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ABSTRACT: The mixed-reference spin–flip time-dependent density functional theory (MRSF-TD-DFT) method eliminates the erroneous spin contamination of the SF-TD-DFT methodology, while retaining the conceptual and practical simplicity of the latter. The availability of the analytic gradient of the energy of the MRSF-TD-DFT response states enables automatic geometry optimization of the targeted states. Here, we apply the new method to optimize the geometry of several $S_1/S_0$ conical intersections occurring in typical organic molecules. We demonstrate that MRSF-TD-DFT is capable of producing the correct double-cone topology of the intersections and describing the geometry of the lowest-energy conical intersections and their relative energies with accuracy matching that of the best multireference wavefunction a\textit{b} initio methods. In this regard, MRSF-TD-DFT differs from many popular single-reference methods, such as, e.g., the linear response TD-DFT method, which fail to produce the correct topology of the intersections. As the new methodology completely eliminates the ambiguity with the identification of the response states as proper singlets or triplets, which is plaguing the SF-TD-DFT calculations, it can be used for automatic geometry optimization and molecular dynamic simulations not requiring constant human intervention.

INTRODUCTION

Conical intersections (CIs) are molecular geometries at which two (or more) adiabatic electronic states of the molecule become degenerate. As the intersecting electronic states at a CI are coupled by the nonvanishing nonadiabatic coupling, CIs provide efficient funnels for the state-to-state population transfer mediated by the nuclear motion. The degeneracy of the intersecting states at a CI is lifted along two directions in the space spanned by the internal molecular coordinates $Q$, which are defined by the gradient difference and derivative coupling vectors (GDV and DCV, respectively) given by

$$x_1 = \frac{1}{2}(\nabla_Q E_{S_1} - \nabla_Q E_{S_0})$$

$$x_2 = \langle \Psi_{S_1} | \nabla_Q | \Psi_{S_0} \rangle$$

for the case of a crossing between the ground ($S_0$) and the lowest excited $S_1$ singlet states. The degeneracy is lifted linearly along the GDV and DCV directions, which lends a double-cone topology to the potential energy surfaces (PESs) of the intersecting states (Figure 1), hence the name. The remaining $3N - 8$ internal coordinates leave the degeneracy intact, thus defining the crossing seam (or the intersection space) of the CI.

Proper description of CIs and their crossing seams is of utmost importance for an accurate modeling of the non-adiabatic processes occurring in the excited states of molecules. Not all computational tools at the disposal of computational chemists are capable of correctly describing the topology of CIs. The most significant requirement is that the computational method in question should produce a nonvanishing nonadiabatic coupling between the intersecting states; this requirement, for the $S_1/S_0$ CIs, is violated by most of the single-reference methods of quantum chemistry. Multireference computational methods are capable of producing the correct topology of CIs (and the correct dimensionality of the CI seams), however, at the expense of very high cost of computations recovering the dynamic electron correlation.

Methods of density functional theory (DFT) include the dynamic electron correlation from the outset. However, the (spin-conserving) linear-response (LR) time-dependent DFT (TD-DFT) methodology, which is perhaps the most popular approach to obtaining excited electronic states of molecules, fails to yield the correct dimensionality of the $S_1/S_0$ CI seam and predicts a linear crossing (i.e., $3N - 7$ dimensional seam) instead (Figure 1). The problem is rooted in the absence of coupling between the $S_0$ state (the

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reference state in the LR formalism) and the excited states (the response states).\textsuperscript{16,17,32} The failure of LR TD-DFT can be corrected by using the spin-flip (SF) TD-DFT formalism,\textsuperscript{33–36} which operates with the SF transitions from a reference state of different multiplicity, e.g., triplet. However, the SF-TD-DFT response excited states are often strongly spin contaminated (i.e., include contributions of states of different multiplicity),\textsuperscript{17–41} which obstructs the identification of the respective states as singlets. This considerably hinders the application of the SF-TD-DFT methodology for automatic geometry optimization and nonadiabatic molecular dynamics (NAMD) simulations, as the targeted state cannot be correctly identified.

Recently, a simple remedy for the spin-contamination problem of SF-TD-DFT was proposed by some of us.\textsuperscript{41} The mixed-reference (MR) SF-TD-DFT method operates with a reference state comprising two high-spin components, $M_S = +1$ and $M_S = -1$, of the triplet state, thus eliminating the bulk of the spin contamination of the response states.\textsuperscript{41} In contrast to other approaches to eliminating the spin contamination of the SF response methodologies, the MRSF-TD-DFT method is conceptually very simple and enables straightforward computation of the analytic gradient of the response state energies,\textsuperscript{42} thus enabling automatic geometry optimization and NAMD simulations. However, before applying the MRSF-TD-DFT methodology on a wide scale, it seems appropriate to evaluate the ability of the method to accurately describe the geometries and relative energies of CIs. In this work, the MRSF-TD-DFT method will be applied to a series of organic molecules, which were studied previously\textsuperscript{18} by the SF-TD-DFT method and, perhaps, the most accurate multireference wavefunction ab initio technique, the multireference configuration interaction with single and double excitations (MRCISD) method.\textsuperscript{20–22} The geometries of the $S_1/S_0$ CIs occurring in these molecules will be optimized with the MRSF-TD-DFT method using the same basis set and exchange-correlation (XC) functional as in the previous studies employing SF-TD-DFT and MRCISD.

## COMPUTATIONAL METHODS

Derivation of the MRSF-TD-DFT methodology\textsuperscript{41} is based on the density-matrix formulation of the TD Kohn–Sham (TD-KS) theory.\textsuperscript{13} In MRSF-TD-DFT, the zeroth-order MR-reduced density matrix (RDM) is defined as an equiensemble of the $M_S = +1$ and $M_S = -1$ components of the triplet state, e.g.,

$$\rho_{0}^{\text{MR}}(x, x') = \frac{1}{2}\{\rho_{0}^{M_S = +1}(x, x') + \rho_{0}^{M_S = -1}(x, x')\}$$  \hspace{1cm} (2)

Due to the particular form of MR-RDM, its idempotency condition is not satisfied. However, it was shown\textsuperscript{41} that this condition can be recovered by the spinor-like spin functions $s_1$ and $s_2$

$$s_1 = \frac{(1 + i)\alpha + (1 - i)\beta}{2}, \quad s_2 = \frac{(1 - i)\alpha + (1 + i)\beta}{2}$$  \hspace{1cm} (3)

where $i$ denotes the imaginary unit. Within the Tamm–Dancoff approximation, the use of MR-RDM in the linear response formalism yields the MRSF-TD-DFT linear response equations for the completely decoupled singlet and triplet excited states\textsuperscript{41}

$$\sum_{rs} (A_{pq,rs}^{(k)} + A_{pq,rs}^{(k)})X_{rs}^{(k)} = \Omega_{(k)}X_{pq}^{(k)}, \quad k = S, T$$  \hspace{1cm} (4)

where $k = S, T$ labels the singlet and triplet states, respectively; $A_{pq,rs}^{(k)}$ is the linear response part of the orbital Hessian matrix; and $A_{pq,rs}^{(k)}$ is a matrix of coupling terms between the configurations originating from different components, $M_S = +1$ and $M_S = -1$, of the mixed reference.\textsuperscript{41,42} $X_{pq}^{(k)}$ and $\Omega_{(k)}$ are the amplitude vectors and the excitation energies with respect to the MR state, respectively.

The effect of using the mixed reference state is illustrated in Figure 2. Recovering the idempotency of MR-RDM of eq 2 with the rotated spin functions of eq 3 allows to describe linear response of the density in terms of electronic configurations shown in the lower panel of Figure 2. Configurations shown with red arrows are missing in the conventional SF-TD-DFT; their absence leads to spin contamination of the SF-TD-DFT response states. These configurations are recovered in MRSF-TD-DFT, and the spin contamination of the response states in MRSF-TD-DFT is nearly completely eliminated.\textsuperscript{41} Configurations shown in Figure 2 with the blue arrows originate from both $M_S = +1$ and $M_S = -1$ components of the mixed reference state and the black and red arrows show the configurations originating from $M_S = +1$ and $M_S = -1$ components, respectively. Although not all electronic configurations can be recovered by using the MR-RDM, the still missing $C \rightarrow V$ configurations (gray arrows in Figure 2) represent high-lying excited states and their effect on the lower part of the excitation spectrum is insignificant.\textsuperscript{41}

The analytic gradient of the MRSF-TD-DFT excited state energies $\Omega_{(k)}$ ($k = S, T$) is obtained using the Lagrangian formalism.\textsuperscript{44,45} Introducing the Lagrangian of an excited state with the energy $\Omega_{(k)}$
The accuracy of the MRSF-TD-DFT method was tested in the calculation of $S_1/S_0$ CIs occurring in several organic molecules (Figure 3 and Table 1). This set of molecules was previously used to benchmark several other methods including the conventional SF-TD-DFT.\textsuperscript{18,54} In the absence of the experimental data on the geometries and relative energies of CIs (which are, probably, impossible to obtain), the results of the MRCDSD/6-31+G** geometry optimizations reported by Nikiforov et al.\textsuperscript{18} are used as the reference data. Due to the smallness of the basis set employed in the MRCDSD calculations in ref 18, convergence with respect to the basis set and the level of inclusion of the dynamic electron correlation was not reached. However, these results are, probably, the best the multireference wavefunction methodology can offer at the moment and, in the absence of more accurate theoretical estimates nor experimental measurements, are used here to evaluate the accuracy of the SF-TD-DFT and MRSF-TD-DFT methods.

The CIs in Figure 3 and Table 1 originate from two types of transitions, the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions between the frontier orbitals.\textsuperscript{18,55} The CIs due to the $\pi \rightarrow \pi^*$ transitions originate in all of the molecules shown in Figure 3, with the exception of ketene. In the latter molecule, as well as the ethylene CI of ethylene and the methylimine CI of methyliminium, the CIs originate due to the $n \rightarrow \pi^*$ transitions. The former CIs can be further distinguished by the geometric distortion occurring at the CI geometry and classified as the twisted—pyramidalized (tw-pyr) or twisted—BLA (tw-BLA; BLA: bond length alternation) CIs.\textsuperscript{18,56} The $S_0$ and $S_1$ states at the geometry of these CIs have distinct electronic characteristics, which are associated with the diradical (Dir) or charge-transfer (CT) nature of the electronic state.\textsuperscript{17,56} Typically, the tw-pyr CIs occur in molecules where the isomerizing $\pi$-bond dissociated by homolytic mechanism and the tw-BLA CIs occur in the case of heterolytic $\pi$-bond dissociation.\textsuperscript{56} The $n \rightarrow \pi^*$ CIs occur due to crossing between a closed-shell lone pair electronic configuration and an open-shell singlet configuration due to the one-electron transition.\textsuperscript{18}

Table 1 collects the relative energies $\Delta E$ (in eV) calculated with respect to the $S_0$ equilibrium conformation. The vertical excitation energies (VEEs) at the Franck–Condon (FC) geometry are also shown in Table 1. For molecules that exist in the trans- and cis-conformations, both FC geometries are shown. The available experimental VEEs or their best theoretical estimates (TBE) are shown in the second column of Table 1. As can be already observed in the earlier study,\textsuperscript{18} the MRCDSD/6-31+G** VEEs may noticeably deviate from the experimental or TBE data. However, it was not possible to afford CI geometry optimization with a larger basis set or a more accurate wavefunction multireference computational methodology.

![Figure 2. Schematic diagram describing the electronic configurations originating from the linear response of the mixed reference state. MR-RDM is defined with RDMs of the $M_s = +1$ and $M_s = -1$ components of mixed reference state shown in the upper panel. Recovering idempotency of MR-RDM enables one to analyze the linear response in terms of the electronic configurations obtained by one-electron spin–flip transitions from each component of the mixed reference state. In the lower panel, the electronic configurations originating in MRSF-TD-DFT are represented by blue, black, and red arrows and categorized by different initial and final MOs of a spin–flip excitation. The blue arrows show configurations originating from both components of the reference. The black and red arrows show configurations generated from $M_s = +1$ and $M_s = -1$ components, respectively. In SF-TD-DFT, only the configurations shown by blue and black arrows are generated. Gray arrows show configurations that cannot be recovered using MR-RDM in MRSF-TD-DFT.](image-url)
In comparison with the MRCISD relative energies, both methods, SF and MRSF, show similar accuracy. The mean absolute deviations (MADs) of the energies reported in Table 1 from the MRCISD energies are 0.38 eV (SF) and 0.41 eV (MRSF). The geometries obtained with the two methods also agree rather well with the MRCISD geometries; the RMSD is 0.070 Å (SF) and 0.067 Å (MRSF). Similar accuracy was displayed by the other methods tested by Nikiforov et al.\textsuperscript{18} However, the SF method shows, in some cases, considerable spin contamination (see the last two columns of Table 1), which can reach $\langle S^2 \rangle \sim 1$. In such cases, identification of the contaminated state as a singlet becomes questionable. The use of naive spin-projection technique\textsuperscript{63,64} in connection with SF destroys proper dimensionality of the CI seam and yields linear instead of conical intersection.\textsuperscript{17,18} The MRSF method eliminates the spin contamination as well as the ambiguity with the identification of the state while preserving the correct $3N-8$ dimensionality of the intersection space.

Visual inspection of the superimposed geometries of the CIs in Figure 3 obtained with the MRCISD (gray color), SF (green), and MRSF (red) shows that in most cases the two TD-DFT methods agree with one another. There are only two cases where SF and MRSF geometries display noticeable deviation from each other. In the case of the tw-pyr CI\textsubscript{49} of the HBI anion, MRSF displays a somewhat greater torsion of the imidazole ring about the methine bridge (Figure 3). However, this does not lead to noticeable alteration of the energetic position of the tw-pyr CI\textsubscript{49} relative to the other CI, tw-pyr CI\textsubscript{48}, or the FC point of HBI (Table 1).

A more considerable deviation of the SF-TD-DFT geometry from both the MRSF-TD-DFT and MRCISD geometries occurs in the tw-BLA CI of the PSB3 cation. The SF-TD-DFT geometry features pronounced pyramidalization of the allylic carbon atom adjacent to the central double bond of PSB3. As was analyzed by Nikiforov et al.,\textsuperscript{18} the excessive pyramidalization of this atom as predicted by SF-TD-DFT is caused by an overestimation of the relative stability of the ionic electronic configuration resulting from the heterolytic breaking of the central $\pi$-bond of PSB3. It is interesting that the MRSF-TD-DFT formalism corrects this deficiency of SF-TD-DFT by simultaneously eliminating noticeable spin contamination, $\langle S^2 \rangle = 0.579$, of one of the intersecting states (Table 1).

The ability of the MRSF method to produce the correct double-cone topology of CIs is illustrated in Figure 4, where the $S_1-S_0$ energy difference as well as the $S_1$ and $S_0$ energies is shown round a loop in the branching plane around the tw-BLA MECI of PSB3. The branching plane vectors, GDV and DCV, were calculated using the algorithm by Maeda et al.,\textsuperscript{47} which yields orthogonal GDV and DCV. The $S_1$ and $S_0$ energies were calculated round a loop with the radius of 0.01 Å centered at the tw-BLA CI of PSB3 with the step of 2°. In Figure 4, the energy differences obtained with the SF-TD-DFT and MRSF-
**CONCLUSIONS**

In this work, we have analyzed the ability of the newly proposed methodology, the MRSF-TD-DFT method, to describe the geometries and relative energies of the CIs originating in organic molecules. The optimized geometries of the CIs were compared with the results of the MRCISD and SF-TD-DFT calculations available in the literature. The most important conclusion of this study is that MRSF-TD-DFT produces the correct double-cone topology of the S1 and S0 states, which is important for the automatic geometry optimization and the NAMD simulations. Correcting the shortcomings of SF-TD-DFT, the MRSF-TD-DFT method predicts the geometries of the CIs studied in this work.

### Table 1. Relative Energies $\Delta E$ (in eV) with Respect to the S0 Equilibrium Conformations and Root-Mean-Square Deviations (RMSD, in Å) of the Geometries Optimized with the DFT Methods with Respect to the MRCISD Optimized Geometries

<table>
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<th>geometry</th>
<th>Lit. $^b$</th>
<th>MRCISD $^e$</th>
<th>$\Delta E$</th>
<th>RMSD $^f$</th>
<th>$\langle S^2 \rangle_{S0}$</th>
<th>$\langle S^2 \rangle_{S1}$</th>
<th>$\Delta E$</th>
<th>RMSD $^f$</th>
<th>$\langle S^2 \rangle_{S0}$</th>
<th>$\langle S^2 \rangle_{S1}$</th>
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<td>Ethylene</td>
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<td>0.0</td>
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<td>4.82</td>
<td>0.077</td>
<td>0.4347</td>
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<td>0.0</td>
<td>0.0</td>
<td>4.52</td>
<td>0.016</td>
<td>0.0102</td>
<td>0.0106</td>
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<td>5.46</td>
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<td>Ketene</td>
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<td>Penta-2,4-dieniminium, PSB3</td>
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<td>4.00</td>
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<tr>
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<td>0.0</td>
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<td>0.0139</td>
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<td>tw-BLA Cl$_{\text{cis}}$</td>
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<td>3.20</td>
<td>0.081</td>
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$^a$For the conformations obtained with SF-TD-DFT, the $\langle S^2 \rangle$ values of the S$_0$ and S$_1$ states are reported. $^b$Theoretical or experimental estimate of $\Delta E$ from the literature. $^c$MRCISD/6-31+G** results from ref 18. $^d$MRSF-TD-DFT/6-31+G** results obtained in this work. $^e$SF-TD-DFT/6-31+G** results from ref 18. $^f$Root-mean-square deviation from the MRCISD geometry. $^g$MRCISD Franck–Condon geometry not available in ref 18. $^h$Energy difference between the S$_0$ equilibrium cis and trans conformations.

**TD-DFT methods are shown; for each method, its own CI geometry and branching plane vectors were used. Both methods correctly predict the nonzero energy differences round the whole loop; hence, the correct double-cone topology is reproduced by both methods. In earlier studies by Gozem et al. $^{17}$ and Huix-Rottlant et al. $^{32}$ it was found that the spin-conserving LR-TD-DFT yields a linear S$_1$/S$_0$ crossing and the S$_1$–S$_0$ energy difference crosses the zero line twice round the loop. As seen in the lower panels of Figure 4, both methods predict a sloped topography of the intersection point. For the other molecules studied in the present work, the loops round the optimized CIs can be found in the Supporting Information. All of the loops reported there confirm the double-cone topology of the CIs optimized with MRSF-TD-DFT.**
The relative energies \( \Delta E \) (kcal/mol; with respect to the MECI energy) of the S\(_1\) (red) and S\(_0\) (blue) states round the loops obtained with the MRSF-TD-DFT (b) and SF-TD-DFT (c) methods. GDV and DCV are measured in Å.

**FIGURE 4.** (a) S\(_1\)/S\(_0\) energy difference (in kcal/mol) calculated round a loop (\( R = 0.01 \) Å) around the PSB3 tw-CLA MECI optimized with the MRSF-TD-DFT (solid line) and SF-TD-DFT (dashed line) methods. (b, c) The relative energies \( \Delta E \) (kcal/mol) with respect to the MECI energy) of the S\(_1\) (red) and S\(_0\) (blue) states round the loops obtained with the MRSF-TD-DFT (b) and SF-TD-DFT (c) methods. GDV and DCV are measured in Å.

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**REFERENCES**


(54) In the previous work, the geometries of Cls in ethylene and PSB3 were optimized using MRSSF in connection with smaller (6-31G*) basis set. However, no systematic comparison with the reference MRCCSD data were made in that work. The present work extends ref 42 by providing such a comparison for a larger set of molecules and using the 6-31+G** basis set.


