

# Breaking the Curse of the Non-Dynamical Correlation Problem: the Spin-Flip Method

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The spin-flip approach to multi-reference situations (e.g., bond-breaking and diradicals) is described. Both closed and open shell singlet states are described within a single reference formalism as spin-flipping, e.g.,  $\alpha \rightarrow \beta$ , excitations from a triplet ( $M_s=1$ ) reference state for which both dynamical and non-dynamical correlation effects are much smaller than for the corresponding singlet state. Formally, the new theory can be viewed as an Equation-of-Motion model where excited states are sought in the basis of determinants conserving the total number of electrons but changing the number of  $\alpha$  and  $\beta$  electrons.

## 1 Introduction

It is difficult to overestimate the importance of electronic structure theory in modern chemistry (1). The design and interpretation of experiments are often aided by high-level *ab initio* calculations of structural, thermochemical, and spectroscopic properties. Additional insight can be derived from the examination of wavefunctions and electron distributions which are produced in electronic structure calculations. Most importantly, high-level calculations can now be carried out almost routinely due to the availability of efficient and user-friendly electronic structure packages. However, in order for electronic structure calculations to be accessible by the general chemical community, the underlying methods should belong to the class of the so called “theoretical model chemistries” (2), or, more loosely, “black-box” methods.

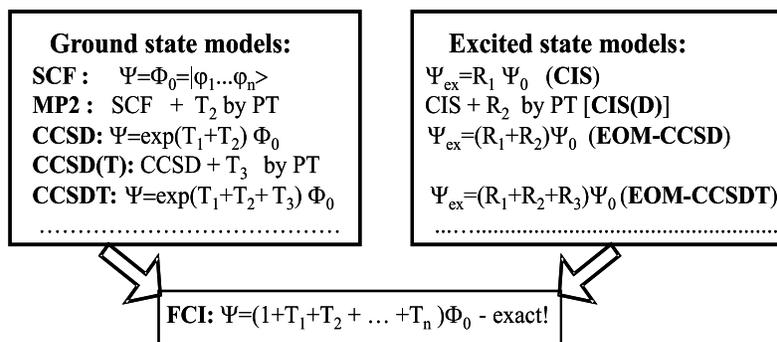


Figure 1: *The hierarchy of approximations to an  $n$ -electron wavefunction. The left panel presents models of increasing complexity for ground state wavefunctions. The emerging hierarchy of excited states' methods is summarized on the right panel. The simplest possible description of an  $N$ -electron wavefunction is given by a single Slater determinant composed of spin-orbitals, i.e., states of pseudo-independent electrons moving in the field of nuclei and a mean field of other electrons [self-consistent field (SCF), or Hartree-Fock (HF) model]. The effects of electron interaction (i.e., correlation) can gradually be turned on by including single, double, and higher excitations ( $T_1$ ,  $T_2$ , etc). This can be done perturbatively, e.g., as in the Møller-Plesset theory (MP), or explicitly, e.g., as in coupled-cluster (CC) methods. The corresponding excited states' models can be derived within the linear response (LR) or equation-of-motion (EOM) formalisms. The resulting wavefunctions have a physically appealing form: excited states are described as electronic excitations from approximate ground state wave functions (the operator  $R_m$  generates all possible  $m$ -electron excitations out of the reference determinant  $\Phi_0$ ). For example, the SCF analog for excited states, the configuration interaction singles (CIS) model, describes excited states as a linear combination of all singly excited determinants. Similarly to the ground state models, accuracy can systematically be improved by including higher excitations. Both series converge to the exact solution of the Schrödinger equation (in a given one-electron basis set) — full configuration interaction (FCI), which, in turn, becomes exact in the limit of the complete one-electron basis set.*

As defined by Pople, “theoretical model chemistry” consists of a pair of well-defined approximations to the exact wavefunction: correlation treatment and one-electron basis set (2). Fig. 1 summarizes a hierarchy of approximate methods for correlation treatment (3, 4) in the ground and excited states. Both the ground state's (left panel) and excited states' (right panel) series converge to the exact solution, and the accuracy of

the description improves with each additional step of sophistication (at the price of increased computational cost, of course). Fortunately, chemically and spectroscopically relevant answers can be obtained within computationally tractable (for moderate-size molecules) models. For example, the coupled-cluster model with single and double excitations (5) augmented by triple excitations treated perturbatively [CCSD(T)] (6) yields highly accurate structural (errors in bond lengths of 0.2-0.3 pm) and thermochemical (errors of less than 1 kcal/mol in reaction enthalpies) data (3). Excitation energies can be calculated with 0.1-0.3 eV accuracy (7) by the excited states' counterpart of CCSD, EOM-CCSD method (8-10). Unfortunately, *the above error bars are valid only for species whose ground state wavefunction is dominated by a single Slater determinant and for excited states dominated by single electron excitations.* This restricts the applications of single-reference (SR) models to well-behaved molecules such as closed-shell species at their equilibrium geometries, leaving many chemically important situations [e.g., transition states, bond-breaking, and diradicals (11)] to the domain of multi-reference methods (12).

In order to understand the origin of the breakdown of the SR methods away from equilibrium, consider the torsional potential in ethylene (Fig. 2). While at its equilibrium geometry ethylene is a well-behaved closed-shell molecule whose ground and  $\pi$ -valence excited states can be described accurately by SR models (except for the doubly excited  $Z$ -state), it becomes a diradical at the barrier, when the  $\pi$ -bond is completely broken (13). Thus, at the twisted geometry all of ethylene's  $\pi$ -valence states ( $N$ ,  $T$ ,  $V$ , and  $Z$ ) are two-configurational, *except for the high-spin components of the triplet.*

The traditional recipe for computing ethylene's torsional potential for the ground and excited states would involve state-by-state (or state-averaged) calculations with the two-configurational SCF (TCSCF) method, the simplest variant of complete active space SCF (CASSCF) (14-16) further augmented by perturbation theory (MRPT) or configuration interaction (MRCI) corrections (12). Recently, this scheme has been reformulated (17-19) employing less expensive coupled-cluster wavefunctions instead of the exponentially expensive CASSCF one. The method, valence optimized orbitals coupled-cluster doubles (VOCCD) (18), is formulated in a SR fashion, however it still (i) relies on an active space selection (20); (ii) involves an orbital optimization step; (iii) requires subsequent inclusion of higher order corrections in a two-step procedure (19); and (iv) is not easily generalized for excited states (21). In this Chapter, we discuss an alternative strategy, the spin-flip (SF) approach, which is a multistate method (i.e., yields several states in one computation), does not require an active space selection and orbital optimization (thus, is genuinely a robust "black-box" type SR method), and treats both non-dynamical and dynamical correlation in one scheme (i.e., is not a two-step procedure).

As mentioned above, the  $M_s = \pm 1$  components of the  $T$ -state of ethylene

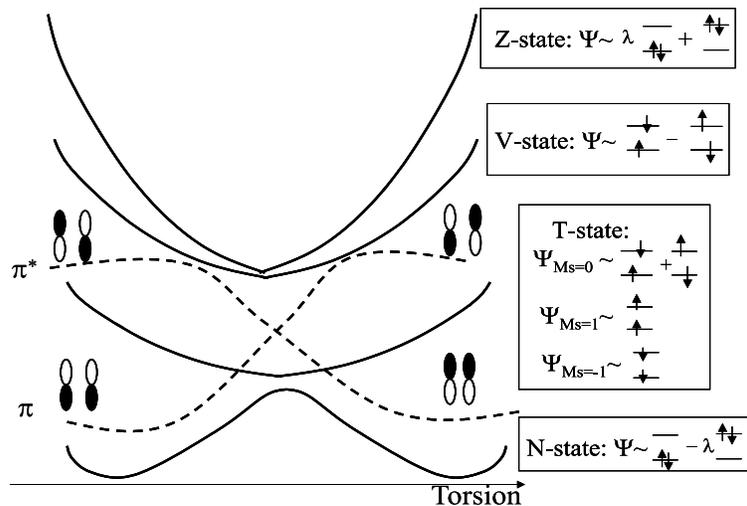


Figure 2: Around equilibrium, the ground state ( $N$ -state) wavefunction of ethylene is dominated by the  $\pi^2$  configuration. However, as a degeneracy between  $\pi$  and  $\pi^*$  develops along the torsional coordinate, the importance of the  $(\pi^*)^2$  configuration increases. At the barrier, where  $\pi$  and  $\pi^*$  are exactly degenerate, the qualitatively correct wavefunction for the  $N$ -state must include both configurations with equal weights. That is why the quality of the SR wavefunctions degrades as the molecule is twisted: even when the second configuration is explicitly present in a wavefunction (e.g., as in the CCSD or CISD models), it is not treated on the same footing as the reference configuration,  $\pi^2$ . The singlet and triplet  $\pi\pi^*$  states (the  $V$  and  $T$  states, respectively) are formally single-electron excitations from the  $N$ -state, and are well described by the SR excited states' models (despite the fact that both the singlet and the  $M_s=0$  component of the triplet are two-configurational and therefore are not accessible by the ground state SR methods). The  $Z$ -state, however, is formally a doubly excited state with respect to the  $N$ -state, and therefore SR models will not treat it accurately. Note that the high-spin  $M_s = \pm 1$  components of the triplet  $T$ -state remain single-determinantal at all the torsional angles. Moreover, all the  $M_s = 0$  configurations employed in the  $N$ ,  $V$ ,  $T$ , and  $Z$  states are formally single-electron excitations which involve a spin-flip of one electron with respect to any of the two high-spin triplet configurations.

(Fig. 2) are single-determinantal at the ground state equilibrium geometry, and remain single-determinantal at all values of the twisting angle. Therefore, they can be accurately described by SR methods at all the torsional coordinates (22). Moreover, all the low-spin  $M_s=0$  determinants from Fig. 2

are formally *single electron excitations from the high-spin triplet state involving a spin-flip of one electron*. This immediately suggests employing the EOM or LR formalism and describing the target  $M_s = 0$  states as spin-flipping excitations from the well-behaved high-spin reference state. This is the essence of the SF approach (23–29).

It should be mentioned that describing ground state wavefunctions as “excited” states with respect to a reference state which is orthogonal to a target wavefunction is a well known approach. For example, the ionized states EOM-CCSD methods have proven very useful for doublet radicals whose theoretical treatment is often plagued by symmetry breaking. In this approach, the ground state CC equations are solved for a *closed shell* cation or anion, and the ground state of the corresponding doublet radical is sought in the basis of determinants which do not conserve the number of electrons, e.g., either in N-1 (EOM ionization potential CC [EOMIP-CC]), or in N+1 (EOM electron affinity CC [EOMEA-CC]) electron basis (30–32). Recently, doubly-ionized/attached EOM models which target diradicals have been presented (33).

## 2 The method

In traditional (non-SF) SR excited states models, the excited state wavefunctions are parameterized as follows (see Fig. 1):

$$\Psi_{M_s=0}^{s,t} = \hat{R}_{M_s=0} \tilde{\Psi}_{M_s=0}^s, \quad (1)$$

where  $\tilde{\Psi}_{M_s=0}^s$  is a closed-shell reference wavefunction, and the operator  $\hat{R}$  is an excitation operator truncated at a certain level of excitation (which should be consistent with the theoretical model employed to describe the reference  $\tilde{\Psi}^s$ ). Note that only excitation operators that do not change the total number of  $\alpha$  and  $\beta$  electrons, i.e.  $M_s=0$ , need to be considered in Eq. (1).

As explained in the Introduction, this scheme breaks down both for ground and excited states when orbitals from occupied and virtual subspaces become near-degenerate, e.g. at the dissociation limit or in diradicals (see Fig. 2). To overcome this problem, the SF model employs a high-spin triplet reference state which is accurately described by a SR wavefunction. The target states, closed and open shell singlets and triplets, are described as spin-flipping excitations:

$$\Psi_{M_s=0}^{s,t} = \hat{R}_{M_s=-1} \tilde{\Psi}_{M_s=+1}^t, \quad (2)$$

where  $\tilde{\Psi}_{M_s=+1}^t$  is the  $\alpha\alpha$  component of the triplet reference state,  $\Psi_{M_s=0}^{s,t}$  stands for the final ( $M_s=0$ ) singlet and triplet states, respectively, and the operator  $\hat{R}_{M_s=-1}$  is an excitation operator that flips the spin of an electron.

In order to distinguish  $\hat{R}_{M_s=-1}$  excitation operators from their non-spin-flipping counterparts, we shall denote  $m$ -electron excitation operators with a spin-flip of one electron as  $U_m$  instead of  $R_m$ . As can be seen from Fig. 2, all the configurations used to describe diradical-type wavefunctions (e.g.,  $N$ ,  $V$ ,  $T$ , and  $Z$  states of ethylene) are formally single excitations with respect to the high-spin component of the triplet ( $|\pi\alpha\pi^*\alpha\rangle$ ).

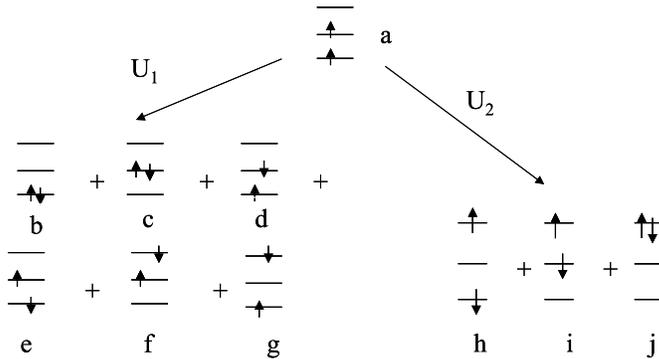


Figure 3: Two electrons in three orbitals system. Configuration (a) is the reference configuration. Single electron excitations with spin-flip produce configurations (b)-(g). Two-electron excitations with a single spin-flip produce configurations (h)-(j). Note that non-spin-flipping excitations or excitations that flip the spin of two electrons produce  $M_s = \pm 1$  configurations, which do not interact through the Hamiltonian with the final  $M_s = 0$  states, and thus are not present in the model.

Fig. 3 shows the reference high-spin configuration and the spin-flipping single and double excitations for two electrons in three orbitals system. Configuration (b) corresponds to a ground-state closed shell singlet. Configurations (c)-(e) are those which become degenerate with (b) at the dissociation limit. They are employed in a description of diradicals' states, e.g., states which can be derived by distributing two electrons over two (nearly) degenerate orbitals ( $N$ ,  $V$ ,  $T$ , and  $Z$  states of twisted ethylene are of this type). It is easy to see that (b)-(e) are treated on an *equal footing* in our model, and that other configurations *do not introduce imbalance in treating (b)-(e)*.

Therefore, the SF ansatz (2) is sufficiently flexible to describe changes in ground state wavefunctions along a single bond-breaking coordinate. Moreover, it treats both closed-shell (e.g.,  $N$  and  $Z$ ) and open-shell ( $V$  and  $T$ ) diradicals' states in a balanced fashion, i.e., without overemphasizing the importance of one of the configurations.

Similarly to traditional excited state theories, the description of the final states can be systematically improved by employing theoretical models

of increasing complexity for the reference wavefunction as summarized in Fig. 4. For example, the simplest SF model employs a Hartree-Fock wavefunction, and the operator  $\hat{U}$  is then truncated at single excitations (SF-CIS or SF-SCF) (23, 29). SF-CIS can be further augmented by perturbative corrections [SF-CIS(D) or SF-MP2] (24). A yet more accurate description can be achieved by describing the reference wavefunction by a coupled-cluster model, e.g., CCSD (28) or OO-CCD (23, 34). In this case, the excitation operator  $\hat{R}$  consists of single and double excitation operators involving a flip of the spin of an electron (23). The corresponding SF equations in spin-orbital form are identical to those of traditional excited state theories, i.e., CIS, CIS(D), EOM-CCSD or EOM-OO-CCD, however, they are solved in a different subspace of determinants: non-SF theories consider only  $M_s=0$  excitation operators, whereas SF operates in the  $M_s=-1$  subspace. The computational cost and scaling of the SF models are identical to those of the corresponding non-SF excited state theories.

Reference:	Method:	Wavefunction:
SCF	SF-SCF (or SF-CIS)	$U_1 \Phi_0$
MP2	SF-MP2 [or SF-CIS(D)]	$U_1 \Phi_0 + T_2$ by PT
CCSD	SF-CCSD	$(U_1+U_2)\exp(T_1+T_2)\Phi_0$
CCSDT	SF-CCSDT	$(U_1+U_2+U_3)\exp(T_1+T_2+T_3)\Phi_0$
.....		

Figure 4: *Hierarchy of the SF models. Similar to the non-SF SR methods, the SF models converge to the exact  $n$ -electron wavefunction when the spin-flipping operator  $\hat{U}$  includes up to  $n$ -tuple excitations. For example, the SF-CCSD model is exact for two electrons.*

Two of the SF models, SF-CISD and SF-DFT, deserve special mention. By using the SF formulation, the CI can be formulated in a rigorously size-consistent way (25, 29). For example, the SF-CISD model is (i) variational, (ii) size-consistent, and (iii) exact for two electrons. So far, this is the only approximate model [except for fully variational CCSD (35) which is prohibitively expensive to be of a practical use] that simultaneously satisfies these three highly desirable properties (2).

Lastly, the SF approach implemented within the time-dependent (TD) density functional theory (DFT) extends DFT to multi-reference situations with no cost increase relative to the non-SF TD-DFT. Similarly to DFT and TD-DFT, the SF-DFT model (27) is formally exact and therefore will yield exact answers with the exact density functional. With the available inexact functionals, the SF-DFT represents an improvement over its non-SF counterparts. It has been shown to yield accurate equilibrium properties and singlet-triplet energy gaps in diradicals (27).

### 3 The spin-flip method for bond-breaking: the ethylene torsional potential

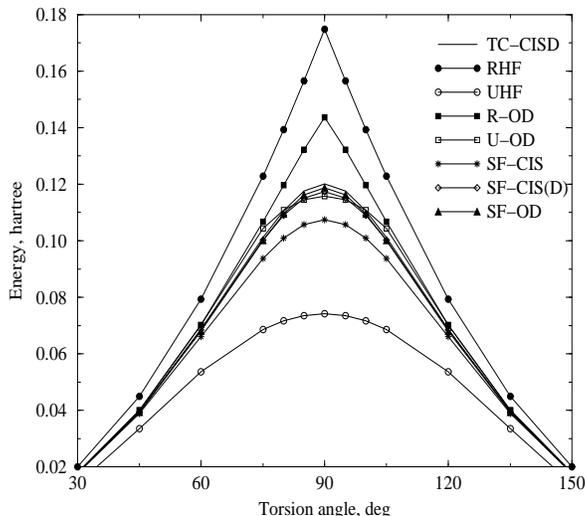


Figure 5: *Ethylene torsion, DZP basis. All curves are shifted such that the energy at  $0^\circ$  is zero. The spin-flip curves do not exhibit an unphysical cusp and are closer to the reference TC-CISD curve than the corresponding spin-restricted and spin-unrestricted models.*

Fig. 5 shows the torsional potential calculated by the SF [SF-CIS, SF-CIS(D), and SF-OD] and non-SF (restricted and unrestricted HF and OD) methods (23, 24, 36). All curves are compared with the TC-CISD curve (24). The unbalanced treatment (within a single reference framework) of  $(\pi)^2$  and  $(\pi^*)^2$  configurations results in unphysical shapes of the PES, i.e., a cusp at  $90^\circ$  and large errors in barrier heights. The spin-unrestricted PESs are smooth; however, the barrier height is usually underestimated, even by the highly correlated methods (36). Moreover, the shape of the unrestricted PES can be quite wrong, for example, the U-OD curve is too flat around the barrier as compared against the TC-CISD one (see Fig. 5). Also, the UHF based wavefunctions are heavily spin-contaminated around the barrier *even for highly correlated methods such as coupled-cluster models* (36). All the SF models produce smooth PESs. Quantitatively, SF-SCF represents a definite advantage over both the RHF and UHF results. Similarly, the SF-OD curve is closer to our reference TC-CISD curve than either R-OD or U-OD. The SF-CIS(D) curve is very close to the more expensive SF-OD one. Similar performance of the SF methods has been observed for

bond-breaking in HF, BH, and F<sub>2</sub> (23–25).

## 4 The spin-flip method for diradicals

Diradicals represent the most clear-cut application of the SF approach because in these systems the non-dynamical correlation derives from a single HOMO-LUMO pair (e.g.,  $\pi$  and  $\pi^*$  in twisted ethylene). In this section we present results for methylene and trimethylenemethane (TMM).

Four low-lying states of methylene are diradical-type states (11) deriving from the distribution of two electrons in the two nearly degenerate orbitals,  $3a_1$  ( $s^x p^y$  hybrid) and  $1b_1$  (out-of-plane p-orbital). The ground state of methylene is triplet  $\tilde{X}^3B_1$ :

$$\tilde{X}^3B_1 \approx (1a_1)^2(2a_1)^2(1b_2)^2(3a_1)(1b_1) \quad (3)$$

The lowest singlets are:

$$\tilde{a}^1A_1 \approx \lambda(1a_1)^2(2a_1)^2(1b_2)^2(3a_1)^2 - \sqrt{1-\lambda^2}(1a_1)^2(2a_1)^2(1b_2)^2(1b_1)^2 \quad (4)$$

$$\tilde{b}^1B_1 \approx (1a_1)^2(2a_1)^2(1b_2)^2(3a_1)(1b_1) \quad (5)$$

$$\tilde{c}^1A_1 \approx \sqrt{1-\lambda^2}(1a_1)^2(2a_1)^2(1b_2)^2(3a_1)^2 + \lambda(1a_1)^2(2a_1)^2(1b_2)^2(1b_1)^2 \quad (6)$$

While the  $\alpha\alpha$  ( $M_s=1$ ) component of the  $\tilde{X}^3B_1$  state (3) is essentially a single-reference wave function, the corresponding singlet  $\tilde{b}^1B_1$  state (as well as the  $M_s=0$  component of the triplet) is a linear combination of two Slater determinants with equal coefficients. Therefore,  $\tilde{b}^1B_1$  state cannot be described within a formalism that uses a single Slater determinant reference. The character of the lowest singlet,  $\tilde{a}^1A_1$ , varies from a single-reference ( $\lambda \approx 1$ ) to the two-configurational ( $\lambda \approx \frac{1}{\sqrt{2}}$ ) wave function. At the  $\tilde{a}^1A_1$  equilibrium geometry, the effect of the second configuration is relatively small, and the  $\tilde{a}^1A_1$  state can be reasonably well described by SR models. The second  $^1A_1$  state,  $\tilde{c}^1A_1$  can be described as a doubly excited state with respect to  $\tilde{a}^1A_1$ . At its equilibrium geometry, the  $\tilde{c}^1A_1$  state requires a two-configurational wave function. Therefore, it is not possible to describe all three singlet states of methylene by a single-reference model. The spin-flip model, however, describes all these states as spin-flipping excitations from the reference  $M_s=1$  triplet  $\tilde{X}^3B_1$  state.

For this small system, we can compare the performance of different methods against the FCI results (37) in a relatively large TZ2P basis. Calculated equilibrium geometries, vibrational frequencies, and adiabatic singlet-triplet gaps for the singlet states of methylene are shown in Table 1. The SF models describe accurately all three singlet states. SF-CIS(D) represents a qualitative improvement over SF-CIS, while the SF-CCSD and SF-OD results follow FCI closely.

Table 1: **Equilibrium geometries, harmonic vibrational frequencies ( $\text{cm}^{-1}$ ), and adiabatic excitation energies (eV) for singlet methylene ( $\tilde{a}^1A_1$ ,  $\tilde{b}^1B_1$ , and  $\tilde{c}^1A_1$  states)<sup>a</sup>.**

Method	$r_e, \text{\AA}$	$\alpha$	$\omega_1(a_1)$	$\omega_2(a_1)$	$\omega_3(b_2)$	$\Delta E_{st}$
$\tilde{a}^1A_1$						
FCI/TZ2P <sup>b</sup>	1.1089	101.89	2899	1404	2971	0.483
SF-SCF/TZ2P	1.0945	104.07	3096	1485	3176	0.883
SF-CIS(D)/TZ2P	1.0974	102.86	3017	1443	3111	0.613
SF-OD/TZ2P	1.1043	102.37	2932	1422	3025	0.514
SF-CCSD/TZ2P	1.1040	102.45	2937	1421	3011	0.517
$\tilde{b}^1B_1$						
FCI/TZ2P <sup>b</sup>	1.0748	141.56	3136	1006	3470	1.542
SF-SCF/TZ2P	1.0624	142.38	3311	1103	3611	1.875
SF-CIS(D)/TZ2P	1.0652	141.59	3243	1082	3546	1.646
SF-OD/TZ2P	1.0716	141.32	3160	1028	3424	1.564
SF-CCSD/TZ2P	1.0716	141.32	3162	1034	3420	1.565
$\tilde{c}^1A_1$						
FCI/TZ2P <sup>b</sup>	1.0678	170.08	3200	666	3531	2.674
SF-SCF/TZ2P	1.0507	174.48	3446	343	3809	3.599
SF-CIS(D)/TZ2P	1.0544	173.73	3374	416	3727	2.953
SF-OD/TZ2P	1.0639	170.14	3238	672	3555	2.715
SF-CCSD/TZ2P	1.0639	170.14	3240	677	3581	2.718

<sup>a</sup> TZ2P basis set from Ref. (37). SF models employ the  $\tilde{X}^3B_1$  ground state as the reference. The SF-CIS, SF-CIS(D), and SF-OD results are from Refs. (24, 25).  $\Delta E_{st}$  are calculated at the FCI/TZ2P optimized geometries.

<sup>b</sup> Ref. (37). One frozen core and one deleted virtual orbital.

Our next example, the TMM diradical, is a more challenging case because its frontier orbitals are exactly degenerate. The  $\pi$ -system of TMM is shown in Fig. 6: four  $\pi$ -electrons are distributed over four molecular  $\pi$ -type orbitals. Due to the exact degeneracy between the two  $e'$  orbitals at the  $D_{3h}$  structure, Hund’s rule predicts the ground state of the molecule to be a triplet  $^3A'_2$  state (similar to the  $T$ -state in ethylene). This is confirmed by both the experimental and theoretical findings (38–43).

The vertical excitation energies are summarized in Fig. 6 (with  $C_{2v}$  symmetry labels) (26, 44). The three lowest singlet states are the diradical singlet states (similar to the  $N$ ,  $V$ , and  $Z$  states of ethylene). However, excited states that derive from excitations of other  $\pi$  electrons are also relatively low in energy. The first closed-shell singlet,  $^1A_1$  and the open-shell singlet  $^1B_2$  (similar to the  $N$  and  $V$  states of ethylene, respectively) are degenerate at the  $D_{3h}$  geometry due to the degeneracy of  $a_2$  and  $2b_1$  orbitals. The second closed-shell singlet  $2^1A_1$  (an analog of the  $Z$ -state) is followed

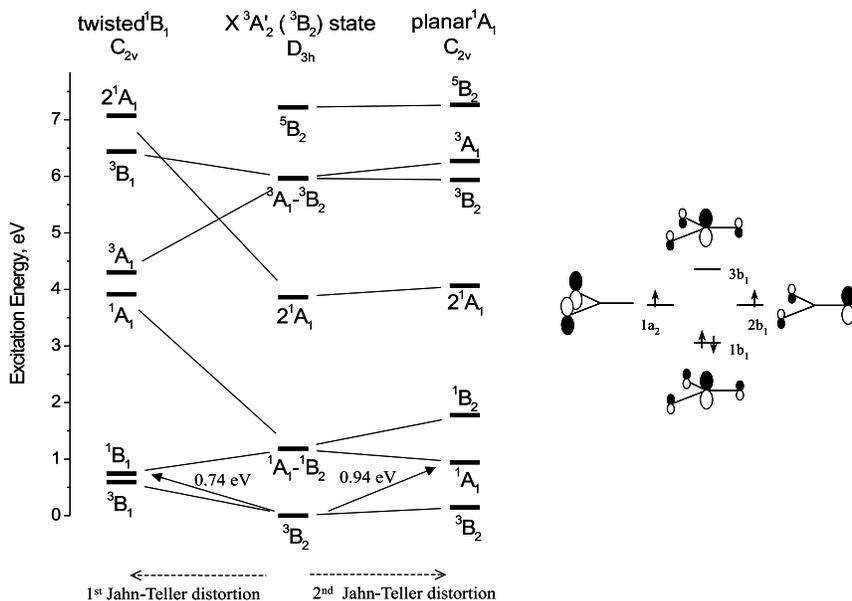


Figure 6: On the right, the  $\pi$ -system of TMM and the electronic configuration of the ground state are shown ( $C_{2v}$  labels are used). The left panel presents electronic states of TMM at the ground state equilibrium  $D_{3h}$  geometry, and at the two Jan-Teller  $C_{2v}$  distorted structures (equilibrium geometries of the  $1^1B_1$  and  $1^1A_1$  states). The corresponding adiabatic singlet-triplet gaps are also shown.

by a pair of degenerate triplets,  $^3A_1$  and  $^3B_2$ , obtained by excitation of one electron from the doubly occupied  $1b_1$  orbital to the  $a_2$  or  $2b_1$  degenerate orbitals. Finally, there is a quintet  $^5B_2$  state in which all  $\pi$ -orbitals are singly occupied. We do not discuss low-lying states derived from electron excitations beyond the TMM's  $\pi$ -system. Several such states appear between the pair of degenerate triplets and the quintet state. The SF-OD model should be augmented by higher excitations to achieve a quantitatively accurate description of these states.

In accordance with the Jahn-Teller theorem, the degeneracy between the degenerate states (closed-shell and open-shell singlets, and a pair of triplets) can be lifted in lower symmetry. The closed-shell singlet is stabilized at the planar  $C_{2v}$  geometry, with one short CC bond. The open-shell singlet prefers an equilibrium structure with one long CC bond and a twisted methylene group. The real minimum of the open-shell singlet is a  $C_2$  structure with a  $79.0^\circ$  twisted methylene group; however, the energy difference between this structure and the  $C_{2v}$  twisted one (the dihedral angle equals  $90.0^\circ$ ) is only

0.001 eV (0.03 kcal/mol). The second  $^1A_1$  state prefers  $D_{3h}$  equilibrium geometry. The adiabatic singlet-triplet energy separations for the three lowest singlet states are 0.74 eV, 0.94 eV, and 3.86 eV for the  $1^1B_1$ ,  $1^1A_1$ , and  $2^1A_1$  states, respectively (26) (at the SF-OD level with the basis set composed of a cc-pVTZ basis on carbons and a cc-pVDZ basis on hydrogens). These energies are very close to the MRPT values (26) of 0.72 and 0.83 eV (for the  $1^1B_1$  and  $1^1A_1$  states, respectively). With regard to experiment, the lowest adiabatic state,  $1^1B_1$ , has not been observed in the photoelectron spectrum (40) because of unfavorable Frank-Condon factors. The experimental adiabatic energy gap (including ZPE) between the ground triplet state and the  $1^1A_1$  state is 0.70 eV. The estimated experimental  $T_e$  is 0.79 eV, which is 0.15 eV lower than the SF-OD estimate.

In our detailed benchmark study (26), we calculated the singlet-triplet energy separations for a large number of systems, i.e., O,C, and Si atoms, O<sub>2</sub>, NH, NF, and OH<sup>+</sup> diatomics, methylene isovalent series (CH<sub>2</sub>, NH<sub>2</sub><sup>+</sup>, SiH<sub>2</sub>, and PH<sub>2</sub><sup>+</sup>), benzynes, and TMM. In all these cases, the SF models performed very well. The SF-OD results are within 3 kcal/mol of the experimental or highly accurate multi-reference values. In most cases the errors are about 1 kcal/mol. Drawing from the performance of single-reference methods for well-behaved molecules, we expect that a perturbative account of triple excitations will bring the corresponding SF-CC model into the *chemical accuracy* range, i.e., < 1 kcal/mol.

## 5 Conclusions

The SF approach extends the applicability of SR methods to bond-breaking problems and to diradicals. Both closed and open shell singlet states are described within a single reference formalism as spin-flipping, e.g.,  $\alpha \rightarrow \beta$ , excitations from the triplet ( $M_s=1$ ) reference state for which both dynamical and non-dynamical correlation effects are much smaller than for the corresponding singlet state. Formally, the new theory can be viewed as an EOM model where the excited states are sought in the basis of determinants conserving the total number of electrons but changing the number of  $\alpha$  and  $\beta$  electrons. A very attractive feature of the new approach is that it is described by equations identical to the EOMEE equations (in spin-orbital form).

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## References

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flexible enough to describe all the major interactions of the valence electrons, e.g., the polarization of  $\sigma$  electrons for the  $\pi\pi^*$  ionic configurations, as in the  $V$ -state of ethylene, etc. The advantage of the VOCCD model is that it enables one to perform full valence active space calculations for much larger systems than it is possible for CASSCF. This eliminates certain arbitrariness involved in the choice of the active space.

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