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Spin-Flip Equation-of-Motion Coupled-Cluster Electronic Structure Method for a Description of Excited States, Bond Breaking, Diradicals, and Triradicals

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ABSTRACT

The spin-flip (SF) approach to multireference situations (e.g., bond breaking, diradicals, and triradicals) is described. Both closed- and open-shell low-spin states are described within a single reference formalism as spin-flipping, e.g., $\alpha \rightarrow \beta$, excitations from a high-spin reference state for which both dynamical and nondynamical correlation effects are much smaller than for the corresponding low-spin state. Formally, the SF approach can be viewed as an equation-of-motion model, where target states are sought on the basis of determinants conserving the total number of electrons but changing the number of α and β electrons.

1. Introduction

High-level calculations of closed-shell molecules can now be carried out almost routinely because of the availability of efficient and user-friendly electronic structure packages featuring a hierarchy of "theoretical model chemistries".[1] The well-defined nature of these approximate methods of solving the electronic Schrödinger equation enables their calibration,[2] thus providing error bars for each model. Using these error bars as criteria for balancing accuracy versus computational cost, a chemist can choose just the right tool for a particular problem at hand and use it in a "black box" fashion.

As defined by Pople, "theoretical model chemistry" consists of a pair of well-defined approximations to the exact wave function: correlation treatment and one-electron basis set.[1] Figure 1 summarizes a hierarchy of approximate methods for correlation treatment[2−4] in the ground and excited states. Both the ground and excited states' 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

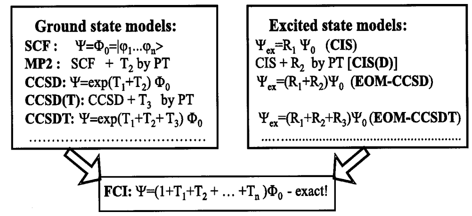

FIGURE 1. Hierarchy of approximations to a *N*-electron wave function. Models of increasing complexity for ground- and excited-state wave functions are presented in the left and right panels, respectively. The simplest description of a *N*-electron wave function is given by a single Slater determinant 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 filed (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 Møller−Plesset (MP) theory, or explicitly, e.g., as in coupled-cluster (CC) methods. The corresponding excited state models can be derived within the linear response (LR) or equation-of-motion (EOM) formalisms, in which the 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 Φ_0). For example, the SCF analogue 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.

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 0.002−0.003 Å) and thermochemical (errors of less than 1 kcal/mol in reaction enthalpies) data.[2] Excitation energies can be calculated with 0.1−0.3 eV accuracy[7] by the excited states' counterpart of CCSD, equation-of-motion for excitation energies (EOM-EE) CCSD method.[8−10] Note that *multi-configurational* excited states, e.g., open-shell singlets, are correctly described by *single-reference* (SR) excited-state models, provided that their wave functions are dominated by single-electron excitations. For example, the two-configurational $^{1,3}\pi \rightarrow \pi^*$ excited states of ethylene are correctly described even at the CIS level, because both configurations, $\pi\alpha\pi^*\beta$ and $\pi\beta\pi^*\alpha$, are single-electron excitations from the ground-state $\pi\alpha\pi\beta$ determinant.

Unfortunately, *the above error bars are valid only for species whose ground-state wave function is dominated by a single Slater determinant and for excited states dominated by single-electron excitations*. This restricted the mainstream applications of SR models to well-behaved molecules such as closed-shell species at their equilibrium geometries, some doublet radicals, or triplet diradicals,

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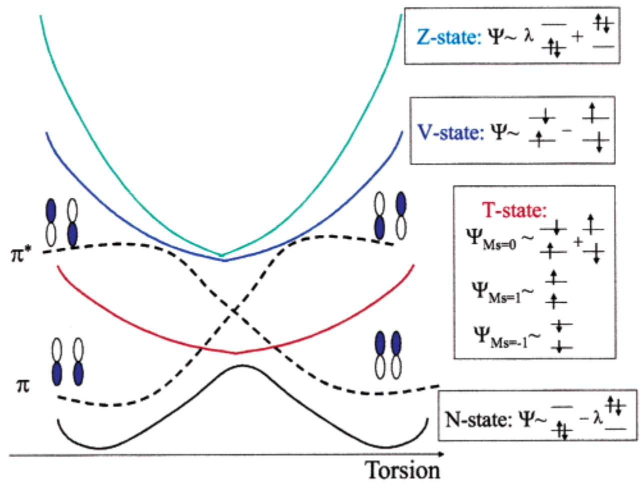

FIGURE 2. Around equilibrium, the ground-state (*N*-state) wave function of ethylene is dominated by the π^2 configuration. However, as a degeneracy between π and π^* develops along the torsional coordinate, the importance of the $(\pi^*)^2$ configuration increases. At the barrier, where π and π^* are exactly degenerate, the qualitatively correct wave function for the *N*-state must include both configurations with equal weights. That is why the quality of the SR wave functions degrades as the molecule is twisted: even when the second configuration is explicitly present in a wave function (e.g., as in the CCSD or CISD models), it is not treated on the same footing as the reference configuration, π^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 of the torsional angles. Moreover, all of the $M_s = 0$ configurations present 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.

leaving many chemically important situations (e.g., transition states, bond breaking, singlet diradicals,[11] and triradicals) to the domain of multireference methods.[12,13]

To understand the origin of the breakdown of the SR methods away from equilibrium, consider the torsional potential in ethylene (Figure 2). Whereas at its equilibrium geometry ethylene is a well-behaved closed-shell molecule whose ground and π-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 π bond is completely broken.[14] Thus, at the twisted geometry, all of ethylene's π-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) further augmented by the perturbation theory (MRPT) or configuration interaction (MRCI) corrections.[12] Similar ideas have also been explored within CC formalism.[15−18]

Here, we discuss an alternative strategy, the spin-flip (SF) approach, which is, as any EOM model, 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 nondynamical and dynamical correlation simultaneously (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) 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 of the torsional coordinates.[19] Moreover, all of the low-spin $M_s = 0$ determinants from Figure 2 are formally *single-electron excitations from the high-spin triplet state involving a spin flip of one electron*. This immediately suggests employing 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[20−26] described below.

2. Equation-of-Motion: A Versatile Electronic Structure Tool

EOM approach[3,8,10,25,27−29] is a powerful and versatile electronic structure tool that allows one to describe many multiconfigurational wave functions within a single-reference formalism.[30] Conceptually, EOM is similar to configuration interaction (CI): target EOM states are found by diagonalizing the so-called similarity transformed Hamiltonian $\bar{H} \equiv e^{-T}He^{T}$:

$$\bar{H}R = ER \tag{1}$$

where T and R are general excitation operators with respect to the reference determinant $|\Phi_0\rangle$. Regardless of the choice of T, the spectrum of $\bar{H}$ is exactly the same as that of the original Hamiltonian H; thus, in the limit of the complete many-electron basis set, EOM is identical to FCI. In a more practical case of a truncated basis, e.g., when T and R are truncated at single and double excitations, the EOM models are numerically superior to the corresponding CI models,[31] because correlation effects are "folded in" in the transformed Hamiltonian. Moreover, the truncated EOM models are rigorously size-extensive,[32,33] provided that the amplitudes T satisfy the CC equations for the reference state $|\Phi_0\rangle$:

$$\langle\Phi_\mu|\bar{H}|\Phi_0\rangle \tag{2}$$

where Φ_μ denotes μ-tuply excited determinants, e.g., $\{\Phi_i^a, \Phi_{ij}^{ab}\}$ in the case of CCSD.

The computational scaling of EOM-CC and CI methods is identical, e.g., both EOM-CCSD and CISD scale as N^6. When different types of excitation operators and references $|\Phi_0\rangle$ are combined, different groups of target states can be accessed as explained in Figure 3. For example, electronically excited states can be described when the

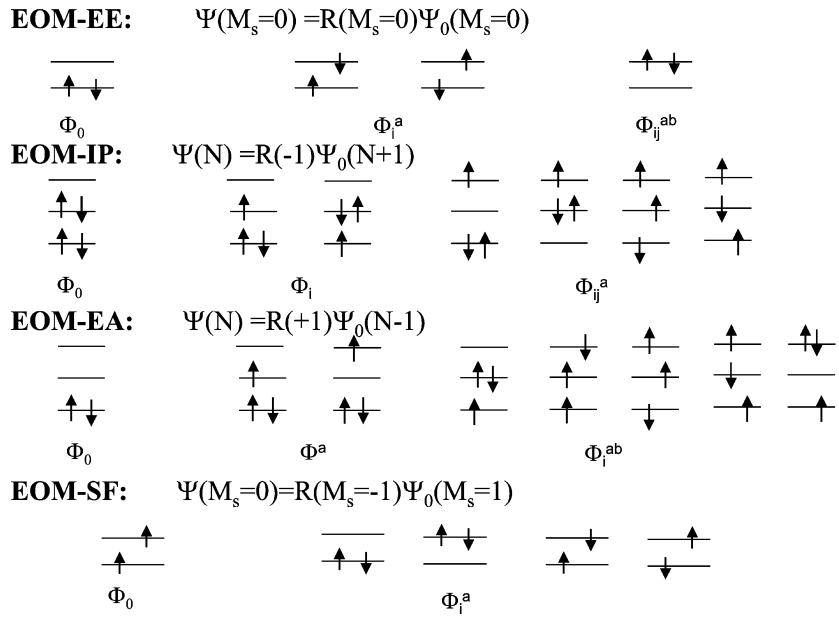

FIGURE 3. In EOM formalism, target states Ψ are described as excitations from a reference state Ψ_0: $\Psi = R\Psi_0$, where R is a general excitation operator. Different EOM models are defined by choosing the reference and the form of the operator R. In the EOM models for electronically excited states (EOM-EE, upper panel), the reference is the closed-shell ground-state Hartree−Fock determinant and the operator R conserves the number of α and β electrons. Note that two-configurational open-shell singlets are correctly described by EOM-EE because both leading determinants appear as single-electron excitations. However, EOM-EE fails when a small HOMO−LUMO gap causes the ground-state wave function to be a mixture of two closed-shell determinants (the reference and the doubly excited one): although both determinants may be present in the target wave function, they are not treated on an equal footing. The second and third panels present the EOM-IP/EA models. The reference states for EOM-IP/EA are determinants for $N + 1/N - 1$ electron states, and the excitation operator R is ionizing or electron-attaching, respectively. Note that both the EOM-IP and EOM-EA sets of determinants are spin-complete and balanced with respect to the target multiconfigurational ground and excited states of doublet radicals. Finally, the EOM-SF method (the lowest panel) employs the high-spin triplet state as a reference, and the operator R includes spin-flip, i.e., does not conserve the number of α and β electrons. All of the determinants present in the target low-spin states appear as single excitations, which ensures their balanced treatment both in the limit of large and small HOMO−LUMO gaps.

reference $|\Phi_0\rangle$ corresponds to the ground-state wave function and operators R conserve the number of electrons and a total spin.[8−10] In the ionized/electron-attached EOM models,[34−36] operators R are not electron-conserving (i.e., include different number of creation and annihilation operators); these models can accurately treat ground and excited states of doublet radicals and some other open-shell systems. For example, singly ionized EOM methods, i.e., EOM-IP-CCSD and EOM-EA-CCSD, have proven very useful for doublet radicals whose theoretical treatment is often plagued by symmetry breaking. Finally, the EOM-SF method[20,25] in which the excitation operators include spin flip allows one to access diradicals, triradicals, and bond breaking without using spin- and symmetry-broken UHF references.

To summarize, the EOM approach enables one to describe many *multiconfigurational* wave functions within a *single-reference* formalism. The EOM models are rigorously size-extensive, and their accuracy can be systematically improved (up to the exact FCI results) by including higher excitations explicitly or perturbatively. Moreover, the EOM methods are *multistate* schemes; several target states are obtained in the single diagonalization step. This results in an improved accuracy because of the built-in error cancellation and greatly simplifies the calculation of coupling elements, such as nonadiabatic or spin−orbit couplings, between the states. Simpler formalism also facilitates implementation of analytic gradients and properties calculations.[10,34,37,38]

3. Spin-Flip Method

In traditional (non-SF) SR excited-states EOM models, the excited-state wave functions are parametrized as follows (see Figure 1):

$$\Psi^{s,t}_{M_s=0} = \hat{R}_{M_s=0}\tilde{\Psi}^{s}_{M_s=0} \qquad (3)$$

where $\tilde{\Psi}^{s}_{M_s=0}$ is a closed-shell reference wave function and the operator $\hat{R}$ is an excitation operator truncated at a certain level of excitation consistent with the theoretical model employed to describe the reference state. Note that only excitation operators that do not change the total number of α and β electrons, i.e., $M_s = 0$, need to be considered in eq 3.

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 Figure 2). To overcome this problem, the SF model employs a high-spin triplet reference state, which is accurately described by a SR wave function. The target

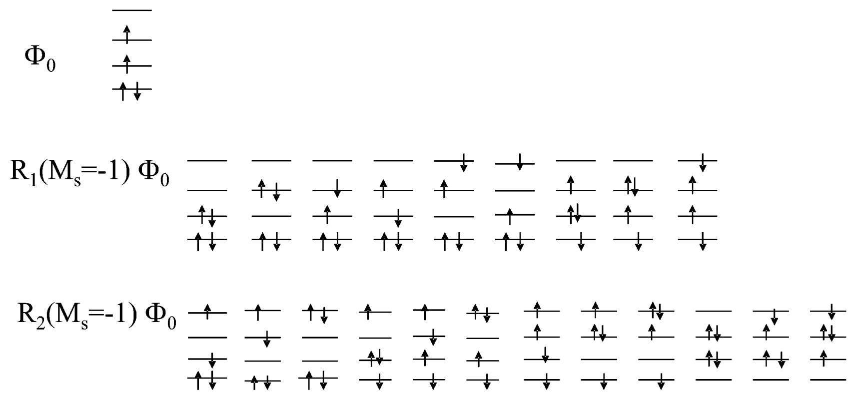

FIGURE 4. Four electrons in four orbitals system. Configuration Φ_0 is the reference configuration. Single-electron excitations with spin-flip produce configurations in the first row. Two-electron excitations with a single spin-flip produce configurations in the second row. Note that non-spin-flipping 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.

states, closed- and open-shell singlets and triplets, are described as spin-flipping excitations

$$\Psi^{s,t}_{M_s=0} = \hat{R}_{M_s=-1}\tilde{\Psi}^{t}_{M_s=+1} \tag{4}$$

where $\tilde{\Psi}^{t}_{M_s=+1}$ is the αα component of the triplet reference state, $\Psi^{s,t}_{M_s=0}$ 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. As can be seen from Figure 2, all of the configurations used to describe diradical-type wave functions (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 4 shows the reference high-spin configuration and the spin-flipping single and double excitations for four electrons in the four orbitals system. The first configuration in the second row corresponds to a ground-state closed-shell singlet. It is followed by the configuration that becomes degenerate with it at the dissociation limit. Two next configurations complete a set necessary to describe all 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 these four configurations are treated on an *equal footing* in our model and that other configurations *do not introduce imbalance in their treating*.

Therefore, the SF ansatz (4) is sufficiently flexible to describe changes in ground-state wave functions along a single bond-breaking coordinate. Moreover, it treats both closed-shell (e.g., *N* and *Z*) and open-shell (e.g., *V* and *T*) diradicals' states in a balanced fashion, i.e., without overemphasizing the importance of one of the configurations.

Note that the SF set of determinants is not a spin-complete set. Whereas all of the closed- and open-shell diradical configurations appear as single excitations (first four in the second row in Figure 4), the counterparts of other single SF determinants (i.e., those which include excitations of electrons from doubly occupied or to the unoccupied MOs) are formally double or triple excitations.

Reference:	Method:	Wavefunction:
SCF	SF-SCF (or SF-CIS)	$R_1\,\Phi_0$
MP2	SF-MP2 [or SF- CIS(D)]	$R_1\,\Phi_0 + T_2$ by PT
CCSD	EOM-SF-CCSD	$(R_1+R_2)\exp(T_1+T_2)\Phi_0$
CCSDT	EOM-SF-CCSDT	$(R_1+R_2+R_3)\exp(T_1+T_2+T_3)\Phi_0$

FIGURE 5. Hierarchy of the SF models. Similarly to the non-SF SR methods, the SF models converge to the exact *n*-electron wave function when the spin-flipping operator $\hat{R}$ includes up to *n*-tuple excitations. For example, the EOM-SF-CCSD model is exact for two electrons.

Thus, when all singles and doubles are included in the SF model, the resulting wave functions are not eigenstates of S^2, i.e., are spin-contaminated. However, the spin contamination is rather small, because the SF excitations within the open shell form a spin-complete set. For example, the values of $\langle S^2\rangle$ for the X^3B_1, $\tilde{a}^1A_1$, $\tilde{b}^1B_1$, and $\tilde{c}^1A_1$ states of methylene at their equilibrium geometries are 1.9991, −0.0011, −0.0007, and −0.0007, respectively, at the EOM-SF-CCSD/TZ2P level using the UHF reference. The spin completeness of SF models can be achieved by including a subset of higher excitations.[26] Although this increases a computational cost of a model, the scaling remains the same.[26] Most importantly, the size-extensivity of SF models is not violated as a result of extending the determinantal subspace.

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 wave function as summarized in Figure 5. For example, the simplest SF model employs a Hartree−Fock wave function, and the operator $\hat{R}$ is then truncated at single excitations (SF-CIS or SF-SCF).[20,26] SF-CIS can be further augmented by perturbative corrections [SF-CIS-(D) or SF-MP2].[21] A yet more accurate description can be achieved by describing the reference wave function by a coupled-cluster model, e.g., CCSD[25] or OO-CCD.[20,39] In this case, the excitation operator $\hat{R}$ consists of single- and double-excitation operators involving a flip of the spin of an electron.[20] Finally, inclusion of triple excitations in the EOM operator R results in the EOM-SF(2,3)[40] model, which is capable of chemical accuracy. The corresponding SF equations in spin−orbital form are identical to those of

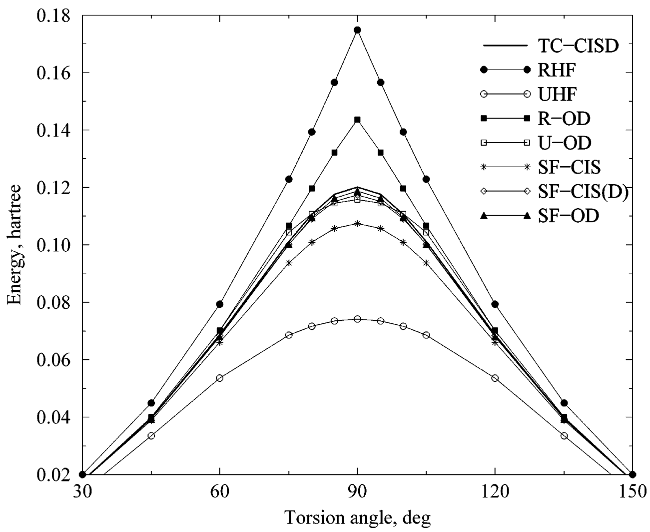

FIGURE 6. Ethylene torsion, DZP basis. All curves are shifted such that the energy at 0° is zero. The spin-flip curves do not exhibit an unphysical cusp and are closer to the reference TC-CISD curve than the corresponding spin-restricted and spin-unrestricted models.

traditional excited-state theories, i.e., CIS, CIS(D), EOM-EE-CCSD or EOM-EE-OOCCD, and EOM-EE(2,3); however, they are solved in a different determinantal subspace: 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.

Two of the SF models, SF-CISD and SF-DFT, deserve special mention. Using the SF approach, CI can be formulated in a rigorously size-extensive way.[22,26,32] For example, the SF-CISD model is (i) variational, (ii) size-extensive, and (iii) exact for two electrons, thus simultaneously satisfying these three highly desirable properties.[1]

Last, the SF approach implemented within the time-dependent (TD) density functional theory (DFT) extends DFT to multireference situations with no cost increase relative to the non-SF TD-DFT. Similar to DFT and TD-DFT, the SF-DFT model[24] 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; e.g., it yields accurate equilibrium properties and singlet−triplet energy gaps in diradicals.[24] All of the above SF models, as well as the corresponding spin-conserving models and analytic gradients for SF-CIS, SF-TDDFT, and EOM-EE/SF-CCSD,[38] are implemented in the *Q-CHEM* electronic structure package.[41]

4. Spin-Flip Method for Bond Breaking: The Ethylene Torsional Potential

Figure 6 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.[20,21,42] All curves are compared with the TC-CISD curve.[21] 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° 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.[42] 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 to the TC-CISD one (see Figure 6). Also, the UHF-based wave functions are heavily spin-contaminated around the barrier *even for highly correlated methods such as coupled-cluster models*.[42] All of 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_2.[20−22]

5. Spin-Flip Method for Diradicals

Diradicals[11,43,44] represent the most clear-cut application of the SF approach because in these systems the nondynamical correlation derives from a single HOMO−LUMO pair (e.g., π and π^* in twisted ethylene). In this section, we present results for trimethylenemethane (TMM), a very challenging case because of the exact degeneracy of its frontier orbitals (for a detailed review of previous TMM studies, see ref 45).

The π system of TMM is shown in Figure 7: four π electrons are distributed over four molecular π-type orbitals. Because of the exact degeneracy between the two e' orbitals at the D_{3h} structure, the ground state of TMM is a $^3A_2'$ state (similar to the *T*-state in ethylene), in agreement with Hund's rule predictions.

The vertical excitation energies are summarized in Figure 7 (with C_{2v} symmetry labels).[23,45] 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 π 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 because of the degeneracy of a_2 and $2b_1$ orbitals (note that CASSCF fails to reproduce this exact degeneracy, unless the state-averaged orbital optimization is performed). The second closed-shell singlet 2^1A_1 (an analogue of the *Z*-state) is followed 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 π orbitals are singly occupied. We do not discuss low-lying states derived from electron excitations beyond the TMM's π system. Several such states appear between the pair of degenerate triplets and the quintet state. The SF-OD and SF-CCSD models should be augmented by higher excitations to achieve a quantitatively accurate description of these states.[40]

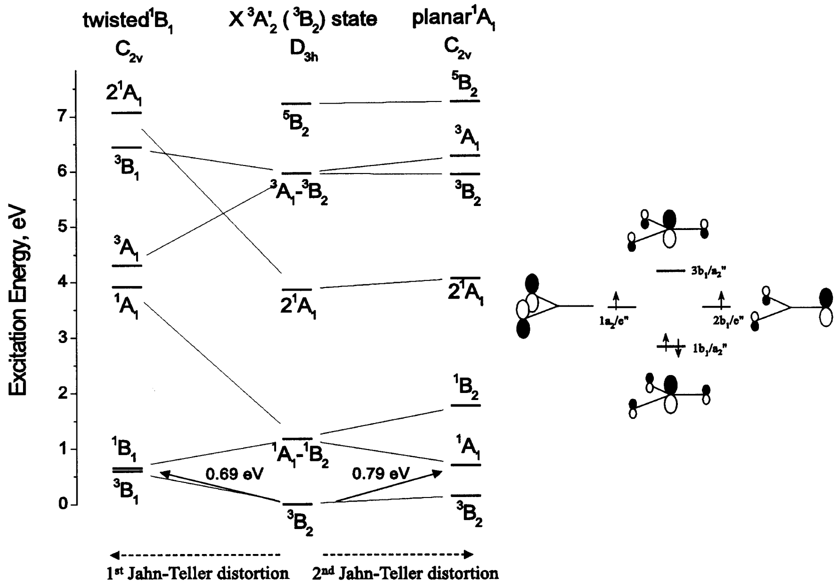

FIGURE 7. On the right, the π system of TMM and the electronic configuration of the ground state are shown (C_{2v} labels are used). The left panel presents electronic states of TMM at the ground-state equilibrium D_{3h} geometry and at the two Jahn–Teller C_{2v} distorted structures (equilibrium geometries of the 1^1B_1 and 1^1A_1 states). The corresponding adiabatic singlet–triplet gaps are also shown.

In accordance with the Jahn–Teller theorem, the degeneracy between the degenerate states (closed- 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 second $^1A_1$ state prefers D_{3h} equilibrium geometry. The EOM-SF-CCSD/EOM-SF(2,3) adiabatic singlet–triplet energy separations for the three lowest singlet states are 0.55/0.70, 0.93/0.79, and 3.86/3.55 eV for the 1^1B_1, 1^1A_1, and 2^1A_1 states, respectively[40] (in the basis set composed of the cc-pVTZ based on carbons and the cc-pVDZ based on hydrogens). These energies are very close to the MRPT values[23] of 0.71 and 0.83 eV (for the 1^1B_1 and 1^1A_1 states, respectively). With regard to the experiment, the lowest adiabatic state, 1^1B_1, has not been observed in the photoelectron spectrum[46] because of unfavorable Franck–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 in excellent agreement with the EOM-SF(2,3) estimate.

In our detailed benchmarks study,[23,40] we calculated the singlet–triplet energy separations for a large number of systems, i.e., O, C, and Si atoms, O_2, NH, NF, and OH^+ diatomics, methylene isovalent series (CH_2, NH_2^+, SiH_2, and PH_2^+), benzynes, and TMM. In all of these cases, the SF models performed very well. The typical errors for EOM-SF-OD/EOM-SF-CCSD are less than 1 kcal/mol, and the maximum error was 3 kcal/mol, as compared to the experimental or highly accurate multireference values. Inclusion of triples in the EOM part brings the error bars down to hundredths of an electronvolt.

6. Triradicals

Triradicals,[47–50] species with three unpaired electrons distributed over three nearly degenerate orbitals, feature even more extensive electronic degeneracies than diradicals. Figure 8 shows valid triradical wave functions with a positive projection of the total spin, i.e., with $M_s = +^3/_2$ and $^1/_2$. Note that only the high-spin component of the quartet state, the first configuration in Figure 8, is single-configurational, while all of the low-spin states are multiconfigurational and are, therefore, not accessible by the traditional ground-state single-reference methods. How-

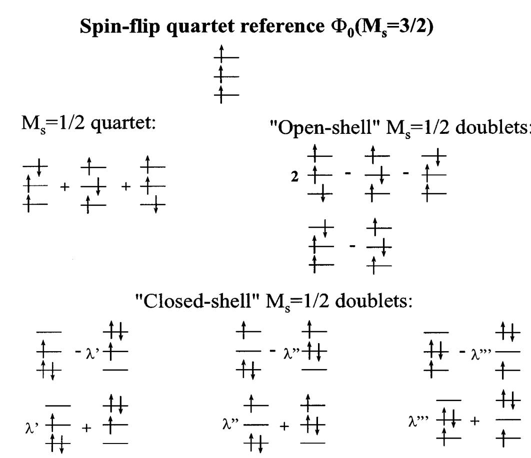

FIGURE 8. Triradicals' wave functions that are eigenfunctions of $\hat{S}^2$. Note that all of the $M_s = {}^1/_2$ configurations present in the low-lying triradical states are formally obtained from the $M_s = {}^3/_2$ reference state by single excitations including a spin-flip. The coefficients λ that define the mixing of closed-shell determinants depend on the energy spacing between the orbitals, while the coefficients of the open-shell determinants are determined solely by the spin-symmetry requirements. Spatial symmetry determines further mixing of the above wave functions.

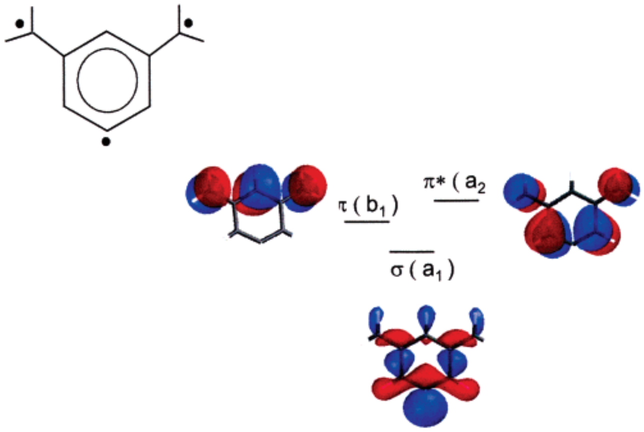

FIGURE 9. Structure and molecular orbitals of DMX.

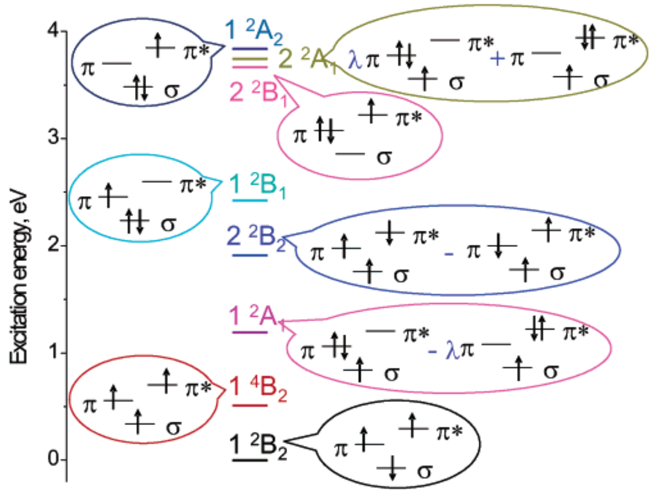

FIGURE 10. Low-lying electronic states of DMX. Note that the closed-shell doublet (1^2B_2 state) in which electrons are distributed in accordance with Aufbau principle is 2.5 eV above the ground state. Another likely candidate for the ground state, the quartet 1^4B_2 state, is 0.5 eV above the open-shell doublet, thus violating Hund's rule.

ever, all of these states can accurately be described by the SF models as:

$$\Psi^{d,q}_{M_s=1/2} = \hat{R}_{M_s=-1}\tilde{\Psi}^{q}_{M_s=3/2} \tag{5}$$

where $\tilde{\Psi}^{q}_{M_s=3/2}$ is the ααα high-spin reference determinant, $\hat{R}_{M_s=-1}$ is an excitation operator that flips the spin of an electron ($\alpha \rightarrow \beta$), and $\Psi^{d,q}_{M_s=1/2}$ stands for the wave functions of the doublet and quartet target states. Because all of the configurations (with $M_s = {}^1/_2$) present in the low-lying triradical states are formally obtained from the $M_s = {}^3/_2$ reference state by single excitations including a spin flip, the SF method provides a balanced description of all of the triradical states from Figure 8.

Note that, although all of the target states, the quartet, the open-shell doublets, and the closed-shell doublets, are multiconfigurational, they are treated by SF within a single-reference formalism.

The SF method enabled recent studies of the electronic structure of triradicals.[48−50] These works focused on interactions between the radical centers in finite size molecules and structural, spectroscopic, and thermochemical signatures of these interactions. For example, we have found that there is a bonding interactions between radical centers in the C_6H_3 isomers that results in considerably tighter equilibrium geometries (i.e., the distance between radical centers can contract by 0.4 Å relative to the parent benzene molecule) and higher vibrational frequencies.[48,49] The energies of these interactions vary between 0.5 and 37 kcal/mol that constitutes approximately one-third of a normal chemical bond.[49] These bonding interactions also determine the multiplicity of the ground state; in all three isomers, multiplicity of the ground state is doublet.

In the 5-dehydro-*m*-xylylene (DMX) triradical[50] shown in Figure 9, the interaction between radical centers is rather weak because of the $\sigma-\pi$ character of the orbitals that host the unpaired electrons. Overall, the interaction between the centers results in an unusual electron arrangement. The ground state of DMX is an *open-shell doublet* state; i.e., the three unpaired electrons are localized at their radical centers and, contrary to Hund's rule, are coupled antiferromagneticaly. Low-lying electronic states of DMX are shown in Figure 10. The dense nature of the DMX electronic spectrum renders MR calculations of this system extremely difficult.

7. Conclusions

The realm of HF → MP2 → CCSD → CCSD(T) → CCSDT → ... hierarchy of approximations to the exact many-electron wave function ends when a wave function acquires considerable multiconfigurational character, e.g., because of a small HOMO−LUMO gap at a dissociation limit or in electronically excited states. Traditionally, these and other chemically important situations were treated by multireference methods that must be tailored to suit a specific problem at hand. The single-reference EOM-CC theory offers an alternative approach to multiconfigurational wave functions, which truly complies with a set of Pople's attributes of a "theoretical model chemistry". The EOM-CC methods are rigorously size-extensive, include both dynamical and nondynamical correlation in a balanced fashion, and describe several electronic states in a single computational scheme. Recently, we introduced a new EOM method, EOM-SF, that extended the applicability of SR EOM-CC methods to bond breaking, diradicals, and triradicals. Both closed- and open-shell type target states are described within a single-reference formalism as spin flipping, e.g., $\alpha \rightarrow \beta$, excitations from the high-spin triplet ($M_s = 1$) or quartet ($M_s = {}^3/_2$) reference state for which both dynamical and nondynamical correlation effects are much smaller than for the corresponding low-spin states. 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 α and β electrons.

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