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Eliminating spin-contamination of spin-flip time dependent density functional theory within linear response formalism by the use of zeroth-order mixed-reference (MR) reduced density matrix

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The use of the mixed reference (MR) reduced density matrix, which combines reduced density matrices of the $M_S = +1$ and $−1$ triplet-ground states, is proposed in the context of the collinear spin-flip-time-dependent density functional theory (SF-TDDFT) methodology. The time-dependent Kohn-Sham equation with the mixed state is solved by the use of spinor-like open-shell orbitals within the linear response formalism, which enables to generate additional configurations in the realm of TD-DFT. The resulting MR-SF-TDDFT computational scheme has several advantages before the conventional collinear SF-TDDFT. The spin-contamination of the response states of SF-TDDFT is nearly removed. This considerably simplifies the identification of the excited states, especially in the “black-box” type applications, such as the automatic geometry optimization, reaction path following, or molecular dynamics simulations. With the new methodology, the accuracy of the description of the excited states is improved as compared to the collinear SF-TDDFT. Several test examples, which include systems typified by strong non-dynamic correlation, orbital (near) degeneracy, and conical intersections, are given to illustrate the performance of the new method. Published by AIP Publishing.

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I. INTRODUCTION

The spin-conserving linear response (LR) time-dependent density functional theory (TDDFT)\(^1\)–\(^7\) based on the conventional single-determinant Kohn-Sham (KS)\(^8,9\) reference state is a widely used methodology for obtaining excitation energies of molecular systems. Although the low-lying excitation energies of molecules are described by the conventional LR-TDDFT with sufficiently high accuracy, there are well-known failures of this methodology, e.g., in describing the energy of long-range charge transfer excitations\(^10\)–\(^14\) excited states with substantial double excitation character\(^15\)–\(^18\) excited states of molecules undergoing bond breaking\(^18\)–\(^20\) and real and avoided crossings between the ground and excited states of molecules\(^21\)–\(^24\). Some of these drawbacks, in particular, the incorrect description of the $S_S/S_1$ conical intersections and poor description of multireference electronic states, can be corrected by the spin-flip (SF) TDDFT formalism\(^25\)–\(^27\) which employs an open-shell high-spin, e.g., triplet, reference state instead of the closed-shell reference of the standard LR-TDDFT. However, the original formulation of SF-TDDFT picks out only one component, e.g., $|\alpha\alpha\rangle$, of the degenerate triplet state as the reference and this leads to a considerable spin-contamination of the resulting ground and excited electronic states\(^28\).

Several approaches have been developed to tackle the spin-contamination problem of the SF-CIS (configuration interaction with single excitations)\(^28\),\(^32\),\(^33\),\(^35\) and the SF-TDDFT\(^36\)–\(^38\),\(^34\). The spin-adaptation techniques were implemented in connection with SF-TDDFT in the Tamm-Dancoff approximation (TDA)\(^29\)–\(^31\) TDA-SF-TDDFT or SF-CIS, resulting in a series of spin-adapted (SA) or spin-complete (SC) methodologies. The application of the tensor equation-of-motion (TEOM) formalism to the derivation of response equations resulted in the formulation of a series of the SA-SF-TD-DFT methodologies\(^36\)–\(^38\),\(^34\).

Perhaps, the most recent example of the latter is the method of Zhang and Herbert\(^34\) who derived SA-SF-DFT equations from the TEOM formalism. It has an advantage of being able to produce correct spin eigenstates by applying tensor operators to a tensor reference. However, the matrix elements of TEOM are evaluated using the Wigner-Eckart theorem, which is not satisfied by the approximate density functionals. Hence, the SA-SF-DFT formalism\(^34\) was derived by introducing an \textit{a posteriori} DFT correction into the SA-SF-CIS equations; see Fig. 1(a).

The main obstacle for obtaining spin-contamination free SF formalism is that including electronic configurations beyond linear response remains a great challenge to TDDFT\(^39\),\(^40\). In this work, the linear response formalism is...
applied to the time-dependent (TD) Kohn-Sham (KS) equation with a mixed state rather than a pure state. It is proposed to use the zeroth-order mixed-reference (MR) reduced density matrix (RDM) which combines RDMs of the $M_S = +1$ and $-1$ triplet-ground states with equal weights. The MR-RDM cannot be applied directly to the TD-KS equation due to the violation of the idempotency conditions. It is shown in this paper that the idempotency of the MR-RDM can be restored by the use of spinor-like open-shell orbitals, which enables one to employ the traditional linear response formalism within the TD-KS equation to obtain the MR-SF-TDDFT equations; see Fig. 1(b). Indeed, the majority of the electronic configurations needed for removing the spin-contamination of SF-TDDFT is recovered by the use of the MR-RDM. A further advantage of the MR-SF-TDDFT formalism is that the analytical derivatives needed for removing the spin-contamination of SF-TDDFT is obtained.

Although the MR-SF-TDDFT response states are (nearly) spin-pure, the absence of coupling between the electronic configurations originating from the $M_S = +1$ and $M_S = -1$ components of the MR-RDM results in an artificial degeneracy between some singlet and triplet response states. A simple \textit{a posteriori} correction is introduced into the MR-SF-TDDFT equations to correct for this deficiency. In the present work, the resulting equations of MR-SF-TDDFT are formulated in connection with the collinear exchange-correlation (XC) kernels.

The use of the non-collinear XC kernels in SF-TDDFT is advocated as a way to provide a partial spin-adaptation of the electronic configurations originating from the SF transitions between the open-shell orbitals. However, the non-collinear formalism does not offer a possibility to introduce non-empirical coupling between the $M_S = +1$ and $M_S = -1$ response configurations. Hence, in this work, the collinear MR-SF-TDDFT formalism is presented and an investigation of a possible use of the non-collinear XC kernels within this formalism is postponed to future work.

The current article is organized as follows. Section II gives a brief overview of the traditional collinear LR SF-TDDFT formalism. The application of the LR formalism to the MR-RDM and the derivation of the MR-SF-TDDFT equations are presented in Sec. III. In Sec. IV, the new formalism is applied to several simple test systems and the advantages as well as disadvantages of MR-SF-TDDFT are discussed.

II. LINEAR-RESPONSE TDDFT AND SF-TDDFT

In this section, we briefly review the standard LR-TDDFT formalism and the collinear SF-TDDFT formalism. The following notations are used throughout this work. Doubly and singly occupied KS spin-orbitals are labeled as $\phi_i^s$, $\phi_i^o$, $\phi_i^v$, $\phi_i^w$, and $\phi_i^{s'}$, $\phi_i^{o'}$, $\phi_i^{v'}$, $\phi_i^{w'}$, respectively, while virtual KS spin orbitals are labeled as $\phi_i^{s''}$, $\phi_i^{o''}$, $\phi_i^{v''}$, $\phi_i^{w''}$. The arbitrary (occupied or virtual) KS spin-orbitals are written as $\phi_i^{s\sigma}$, $\phi_i^{o\sigma}$, $\phi_i^{v\sigma}$, $\phi_i^{w\sigma}$, respectively. The superscript $\sigma_p$ denotes the index for the spin function of the molecular orbital $p$. All two-electron integrals are written in chemists’ notation. Furthermore, the closed, open, and virtual orbital spaces are denoted as $C$, $O$, and $V$, respectively. The summation index $n$ refers to $n$th and $(n+1)$th molecular orbitals representing the two orbitals in $O$ space, where $2n$ is the number of electrons. For the rest of discussions, O1 and O2 are used instead of $n$ and $n + 1$.

A. Derivation of LR-TDDFT by the use of idempotency of the density matrix

The conventional LR-TDDFT formalism can be derived from the exact TD-KS theory by imposing an idempotency condition on the density matrix. Within the TD-KS formalism, the time-dependent reduced density matrix (RDM) $\rho(t, x, x')$ can be decomposed in terms of the time-independent KS spin-orbitals $\phi_p^{s\sigma}$ (the solutions of KS equations at $t = 0$) as

$$\rho(t, x, x') = \sum_{p,\sigma} P_{p\sigma,q\sigma} \rho(t, x, x') \phi_p^{s\sigma}(x) \phi_q^{s\sigma}(x'),$$

(2.1)

where $x$ denotes both the position and spin of the electron, $x = (r, \sigma)$, and $P_{p\sigma,q\sigma}(t)$ is the discrete representation of the RDM, denoted as the density matrix, in the following. The diagonal part of the RDM (2.1) is required to be equal to the density of a system of 2N interacting electrons

$$\rho(t, x, x) \equiv \sum_{p,\sigma} P_{p\sigma,q\sigma} \rho(t, x, x') \phi_p^{s\sigma}(x) \phi_p^{s\sigma}(x'),$$

(2.2)

at each instance of $t$ and $x$. As the TD-KS non-interacting wavefunction is represented by a single KS determinant, the RDM (2.1) satisfies the idempotency relation

$$\rho(t, x, x') = \int dx'' \rho(t, x, x'') \rho(t, x'', x'),$$

(2.3)

which becomes

$$P_{p\sigma,q\sigma} = \sum_{i,\tau} P_{p\sigma,i\tau} P_{i\tau,q\sigma},$$

(2.4)

for the density matrix $P$.

From the TD-KS equations, the equations of motion (EOMs) for the density matrix ($P_{p\sigma,q\sigma}$) can be derived in the form

$$\partial_t \rho_{p\sigma,q\sigma} = \sum_{i,\tau} \left( F_{p\sigma,i\tau} P_{i\tau,q\sigma} - P_{p\sigma,i\tau} F_{i\tau,q\sigma} \right),$$

(2.5)

where

$$F_{p\sigma,q\sigma} = \int dx'' \rho_{p\sigma}(x'') \left( \frac{1}{2} \nabla^2 - \sum_A \frac{Z_A}{|r - R_A|} - \frac{\delta A_{XC}[\rho]}{\delta \rho(t, x)} \phi_q^{s\sigma}(x) \right) dx.''
$$

(2.6)
are the elements of the Fock matrix at time $t$. Within the adiabatic approximation, the exchange-correlation (XC) part $\Delta^X^C$ of the action functional is replaced by the XC functional of time-independent DFT evaluated with the density $\rho_i$ at time $t$, $\Delta^X^C[\rho_i] \delta r(x,t) \equiv \Delta^X^C|[\rho_i]/\delta r_i(x)$. In the case of approximate hybrid XC functionals, the Fock matrix $F_{\text{per,qr}}$ becomes

$$ F_{\text{per,qr}} = \int dx \phi_p^{\sigma \ast} \phi_q^{\sigma} \left[ \frac{1}{2} t_{p \sigma}^2 - \sum_{\lambda} \frac{Z_{\lambda}}{|r - R_{\lambda}|} \right] \phi_q^{\sigma \ast} \phi_q^{\sigma} + (1 - c_H) \int dx \phi_p^{\sigma \ast} \phi_q^{\sigma} \frac{\delta^X^C[\rho_i]}{\delta r_i(x)} + \sum_{\text{occ}} P_{\text{exc,exc}} \int dx \int dx' \phi_p^{\sigma \ast} (x) \phi_q^{\sigma \ast} (x') \times \frac{1}{|r' - r|} \phi_q^{\sigma \ast} (x') \phi_q^{\sigma \ast} (x), \quad (2.7) $$

where $P(x, x')$ is the permutation (exchange) operator and $c_H$ is the mixing coefficient for the exact (Hartree-Fock, HF) exchange; $c_H = 0$ or 1 recovers the pure DFT or pure HF limits of Eq. (2.7), respectively.

When a time-dependent one-electron external perturbation, e.g., a time-dependent electric field, with a strength $E$ acts on the system, the first-order density matrix

$$ P_{\text{exc,exc}} = \int dx \int dx' \phi_p^{\sigma \ast} (x) \phi_q^{\sigma \ast} (x') \times \frac{1}{|r' - r|} \phi_q^{\sigma \ast} (x') \phi_q^{\sigma \ast} (x), \quad (2.13) $$

yields the idempotency relations for the zeroth-order (the first term on the left-hand side) and the first-order (the second term) density matrices. The former relation is satisfied by any pure state represented by a single Slater determinant. For example, SF-TDDFT uses the $M_S = +1$ component of the triplet state where the elements of the density matrix are given by

$$ P_{\text{exc,exc}}^{(0)} = P_{\text{exc,exc}}^{(0)} + P_{\text{exc,exc}}^{(1)} + P_{\text{exc,exc}}^{(1)} - P_{\text{exc,exc}}^{(1)} = 1, \quad P_{\text{exc,exc}}^{(0)} + P_{\text{exc,exc}}^{(1)} = 1, \quad P_{\text{exc,exc}}^{(0)} - P_{\text{exc,exc}}^{(1)} = 0. \quad (2.14) $$

Equation (2.14) defines projections of the density matrix onto the subspace of the occupied MOs, $P_{\text{ocq,ocq}}^{(0)}$ and $P_{\text{ocq,ocq}}^{(1)}$, and onto the unoccupied MOs, $P_{\text{ucq,ucq}}^{(1)} - P_{\text{ocq,ocq}}^{(0)}$. The zeroth-order RDM. In substituting Eq. (2.11) into the second term on the left-hand side of Eq. (2.13) yields the first-order idempotency relation

$$ \sum_{\text{exc}} (d_{\text{exc,exc}}^{(0)} - d_{\text{exc,exc}}^{(1)} + d_{\text{exc,exc}}^{(1)}) = d_{\text{exc,exc}}^{(0)}, \quad (2.15) $$

from which the amplitude matrix $d_{\text{exc,exc}}^{(0)}$ can be represented as

$$ d_{\text{exc,exc}}^{(0)} = X_{\text{exc,exc}} + Y_{\text{exc,exc}}, \quad (2.16) $$

where

$$ X_{\text{exc,exc}} = \sum_{\text{ocq,ocq}} (\delta_{\text{ocq,exc}} - P_{\text{ocq,ocq}}^{(1)})M_{\text{ocq,ocq}}, \quad (2.17) $$

$$ Y_{\text{exc,exc}} = \sum_{\text{ucq,ucq}} P_{\text{exc,exc}}^{(1)}M_{\text{exc,exc}}(\delta_{\text{ocq,exc}} - P_{\text{exc,exc}}^{(0)}), \quad (2.18) $$

and $M_{\text{exc,exc}}$ is a matrix to be defined in the following. The matrix $X_{\text{exc,exc}}$ has non-zero elements between the occupied $\text{ocq}$ and occupied $\text{ocq}$ MOs and corresponds to one-electron excitations, whereas the matrix $Y_{\text{exc,exc}}$ has non-zero elements for the occupied $\text{ocq}$ and unoccupied $\text{ucq}$ MOs and corresponds to one-electron de-exitations.

SF-TDDFT employs TDA, within which the de-excitation matrix $X$ is neglected.

![FIG. 2. A schematic diagram of SF-TDDFT.](image-url) The upper panel depicts the high-spin triplet reference and the corresponding zeroth-order RDM. In the lower panel, a complete set of electronic configurations considered in SF-TDDFT is given. Electronic configurations which can be generated by spin-flip linear responses (spin-flip one-electron transitions) from the zeroth-order RDM are given by black arrows in four types. Configurations unable to be obtained in the linear responses of SF-TDDFT are given by gray dashed arrows.
dashed arrows are missing in the amplitude equations of the collinear SF-TDDFT. Hence, the excitation space defined by SF-TDDFT is incomplete and spin-contaminated, as the individual configurations shown in Fig. 2 are not eigenfunctions of the total spin $S^z$.

**B. Equations of motion of SF-TDDFT**

Substituting Eqs. (2.9) and (2.10) into the EOM Eq. (2.5) and collecting the terms of zeroth and first order in the perturbation parameter $\lambda$ lead to EOM for the density matrix $P^{(0)}$ and $P^{(1)}$. The zeroth-order EOM

$$\sum_{\sigma r} \left( F_{\sigma r}^{(0)} P^{(0)}_{\sigma r} - P^{(0)}_{\sigma r} F_{\sigma r}^{(0)} \right) = 0$$

(2.19)

is trivially satisfied by the restricted open-shell (ROHF) density matrix. The EOM for the first-density order

$$\sum_{\sigma r} \left( F_{\sigma r}^{(1)} P^{(1)}_{\sigma r} - P^{(1)}_{\sigma r} F_{\sigma r}^{(1)} \right) + i \frac{\partial}{\partial t} P^{(1)}_{\sigma r} = 0$$

(2.20)

enables one to obtain the excitation amplitudes $X_{\sigma r, s \sigma'}$. Substituting Eqs. (2.11), (2.12), (2.17), and (2.18) into Eq. (2.20) and applying the TDA results in an eigenvalue equation,

$$\sum_{\sigma r, s \sigma'} A_{\sigma r, s \sigma'} X_{\sigma r, s \sigma'} = \sum_{\sigma r, s \sigma'} \omega_{\sigma} \delta_{\sigma r, s \sigma'} X_{\sigma r, s \sigma'},$$

(2.21)

for the excitation frequencies $\omega_{\sigma}$ to the $\sigma$th excited state and the respective excitation amplitudes $X_{\sigma r, s \sigma'}$. In Eq. (2.21), $\delta_{\sigma r, s \sigma'} = \delta_{\sigma r} \delta_{s \sigma'}$ and the orbital Hessian matrix $A_{\sigma r, s \sigma'}$ is given by

$$A_{\sigma r, s \sigma'} = F_{\sigma r, s \sigma'} - F_{s \sigma r, \sigma \sigma'} + \frac{\partial F_{\sigma r, s \sigma'}}{\partial P_{s \sigma r, \sigma \sigma'}},$$

(2.22)

where the partial derivative of the Fock matrix with respect to the density matrix on the right-hand side is given by

$$\frac{\partial F_{\sigma r, s \sigma'}}{\partial P_{s \sigma r, \sigma \sigma'}} = (pq|sr) \delta_{\sigma r, \sigma'} \delta_{s \sigma'} - c_H((pq|rs) \delta_{\sigma r, \sigma'} \delta_{s \sigma'} + (1 - c_H) f_{XC}^{pq|rs} \delta_{\sigma r, \sigma'} \delta_{s \sigma'}.$$

(2.23)

In Eq. (2.23), $(pq|sr)$ is the two-electron integral in the Mulliken (or chemist's) notation and the matrix elements of the exchange-correlation kernel $f_{XC}^{pq|rs}$ are given by

$$f_{XC}^{pq|rs} = \int dxd'y \phi_p^{\sigma} (x) \phi_q^{\sigma'} (x) \delta^2 E_{XC} [\rho] \frac{\delta}{\delta \rho(x)} \frac{\delta}{\delta \rho(x')},$$

(2.24)

When using a collinear XC kernel $f_{XC}$ in SF-TDDFT, only the exact exchange part remains in Eq. (2.23) due to the spin symmetry requirements, thus leading to

$$\frac{\partial F_{\sigma r, s \sigma'}}{\partial P_{s \sigma r, \sigma \sigma'}} = -c_H((pq|rs) \delta_{\sigma r, \sigma'} \delta_{s \sigma'}.$$

(2.25)

**III. SPIN-FLIP TDDFT WITH MIXED REFERENCE, MR-SF-TDDFT**

**A. Definition of a mixed-reference reduced density matrix**

As discussed in the end of Sec. II A, one of the main sources of spin-contamination in SF-TDDFT is the missing electronic configurations (and the respective amplitudes) shown by the gray arrows as type II, III, and IV in Fig. 2. In this work, it is proposed to eliminate the bulk of the spin-contamination of the SF-TDDFT response states by using an RDM of an equiensemble of the $M_S = +1$ and $M_S = -1$ components of the triplet state,

$$\rho_{0 \chi}^{MR} = \frac{1}{2} \{ \rho_{0 \chi}^{M_S = +1} + \rho_{0 \chi}^{M_S = -1} \}.$$

(3.1)

As shown in Fig. 3, the use of this mixed-reference (MR) RDM introduces many of the electronic configurations missing in SF-TDDFT and largely eliminates the spin-contamination of the response states.

It is noteworthy that not all of the electronic configurations shown in Fig. 3 can be recovered by the use of the MR-RDM (3.1). Thus, four out of six type IV configurations (four configurations shown with the gray arrows in Fig. 3) are still unencountered. Typically, these configurations represent high lying excited states and make insignificant contributions to the low lying states of molecules. Hence, the effect of the missing configurations for the spin-contamination of the SF-TDDFT response states is expected to be relatively small. Although the missing type IV configurations could be included by adding the $M_S = 0$ component of the triplet to the mixed reference, this would require to handle with a number of non-flip transitions along with the spin-flip ones; this endeavour is postponed to future work.

According to Sec. II, to be able to derive the TD-KS equations with the new density matrix, the matrix should satisfy the condition of idempotency. Although each of the RDMs of the $M_S = +1$ and $M_S = -1$ components of the triplet is idempotent, their ensemble, Eq. (3.1), is not, i.e.,

![FIG. 3. A schematic diagram of mixed-reference (MR) SF-TDDFT. The upper panel shows the zeroth-order MR-RDM which is a combination of $M_S = 1$ and $−1$ RDMs. In the lower panel, electronic configurations which can be generated by spin-flip linear responses from the MR-RDM are given by black arrows in four types. Configurations unable to be obtained in the linear responses of MR-SF-TDDFT are given by gray dashed arrows.](image-url)
\[
\sum_{\beta} p_{\alpha \sigma}(0)^{MR}_{\text{O1a} \alpha \sigma} p_{\alpha \sigma}(0)^{MR}_{\text{O1} \alpha \sigma} = p_{\alpha \sigma}(0)^{MR}_{\text{O1a} \alpha \sigma} + p_{\alpha \sigma}(0)^{MR}_{\text{O1} \alpha \sigma} - \frac{1}{2} p_{\alpha \sigma}(0)^{MR}_{\text{O1a} \alpha \sigma} \neq p_{\alpha \sigma}(0)^{MR}_{\text{O1} \alpha \sigma} \tag{3.2}
\]

where \(p_{\alpha \sigma}(0)^{MR}_{\text{O1a} \alpha \sigma} = p_{\alpha \sigma}(0)^{MR}_{\text{O1} \alpha \sigma} = p_{\alpha \sigma}(0)^{MR}_{\text{O1a} \alpha \sigma} = 1/2\) are the open-shell blocks of the MR-RDM; see Sec. 1 of the supplementary material for more detail.

The formal idempotency of the MR-RDM can be recovered by introducing mixed-spin orbitals, in the following labeled by mixed-spin labels \(s_1\) and \(s_2\),

\[
s_1 = \frac{(1 + i)\alpha + (1 - i)\beta}{2}, \quad s_2 = \frac{(1 - i)\alpha + (1 + i)\beta}{2}.
\tag{3.3}
\]

The new mixed spin O orbitals \(\phi_{O1k}^{\sigma}\), \(k = 1, 2\), are orthonormal among themselves and with respect to the C and V orbitals, yield the same RDM as in Eq. (3.1), and make the new RDM idempotent; see Sec. 2 of the supplementary material for detailed derivation.

**B. EOM for excitation amplitudes from MR RDM**

As the redefined MR-RDM is idempotent, the new excitation amplitudes can be defined with the zeroth-order density matrix as Eq. (2.17); i.e.,

\[
X_{\alpha \beta}^{MR} = \sum_{\sigma, \sigma'} \left( \delta_{\sigma, \sigma'} p_{\alpha \sigma}(0)^{MR}_{\text{O1} \alpha \sigma} \right) M_{\sigma, \sigma', \alpha \beta}^{\text{O1}} p_{\beta \sigma}(0)^{MR}_{\text{O1} \alpha \sigma}.
\tag{3.4}
\]

Subsequently, within TDA, the excitation energy to the \(j\)th state \(\omega_j\) and the respective new amplitudes \(X_{\alpha \beta}^{MR}\) are obtained from the similar eigenvalue equation Eq. (2.21) with the orbital Hessian matrix Eq. (2.22) as in the collinear SF-TDDFT case; the only difference is that the spin functions of KS MOs in O space in Eq. (3.3) are to be substituted there.

The excitation amplitudes \(X_{\alpha \beta}^{MR}\) of each from \(M_S = 1\) and \(-1\) references are given in the first and second columns of Table I, respectively. The spin-flip (SF), \(\alpha \rightarrow \beta\) and \(\beta \rightarrow \alpha\), amplitudes resulting in the configurations with \(M_S = 0\) are shown on the white background, the non-flip (NF), \(\alpha \rightarrow \alpha\) and \(\beta \rightarrow \beta\), amplitudes with \(M_S = \pm 1\) are shown on the light gray background, and the SF amplitudes with \(M_S = \pm 2\) are shown on the dark gray background. These eighteen types of excitation amplitudes \(X_{\alpha \beta}^{MR}\) are entangled in the nine types of the new excitation amplitudes \(X_{\alpha \beta}^{MR}\) in the third column; for each row, two \(X_{\alpha \beta}^{MR}\) are entangled in \(X_{\alpha \beta}^{MR}\).

Of the nine types of the \(X_{\alpha \beta}^{MR}\) amplitudes shown in Table I, the last two amplitudes, \(X_{\alpha \alpha}^{MR}\) and \(X_{\beta \beta}^{MR}\), do not contain \(M_S = 0\) excitation amplitudes and they are dropped in EOM for the new excitation amplitudes. In EOM for the remaining \(X_{\alpha \beta}^{MR}\) amplitudes, the contributions of SF excitations with \(M_S = 0\) are mixed with those of the SF and NF excitations with \(M_S = \pm 1, \pm 2\). The separation of EOM for these \(M_S = 0\) and \(M_S \neq 0\) amplitudes can be done with the definitions of separated excitation amplitudes and by substitutions of the definitions. A detailed description of this separation is given in Secs. 3 and 4 of the supplementary material.

The eigenvalue equation for the remaining seven excitation amplitudes with \(M_S = 0\) can be represented in a concise notation as

\[
AX_j = \omega_j X_j,
\tag{3.5}
\]

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<th>(M_S = +1) reference</th>
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where 

\[
X_j = \begin{pmatrix}
X_{\alpha \alpha}^{MR} + X_{\beta \beta}^{MR} & X_{\alpha \alpha}^{MR} + X_{\beta \beta}^{MR} & X_{\alpha \alpha}^{MR} + X_{\beta \beta}^{MR} & X_{\alpha \alpha}^{MR} + X_{\beta \beta}^{MR} & X_{\alpha \alpha}^{MR} + X_{\beta \beta}^{MR} & X_{\alpha \alpha}^{MR} + X_{\beta \beta}^{MR} & X_{\alpha \alpha}^{MR} + X_{\beta \beta}^{MR} & X_{\alpha \alpha}^{MR} + X_{\beta \beta}^{MR} & X_{\alpha \alpha}^{MR} + X_{\beta \beta}^{MR}
\end{pmatrix}.
\tag{3.6}
\]

The excitation-amplitude vectors \(X_{\alpha \alpha}^{MR} + X_{\beta \beta}^{MR}\) and \(X_{\alpha \alpha}^{MR} + X_{\beta \beta}^{MR}\) originate from \(M_S = +1\), whereas the \(X_{\alpha \alpha}^{MR} + X_{\beta \beta}^{MR}\) vectors from \(M_S = -1\). The \(X_{\alpha \alpha}^{MR} + X_{\beta \beta}^{MR}\) vectors from the type I configurations in Fig. 3 originates from both the components of the reference.

The blocks of the orbital Hessian matrix \(I_{km}\) are labeled by indices \(k, m \in [1, 7]\), where \(k (m)\) are the ordinal numbers of the blocks of the \(X_j\) vector [in the order of their appearance in Eq. (3.6)]. The \(A_{km}\) blocks \((k, m = 1, 2, 3)\) represent couplings between \(\alpha \rightarrow \beta\) and \(\alpha \rightarrow \beta\) excitations, and the \(A_{km}\) blocks \((k, m = 5, 6, 7)\) are couplings between \(\beta \rightarrow \alpha\) and \(\beta \rightarrow \alpha\). When using a collinear XC kernel, couplings between \(\alpha \rightarrow \beta\) and \(\beta \rightarrow \alpha\) excitations vanish; see Sec. 6 of the supplementary material. Spin-contamination for type II and III configurations is completely eliminated by the additional configurations and proper symmetric relations in the corresponding elements of the Hessian matrix.

The use of a collinear XC kernel introduces an additional source of spin-contamination for type I configurations: The magnitude of the amplitudes \(X_{\alpha \alpha}^{MR} + X_{\beta \beta}^{MR}\) and \(X_{\alpha \alpha}^{MR} + X_{\beta \beta}^{MR}\) should be identical, see Fig. 4, to yield properly spin-adapted configurations. However, spin-flip excitations from different orbitals may lead to a certain asymmetry in the magnitudes of these amplitudes and to an imperfect spin-adaptation of the respective configurations.

As discussed previously, the type I configurations are generated from both the \(M_S \pm 1\) and \(-1\) components of the MR RDM. However, we noticed that there is no one-to-one correspondence between excitation amplitudes and configurations, and it relates to the spin contamination of the type I amplitude.
By imposing these correspondences, important symmetries are recovered, which completely eliminate this type of the spin-contamination. Detailed discussions are given in Sec. 5 of the supplementary material. For convenience, the electronic configurations originating from the SF transitions among the O orbitals are labeled as G (ground), D (double), L (left), and R (right) in the order of type I configurations shown in Fig. 3.

Using the aforementioned symmetry relations, the response equations are separated into two independent sets

\[ A_T X'_I = \omega_T X'_T, \]  
\[ A_S X'_S = \omega_S X'_S, \]

for the triplet (T) and singlet (S) excited states. In these equations, the excitation amplitude vectors are

\[ X'_I \equiv \begin{pmatrix} (X_{O_1O_2a} + X_{O_1O_2b}) / \sqrt{2} \\ (X_{O_1O_2a} + X_{O_1O_2b}) / \sqrt{2} \\ (X_{O_2O_1a} + X_{O_2O_1b}) / \sqrt{2} \\ (X_{O_2O_1a} + X_{O_2O_1b}) / \sqrt{2} \end{pmatrix}, \]

\[ X'_S \equiv \begin{pmatrix} X_{O_1O_2a} - X_{O_1O_2b} / \sqrt{2} \\ X_{O_1O_2a} - X_{O_1O_2b} / \sqrt{2} \\ X_{O_2O_1a} - X_{O_2O_1b} / \sqrt{2} \\ X_{O_2O_1a} - X_{O_2O_1b} / \sqrt{2} \end{pmatrix}. \]

Detailed description of the \( A_T \) and \( A_S \) matrices is given in Sec. 8 of the supplementary material.

The new response Eqs. (3.7) and (3.8) yield spin-adapted excited states, where the spin-contamination due to missing configurations of the type I, II, and III, see Fig. 3, is completely removed. Hence, the clean separation of triplet and singlet states is achieved in MR-SF-TDDFT, which is an advantage before the collinear SF-TDDFT formalism.

For the type IV configurations, only one missing configuration (out of five) is recovered in MR-SF-TDDFT and spin-adaptation of this type of configurations remains incomplete. However, as discussed in Sec. III A, the contribution of these configurations into the low lying excited states is expected to be small and the resulting spin-contamination is insignificant. When calculating the expectation values of the \( S^2 \) operator, see Sec. 7 of the supplementary material, the contributions of the missing configurations are not taken into account.

C. Coupling between spin-paired amplitudes

The MR-SF-TDDFT formalism outlined so far represents the exact solution of the linear response formalism with the MR-RDM. Although the use of the MR-RDM eliminates the bulk of the spin-contamination of the conventional SF-TDDFT, there is little effect of the use of the MR state on the energies of the response states. As the spin-paired configurations originate from different components, with \( M_S = +1 \) and \( M_S = -1 \), of the MR state, they are uncoupled within the SF-TDDFT formalism; see Figs. 5(a) and 5(b).

In the SC-SF-CIS method of Sears, Sherrill, and Krylov,28 coupling between the spin-paired configurations is introduced by the use of a restricted active space CI procedure. Within the CI method, the matrix elements between the spin-paired configurations do not vanish, as follows from the application of Slater-Condon rules.51,52 As there is no simple way of reintroducing the couplings while staying within a strict SF-TDDFT formalism, in this work, we adopt the approach of Sears, Sherrill, and Krylov28 and introduce the couplings through the application of the Slater-Condon rules to the matrix elements between the spin-paired configurations; see Figs. 5(c) and 5(d). The respective block-matrices of the pairing strengths \( C_{pq} \) are introduced to the orbital rotation Hessian.

A complete list of the pairing strength matrices \( C_{pq} \) is given in Sec. 6 of the supplementary material. Here, we illustrate their calculation using \( C_{11} \) as an example,

\[ (C_{11})_{\alpha i \omega j} = c \langle \Psi_{M_S=+1}^{\alpha} | H | \Psi_{M_S=-1}^{\omega} \rangle. \]

In Eq. (3.11), \( \Psi_{M_S=+1}^{\alpha} \) and \( \Psi_{M_S=-1}^{\omega} \) are the configurations originating from the SF transitions from the \( M_S = +1 \) and \( M_S = -1 \) components of the mixed reference state and \( c \) is an arbitrary constant. Here, this constant is chosen equal to the fraction of the exact HF exchange in the density functional, i.e., \( c = \epsilon_H \), which significantly improves the degeneracy of the multiplet components of a Be atom, as shown in Sec. IV. However, a further study is necessary to determine the appropriate form of the pairing strengths. The use of the pairing strengths \( C_{pq} \) does not change the general form of the MR-SF-TDDFT equations (3.7) and (3.8); see Sec. 8 of the supplementary material.
IV. RESULTS AND DISCUSSION

The developed MR-SF-TDDFT method was tested in the calculation of four different atomic and molecular systems, which cover a range of multi-reference problems ranging from the description of atomic multiplets to bond breaking and to $S_1/S_0$ conical intersections. The test calculations employ the BH&HLYP density functional in connection with the 6-31G or cc-pVTZ basis set, as noted below. The MR-SF-TDDFT and the SF-TDDFT calculations with the collinear XC kernels were performed using a local development version of the GAMESS-US program.

A. Be atom

The Be atom has the $1^1S$ ground state arising in the configuration $1s^2$. The low-lying excited states of Be are the $3^1P_{x,y,z}$ and the $1^3P_{x,y,z}$ states arising in the configuration $1s^22s^12p_1^1$, $k = x, y, z$. The SF-TDDFT and the MR-SF-TDDFT calculations use the $3^1P_1$ state ($1s^22s^12p_1^1$) as the reference state. With this choice of reference, the $X_{M_S=1}$ and $X_{M_S=0}$ amplitudes generate the $1^1P_z$ and $3^1P_z$ states, while the rest of the $P$ states are produced by the $X_{M_O=1}$ and $X_{M_O=0}$ amplitudes.

The results of the calculations are collected in Table II. The MR-SF-TDDFT(0) represents MR-SF-TDDFT where the pairing strength, see Sec. III C, is neglected. The SF-TDDFT, MR-SF-TDDFT(0), and MR-SF-TDDFT yield nearly identical energy for the $1^1S$ ground electronic state. However, there remains residual spin-contamination in the SF-TDDFT state, whereas both MR-SF-TDDFT(0) and MR-SF-TDDFT produce pure spin states.

The collinear SF-TDDFT method yields relatively the minor spin-contamination of the $1^3P_z$ and $3^1P_z$ components, for which the excitation amplitudes arise in the O orbital subspace; see Fig. 2. However, the $3^1P_z$ components, which are described by the amplitudes arising in the V subspace, are strongly spin-contaminated; $\langle S^2 \rangle = 1.0$, which is typical for mixtures of the true singlet and triplet states. As a result, there are absences of $1^1P_{x,y}$ components. Strictly, one cannot say the strongly spin-contaminated states as neither singlet nor triplet states. Hence, an erroneous energy splitting between the $(x, y)$ components and $z$ component of the $3^1P$ and $1^3P$ multiplets is predicted by SF-TDDFT, 0.811 eV and 1.247 eV, respectively.

Although the removal of the spin-contamination by MR-SF-TDDFT(0) does not improve the energies of the multiplet components, the $1^1P_{x,y}$ and $3^1P_{x,y}$ can now be distinguished.

The use of the pairing strengths in MR-SF-TDDFT lifts the degeneracy of these components of the $1^1P$ and $3^1P$ multiplets; see the fourth column in Table II. The magnitude of the splitting between the components of the same multiplet with the non-zero pairings is considerably reduced as compared to SF-TDDFT; the $3^1P_{x,y}$ and $3^1P_z$ splitting is now 0.233 eV, and the $1^1P_{x,y}$ and $1^3P_z$ splitting is reduced to 0.223 eV. It can be expected that the residual splitting between the $(x, y)$ and $z$ components can be further reduced by considering more accurate expressions for the pairing strengths than simple Eq. (3.11) used here.

To understand the origin of the residual splitting, calculations with 100% HF exchange instead of the XC functional (labeled MR-SF-CIS in Table II) were performed. The use of the self-interaction free HF exchange completely eliminates the erroneous splitting between the $3^1P_{x,y}$ and $3^1P_z$ components and reduces the $1^3P_{x,y}$ and $1^3P_z$ splitting to only 0.09 eV. This indicates that the bulk of the splitting between the multiplet components is caused by the effect of the self-interaction error of the density functional. The remaining tiny splitting between the components of the $1^1P$ multiplet is probably caused by the incompleteness of the mixed reference. A systematic investigation on the splittings is currently undertaken in a separate study.

B. Ethylene

When the double bond of ethylene is subject to torsion, the $\pi$-component of this bond is broken near $90^\circ$ torsion and the ground singlet electronic state (N) of ethylene acquires a strong multi-reference character. The singlet excited states obtained in the $(\pi, \pi^*)$ orbital space, the V and Z states, form an avoided crossing with the N state. This situation is poorly described by the standard KS formalism and the linear-response spin-conserving TDDFT formalism.

The SF-TDDFT and MR-SF-TDDFT calculations of the singlet N, V, and Z states of ethylene employed the $[\ldots, \pi^1\pi^1]$ triplet reference state. The potential energy curves of these states obtained with the SF-TDDFT (red curves) and MR-SF-TDDFT (black curves) methods along the rigid torsion coordinate are shown in Fig. 6. There is a very close agreement between the two methods for the relative energies of these states; the red and black curves coincide for practically all values of the torsion angle. However, the SF-TDDFT states are strongly spin-contaminated, $\langle S^2 \rangle$ up to ca. 0.3, as shown by the dashed red curves in Fig. 6. The spin-contamination is completely absent in the singlet states produced by

<table>
<thead>
<tr>
<th>State</th>
<th>SF-TDDFT</th>
<th>MR-SF-TDDFT(0)</th>
<th>MR-SF-TDDFT</th>
<th>MR-SF-CIS</th>
</tr>
</thead>
<tbody>
<tr>
<td>$1^1S$</td>
<td>$-14.650,997,(0.0003)$</td>
<td>$-14.650,997,(0.00)$</td>
<td>$-14.650,988,(0.00)$</td>
<td>$-14.583,980,(0.00)$</td>
</tr>
<tr>
<td>$3^1P_x$</td>
<td>2.877 (1.98)</td>
<td>2.899 (2.00)</td>
<td>2.900 (2.00)</td>
<td>2.107 (2.00)</td>
</tr>
<tr>
<td>$3^1P_{x,y}$</td>
<td>3.688 (1.00)</td>
<td>3.688 (2.00)</td>
<td>2.667 (2.00)</td>
<td>2.107 (2.00)</td>
</tr>
<tr>
<td>$1^3P_z$</td>
<td>4.935 (0.02)</td>
<td>4.913 (0.00)</td>
<td>4.913 (0.00)</td>
<td>6.042 (0.00)</td>
</tr>
<tr>
<td>$1^3P_{x,y}$</td>
<td>3.688 (0.00)</td>
<td>4.690 (0.00)</td>
<td>5.952 (0.00)</td>
<td></td>
</tr>
</tbody>
</table>
the MR-SF-TDDFT method; see black dashed lines in Fig. 6.

C. HF molecule

The potential energy curves of the ground electronic state of the HF molecule were calculated using the SF-TDDFT and MR-SF-TDDFT methods along the bond stretching coordinate and are shown in Fig. 7 along with the respective expectation values of the spin, \( \langle S^2 \rangle \). The triplet \( ^3\Sigma^+ \) state \( \left[ \left( \pi_1^2 \pi_2^2 \pi_1^1 \pi_2^1 \right) \right] \) is used as the reference state. Near the equilibrium H–F bond length, both methods yield nearly identical relative energies of the ground state. Although the ground \( ^1\Sigma^+ \) state of HF is a closed-shell state, the SF-TDDFT method yields a small spin-contamination near the equilibrium geometry. The spin-contamination increases rapidly as the H–F bond is stretched, and at \( R = 3.4 \) Å, the total spin \( \langle S^2 \rangle \) reaches a value typical for a 50:50 mixture of true singlet and true triplet states, \( \langle S^2 \rangle = 1 \). The MR-SF-TDDFT method yields a pure-spin singlet ground state as evidenced by the zero expectation value of the total spin; see the dashed black line in Fig. 7. A small difference between the relative energies produced by SF-TDDFT and MR-SF-TDDFT is seen on the range of 1.5–2.5 Å, which is likely caused by the spin-contamination of the SF-TDDFT reference state and the response state.

D. Conical intersection of penta-2,4-dieniminium cation

The penta-2,4-dieniminium cation (PSB3) is a model of the retinal chromophore often used to test computational methods for their ability to correctly describe the topology of the conical intersections between the \( S_0 \) and \( S_1 \) states.\(^{22,23,62-64}\) The conventional spin-conserving linear-response TDDFT fails to produce the correct double cone topology of conical intersections,\(^{22-24,65}\) whereas SF-TDDFT does this correctly.\(^{23,65,66}\) However, SF-TDDFT shows the pronounced spin-contamination of the excited states, which complicates considerably the identification of the relevant states for automatic geometry optimization or molecular dynamics.\(^{22}\)

Here, we use the geometry of the minimum energy conical intersection (MECI) of PSB3 obtained by the SF-BH&HLYP/6-31+G** method\(^{65}\) to test the ability of MR-SF-TDDFT to describe conical intersections. The analytic energy gradient is not yet available for the MR-SF-TDDFT method; hence, only single point calculations are carried out here. In these calculations, the same basis set and density functional as in Ref. 65 are used, i.e., the 6-31+G** and BH&HLYP. The \( \pi\pi^* \) triplet state \( (T_1) \) is used as the reference. The energies of the \( S_0 \) and \( S_1 \) states at the geometry of the SF-BH&HLYP/6-31+G** MECI are reported in Table III. As expected, the SF-TDDFT \( S_0 \) and \( S_1 \) energies are degenerate at the MECI geometry. However, there is a small, ca. 0.3 kcal/mol, \( S_1/S_0 \) gap between the MR-SF-TDDFT energies. This is not unexpected, as the geometry used is not optimized with this method. The small gap however indicates that a CI can indeed be present nearby. The most important observation from the results of Table III is that the noticeable spin-contamination of the SF-TDDFT singlet states completely disappears in MR-SF-TDDFT.

V. CONCLUSIONS

A new method in the context of the collinear spin-flip linear response TDDFT is proposed, which employs an equiensemble of the \( M_3 = +1 \) and \( M_3 = -1 \) components of the triplet state as a (mixed) reference state. The TD-KS equation with the mixed state can be solved within linear response formalism by the use of spinor-like open-shell orbitals. It is a novel attempt to add configurations within the realm of TD-DFT. The new MR-SF-TDDFT method has a number of advantages before the collinear SF-TDDFT methodology. The method nearly eliminates the spin-contamination of the
response states, thus simplifying the identification of the relevant excited states; this is especially important for applications such as the automatic geometry optimization, reaction path following, or molecular dynamics simulations.

The MR-SF-TDDFT method is tested on a number of systems, where multi-reference effects are important for the electronic structure of the ground and excited singlet states. For the low-lying excited states of beryllium, the new method eliminates completely the spin-contamination of the 1P and 1P states. Besides that, the erroneous splitting between the 3P, 1P, and 1P triplet and singlet states. As this is achieved without a considerable increase of the SF-TDDFT computational cost, the new method enables clean separation between the triplet and singlet states. This is true for the conical intersection in the penta-2,4-dieniminium cation (PSB3), where the S and T1 dissociation of hydrogen fluoride. The MR-SF-TDDFT and SF-TDDFT results. The same is true for the conical intersection curves of chemical bonds, which was tested on the dissociation curves of chemical bonds, which was tested on the electronic structure of the ground and excited singlet states. As this is achieved without a considerable increase of the SF-TDDFT computational cost, the new method seems very well suited for molecular dynamics simulations of the excited states.

A further study of the pairing strengths and an application of noncollinear XC kernel are necessary to obtain better energy curves. Overall, MR-SF-TDDFT is a promising method for excited-state ab initio MD simulations and non-adiabatic MD simulations. The formulation and implementation of analytical energy derivatives of response states are currently under development.

SUPPLEMENTARY MATERIAL

A supplementary material with eight sections is supplied, which contains the detailed derivations and informations.

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