupied–unoccupied  $\beta$ -spin blocks, constraining drastically the singly excited space. Note that each block of the 1-TDM between SF states could be diagonalized to provide SF natural transition orbitals. This will be the subject of a future study on indenofluorenes and expanded quinoidal analogues.<sup>41</sup> The SFstate-to-SF-state oscillator strength

where

$$f_{mn} = \frac{2}{3}(\omega_m - \omega_n)\vec{\mu}_{mn}\cdot\vec{\mu}_{nm}$$
(11)

allows one to compute optical excitation spectra in the dipolelength formalism. Additionally, a SF version of the tight-binding sTD-DFT-xTB method<sup>21</sup> has been implemented. Here, the effective Fock exchange parameter in the sTDA part is changed to  $a_x = 0.36$ , whereas  $y_{\alpha \to \beta} = 3.0$ . For clarity, it is noted that the monopole correction  $\Delta_K$  for the "exchange-type" (Coulomb response) integrals is zero in SF-sTD-DFT-xTB. The vTB and xTB parts remain unchanged compared to the original formulation for open-shell systems.<sup>21</sup>

**2.2. Computational Details.** Both SF-sTD-DFT and SF-sTD-DFT-xTB methods are implemented in the sTDA program,<sup>19</sup> allowing to compute SF-state-to-SF-state transitions. Computation times of these methods are similar to those at the sTDA and sTDA-xTB levels. For more information on the computational performance see the original sTDA and sTDA-xTB publications.<sup>19,21</sup>

Except for PQM, the eight smaller diradicals, and the two faceto-face singlet diradicaloids, all geometries of the first SF state were optimized at the SF-TD-DFT/B5050LYP/cc-pVDZ level of theory. The geometry of PQM is taken from ref 42. Geometries of the first SF state of trimethyl-methane, o-benzyne, *m*-benzyne, *p*-benzyne,  $\alpha$ ,2-didehydrotoluene,  $\alpha$ ,3-didehydrotoluene,  $\alpha$ ,4-didehydrotoluene, and *m*-xylylene were taken from ref 13 as well as their energies at the EOM-SF-CCSD(dT) and SF-TD-DFT(non-collinear)/B5050LYP levels using the ccpVTZ basis set. The two face-to-face singlet diradicaloids (Figure 4) were optimized with the GFN2-xTB method.<sup>43</sup> To parameterize  $y_{\alpha \rightarrow \beta}$  as a function of the amount of exact exchange, our benchmark study was carried out on the two first SF states determined with the B5050LYP,<sup>10</sup> B3LYP,<sup>44</sup> PBE0,<sup>45</sup> PBE50, and BHandHLYP<sup>46</sup> exchange-correlation functionals. Because the cc-pVDZ basis set was used for parameterization, it is possible that  $y_{\alpha \to \beta}$  is not optimal for other basis sets. However, the expected effects are on the order of a few tenth of an eV or less and hence smaller that the intrinsic accuracy of the method.

All optimizations, SCF, and SF-TD-DFT calculations were done with the Q-Chem  $5.1^{47}$  quantum chemistry package. The SF-sTD-DFT calculations were computed by the sTDA program.<sup>19</sup> All excitations up to 7 eV were computed for all absorption spectra with sTDA. For the benchmark set, only the first 15 SF states were calculated using the SF-TD-DFT method. To model the absorption spectra, transition strengths were broadened by Gaussians with a half width at 1/e maximum of 0.1-0.2 eV to best reproduce the experimental absorption bands.

Apart from the aforementioned systems, we study a PBI in Section 3.5. Here, all optimizations and ground state calculations were done with the TURBOMOLE suite of programs (version 7.2).<sup>48–50</sup> The geometry was optimized at the PBEh-3c level of theory<sup>51</sup> and verified as minima by a harmonic frequency calculation. Single-point energy calculations were then computed with the BHandHLYP<sup>46</sup> functional employing the def-TZVP<sup>52</sup> basis set, with extra diffuse functions on the oxygen atoms (option *flat 2sp* in TURBOMOLE) and the COSMO<sup>53</sup> implicit solvation model ( $\epsilon = 8.93$ ).

### 3. RESULTS AND DISCUSSION

**3.1. Benchmark Set: Excitation Energies.** To benchmark the SF-sTD-DFT method with the SF-TD-DFT level as a reference, we consider *vertical* singlet—triplet energy gaps where,

except for PQM, geometries of the first SF state were taken. We did not make any comparison to experimental gaps as they are related to *adiabatic* excitation energies. They are dependent on the equilibrium geometries of both states and include zero-point energy corrections.<sup>6</sup> The complete basis set limits should ideally be employed as well. To avoid these additional complexities and uncertainties, we prefer to compare our simplified method directly to the non-approximated one. Figure 5 compares



**Figure 5.** Singlet-triplet energy gaps for the nine benchmark compounds obtained at both SF-TD-DFT levels with collinear and noncollinear exchange-correlation kernels in comparison with the sTD-DFT method.

singlet—triplet energy gaps (first SF excitation energy) obtained with B5050LYP exchange correlation functional for SF-sTD-DFT, SF-TD-DFT/collinear, and SF-TD-DFT/noncollinear methods. Except for compound 8 (OZ-TIPS) for which the gap is almost zero, the proposed parameterization seems to reproduce well all trends. Considering a collinear exchange correlation kernel as a reference, we observe a maximum averaged deviation (MAD) of 0.084 eV and a root mean square deviation (RMSD) of 0.159 eV. With a MAD of 0.076 eV and a RMSD of 0.101, the simplified scheme slightly better reproduces SF-TD-DFT values obtained with a noncollinear exchange correlation functional which is supposed to be more accurate. Considering energy gaps between the triplet reference and the second SF states (Figure 6), the agreement is even better with an



**Figure 6.** Energy gaps between the second SF state and the triplet reference for the nine benchmark compounds obtained at both SF-TD-DFT levels with collinear and noncollinear exchange–correlation kernels in comparison with the sTD-DFT method.

MAD of 0.064 eV (RMSD = 0.128 eV) with respect to the SFTD-DFT/collinear level of theory and an MAD of 0.058 eV (RMSD = 0.073 eV) for the noncollinear variant. Similarly, good agreement is observed for the other exchange correlation functionals (Figures S1-S8). Same observations can be done for the third and fourth SF states (see Figure 7). Note that for the





third SF state of the three bisanthene molecules, we have a similar underestimation by the SF-sTD-DFT method with respect to the unsimplified scheme. For this set of nine diradicals, we can conclude that the parameterization is robust for a wide range of Fock exchange mixing values. The next step is to investigate how the SF-sTD-DFT method is able to reproduce experimental absorption spectra of diradicals.

**3.2. Benchmark Set:** Absorption Spectra. Figure 8 compares experimental spectra<sup>24–27</sup> to SF-TD-DFT, SF-sTD-DFT, and SF-sTD-DFT-xTB results. Because only the first 15 states were computed at the SF-TD-DFT level of theory, the higher energy parts of the spectra could not be reproduced. We used the BS050LYP exchange correlation functional because it showed the best performance in the original SF-TD-DFT publication.<sup>10</sup> It is possible that better agreement could be



Figure 8. Experimental absorption spectra<sup>24-27</sup> for compounds 2 to 9 compared to SF-TD-DFT and SF-sTD-DFT/B5050LYP/cc-pVDZ calculations. For clarity, we have omitted the comparison with the SF-TD-DFT method for the three meso-substituted bisanthene derivatives.

achieved with other functionals but this will not be explored in this work. Note that all absorption spectra were recorded in solution and that solvent effects are not included in the simulations. Furthermore, the impact of a finite temperature on the population of higher vibrational or electronic states is neglected. The aim of our work here is to show possible method capabilities and not to obtain the best agreement with the experiment. Tri-PQM is the largest molecule of this set. The SFsTD-DFT calculation used 2300 basis functions to compute 327 SF states in 1.3 min on an eight-core desktop computer (Intel core i7-6700, 3.40 GHz). In comparison, the SCF part took 192.45 min on a 28-core cluster node. The semiempirical variant SF-sTD-DFT-xTB used 1028 basis functions to compute 249 SF states in 0.4 min on the same 8-core computer. The full SF-TD-DFT calculation to compute 15 SF states took 2305.62 min on a 28-core cluster node. Considering di-PQM, the experimental spectrum is dominated by one main band at 620 nm. The SFsTD-DFT-xTB method perfectly matches the energy position of the peak (exp.: 2.00 eV, SF-sTD-DFT-xTB: 1.99 eV) with a slightly lower extinction coefficient ( $\epsilon$ ). A blue shift of 63 nm (0.22 eV) is observed at the SF-sTD-DFT level (2.22 eV) with a slightly higher  $\epsilon$  value. Surprisingly, the SF-TD-DFT method (2.36 eV) provides the worst agreement with a wavelength shift of almost 100 nm (0.36 eV) and largely overestimates the cross section. For tri-PQM, although the SF-sTD-DFT method performs as good as for di-PQM, its xTB variant strongly underestimates the intensity of the first peak. The nonsimplified scheme provides a similar agreement as for the SF-sTD-DFT method in reproducing the main band  $\epsilon$  located at 840 nm but strongly overestimates the small band observed at 616 nm. For the teranthene derivative, the best agreement is obtained by the SF-sTD-DFT method (1.48 eV, exp.: 1.42 eV). Its xTB variant shows a similar accord (1.56 eV). The SF-TD-DFT method (1.66 eV) blue shifts the main absorption band by 126 nm but the  $\epsilon$  value seems in better agreement with the experiment. Note that we could have chosen a smaller band broadening width, providing a slightly better agreement for simplified methods. Considering the three meso-substituted bisanthenes, we only present the comparison with the SF-sTD-DFT method to have a more readable graph. Because absorptions are normalized, only the band position is of interest. The simplified method reproduces trends when changing the meso-substituted groups, with the same systematic energy shift as observed experimentally. For the two Z-shaped zethrenes, the SF-sTD-DFT method provides the best agreement with respect to the experiment. Its semiempirical xTB variant shows excitation energies similar to the SF-sTD-DFT scheme but the  $\epsilon$  values are of poor quality. The SF-sTD-DFT/B5050LYP/cc-pVDZ method outperforms the full scheme to reproduce absorption spectra for this set of diradicals while drastically reducing the computational effort. This is probably due to the modified response integrals, which are asymptotically correct at long range, but increased in magnitude at short range in SF-sTD-DFT, thus leading to more red-shifted excitation energies. The  $\sqrt{2}$  factor used in transition dipole moments further improves intensities with respect to experimental ones.

**3.3. Eight Small Diradicals.** Each of the eight small diradicals taken from 13 has either a low-spin triplet or singlet ground state that could only be determined by multireference methods. Krylov and co-workers<sup>13</sup> used both EOM-SF-CCSD(dT) and SF-TD-DFT methods to determine their total ground state energies. Trimethyl-methane,  $\alpha$ ,2-didehydrotoluene,  $\alpha$ ,3-didehydrotoluene,  $\alpha$ ,4-didehydrotoluene, and

m-xylylene have a low-spin triplet ground state, whereas o-benzyne, m-benzyne, and p-benzyne have a diradical singlet ground state. Figure 9 presents ground state total energy



**Figure 9.** Total ground state energy deviations obtained at both SF-TD-DFT with a noncollinear exchange–correlation kernel and SF-sTD-DFT levels with respect to EOM-SF-CCSD(dT) reference energies<sup>13</sup> for the eight small diradicals.

deviations at both SF-TD-DFT with a noncollinear exchangecorrelation kernel<sup>13</sup> and SF-sTD-DFT levels with respect to EOM-SF-CCSD(dT) reference energies.<sup>13</sup> Results obtained at the simplified level are very similar to those using the full scheme and show the same deviation with respect to the EOM-SF-CCSD(dT) level. We obtained a MAD of 0.490 a.u. for energy deviations at the SF-sTD-DFT level with respect to the reference, slightly lower than that for the full scheme (0.501 a.u.). RMSDs are of the same order: 0.495 and 0.502 a.u. for the simplified and the full scheme, respectively. This demonstrates that our parameterization is also consistent for smaller diradicals outside the initial benchmark set. The next subsection will show another application outside the initial benchmark set considering the two largest systems in this publication.

3.4. µ-Hydroxo-bridged Dimers of Corrole Tape Ga(III) Complexes Derivatives. Figure 10 presents experimental absorption spectra for two  $\mu$ -hydroxo-bridged dimers of corrole tape Ga(III) complex derivatives<sup>28</sup> and compares them to SFsTD-DFT/B5050LYP/cc-pVDZ and SF-sTD-DFT-xTB results. On the basis of ESR and SQUID measurements, as well as theoretical calculations, Ooi et al.<sup>28</sup> assigned these systems as singlet systems where both corrole tape Ga(III) complexes are well-separated radicals. The two spectra are very alike, not affected by the change of substituents. With 2976 and 4616 basis functions, respectively, the SF-sTD-DFT/B5050LYP/cc-pVDZ calculations on these two systems are the largest considered in this work. The 938 and 1102 SF states were computed in 3.0 and 7.6 min, on an eight-core desktop computer (Intel Core i7-6700, 3.40 GHz). The xTB calculations took only 1.2 and 2.5 min, respectively. For the first compound, the SF-sTD-DFT method reproduces well band positions experimentally observed at 926, 616, 457, and 333 nm but the small bands at 1150 and 733 nm are missing. With the xTB variant, the band at 1150 nm is recovered, whereas bands are 733 and 616 nm are not reproduced. This discrepancy is probably due to additional approximations in the xTB Hamiltonian. Qualitatively, the spectral shape is well reproduced even if intensities of higher energy peaks are not so well described. This is expected because the SF configuration space is too much truncated to treat correctly higher energy states. The same observations can be drawn for the second molecule. Treating such large diradical systems is a real challenge for quantum chemistry, and here, we provide a very efficient way to approach the problem. The







**Figure 11.** Experimental absorption spectrum<sup>29</sup> of the PBI biradical to spectra computed by SF-sTD-DFT and spin-preserving UsTDA-DFT. A high-spin triplet reference ( $S_z = 1$ ) BH&HLYP/def-TZVP' + COSMO ( $\epsilon = 8.93$ ) reference has been used throughout, and no shifts were applied. The experimental spectrum is given in arbitrary units.

comparison could be improved by using other exchange correlation functionals, more extended basis sets, including solvent effects, and dealing with temperature-dependent vibrational and electronic state populations.

3.5. Perylene Bisimide Biradical. We next turn our attention to a PBI biradical, which was synthesized by Würthner and co-workers.<sup>29</sup> On the basis of temperature-dependent nuclear magnetic resonance (NMR) spectroscopy measurements, it was concluded that this system is an open-shell singlet molecule at low temperatures, whereas the triplets become the predominant spin state at room temperature. An UV/vis absorption was recorded at room temperature for this system. It is shown here that the simplified TD-DFT framework, that is, the spin-preserving and SF variants, can complement experimental absorption spectroscopy to identify the spin-state of such diradical systems. In Figure 11, we compare the experimental UV/vis spectrum (recorded at room temperature) to spectra computed with SF-sTD-DFT and spin-preserving unrestricted sTDA-DFT. Both calculations start from a highspin triplet reference determinant.

It can be seen that—apart from a slight red shift—the spinpreserving UsTDA-DFT spectrum fits much better to the distinctive bands that are also visible in the experimental spectrum (peaks around 1.6, 2.5, and 3.4 eV). The SF spectrum starts already at lower energies and shows a very different band shape compared to the experiment. This and the better agreement of UsTDA-DFT suggest that at room temperature, there are mostly triplet diradicals present, which dominate the absorption spectrum. This is in agreement with the findings from the temperature-dependent NMR study in ref 29. For a conclusive statement, temperature-dependent UV/vis measurement would be necessary to observe if the absorption spectrum changes in a way that resembles the SF-sTD-DFT computed spectrum. Note that spin-contaminated spurious states could also be present in both computed spectra. In such cases, SA-SF-TD-DFT<sup>8</sup> or mixed-reference SF-TD-DFT<sup>9</sup> methods could be used instead but at the price of a quite larger computational cost. The evaluation of the spin contamination is currently not implemented in the sTDA program.

**3.6. Limitations for Higher-Energy Excitations.** From Figure 1, it can be deduced that the type I determinants form an



**Figure 12.** Spectra of indigo computed based on a PBE0/def-TZVP reference. The spectra are computed by sTDA, SF-sTD-DFT, and SF-sTD-DFT with restricted orbitals. The latter and the sTDA (dark red) are based on a restricted closed-shell DFT calculation. For the SF-sTD-DFT calculation based on this reference, the orbital occupation has manually been changed to a triplet high-spin occupation (green dotted). The blue line refers to SF-sTD-DFT based on high-spin triplet reference ( $S_z = 1$ ) computed at the UPBE0/def-TZVP level. All spectra were shifted such that the first visible band is found at 2.6 eV, which is the excitation energy computed at the TDA-PBE0/def-TZVP level.<sup>19</sup>

active space (2 electrons in 2 orbitals). If spin contamination is absent, spin-pure configurations could be formed within this active space. However, spin contamination and the incomplete determinant space for the other types (see Figure 1) make the description of the remaining higher lying states questionable. This is the major drawback of the SF-TD-DFT method and is not inherent to the present simplified version. Though, as mentioned in the Introduction, several ways<sup>8,9</sup> already exist to circumvent this. To obtain insight about the effect on the absorption spectra, we have computed absorption spectra of indigo, which has a closed shell ground state (see Figure 12). The spectra were computed based on a PBE0/def-TZVP<sup>45,52</sup> reference, with sTDA being based on a closed shell determinant and SF-sTD-DFT on a high-spin triplet determinant. We also considered SF-sTD-DFT based on restricted orbitals from the closed shell ground state calculation, which was manually turned to a high spin by flipping the highest occupied molecular orbital-lowest unoccupied molecular orbital occupations. The purpose of this comparison is to verify which part of the single excitation spectrum could be recovered within the SF-sTD-DFT framework for a realistic test case. The SF-sTD-DFT spectra differ significantly from the sTDA spectrum, and apart from the lowest excitation, only very few visible peaks are recovered. The other visible peaks in the SF-sTD-DFT case (blue curve) always involve SF excitation to the lowest unoccupied spin-down orbital. If restricted orbitals are used, these peaks are also found, but a few additional ones as well. The latter involves SF excitations from the highest occupied spin-up orbital. Note that an excitation from the first SF state can be seen as moving the hole created by the SF procedure in the occupied–occupied  $\alpha$ space and the electron in the unoccupied–unoccupied  $\beta$  space (see eq 10). This drastically reduces the singly excited space with respect to a normal TD-DFT/TDA procedure. Hence, spectra obtained with the SF-sTD-DFT method beyond the "active space" (type I) could be of poor quality, like for this closed-shell system. A deeper discussion or a correction for this shortcoming

is beyond the scope of this work, but one should be aware of this drawback if higher-energy excited states are of interest.

#### 4. CONCLUSIONS

In this contribution, we presented the first SF-sTD-DFT implementation to compute absorption spectra of very large diradical systems. This method was complemented by the SFsTD-DFT-xTB tight-binding variant to treat even larger systems. A benchmark set of nine diradicals was used to provide a robust parameterization of the method. Using the B5050LYP exchange correlation functional, we obtained a MAD of only 0.076 eV with respect to the unapproximated, noncollinear SF-TD-DFT level of theory. Similarly, good agreements were also obtained for a few other tested functionals. The required computation times are negligible with respect to the preceeding SCF step. In comparison to experimental absorption spectra for this set of compounds, the SF-sTD-DFT/B5050LYP/cc-pVDZ method outperformed the full scheme while drastically reducing the computational effort. We argued that this is due to asymptotically correct response integrals used in SF-sTD-DFT and to the correction factor of  $\sqrt{2}$  used in the calculation of transition moments. Overall, both SF methods seem to be well suited to treat diradicals in low-lying excited states with small spin contamination, whereas higher excited states suffer from the inherent truncation of the singly excited space. In addition to these diradical systems, smaller molecules from ref 13 were also characterized giving similar energy deviations as for the full scheme with respect to the EOM-SF-CCSD(dT) reference method. Two very large  $\mu$ -hydroxo-bridged dimers of corrole tape Ga(III) complexes were also considered to challenge our method. In only about 8 min computation time, we were able to obtain the absorption spectrum at the sTD-DFT/B5050LYP/ cc-pVDZ level of theory considering 4616 basis functions in the calculation. Good qualitative agreement with experimental spectra was observed, especially for low-lying states, even with the "low-cost" xTB variant. Finally, the absorption spectrum of a perylene bisimide biradical was characterized. The comparison

between the high-spin triplet spectrum and the one determined at the SF-sTD-DFT level comforts the experimental finding that at room temperature, mostly triplet diradicals are present in solution.

Considering all of the missing configurations in the SF-TD-DFT approach, one could argue that this is probably not the best method to treat absorption spectra which often encompass relevant high-energy bands. However, for huge diradicals in lowspin states, its simplified counterpart is the only viable method, at least for low-lying excitations. Experimentalists working with diradical are very often facing the question on the electronic character of the species observed in solution. Now, by simply recording the absorption spectrum, a confrontation to SF-sTD-DFT(-xTB) calculations could be applied routinely, yielding reasonable hints if a singlet diradical or a triplet one or a closedshell molecule is present. Furthermore, the SF-sTD-DFT method is a very cheap way to provide good spin symmetry for states that are usually not well treated by DFT.

#### ASSOCIATED CONTENT

#### **Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpca.9b03176.

Appendix providing a justification of the use of a factor  $\sqrt{2}$  in eq 10; comparisons of singlet-triplet energy gaps (first and second SF excitation energies) obtained with B3LYP, PBE0, PBE50, and BHandHLYP exchange correlation functionals for SF-sTD-DFT and SF-TD-DFT methods (PDF)

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#### Notes

The authors declare no competing financial interest.

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