Perturbative corrections to the equation-of-motion spin–flip self-consistent field model: Application to bond-breaking and equilibrium properties of diradicals

Anna I. Krylov  
Department of Chemistry, University of Southern California, Los Angeles, California 90089-0482

C. David Sherrill  
Center for Computational Molecular Science and Technology, School of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, Georgia 30332-0400

(Received 9 August 2001; accepted 29 November 2001)

We present perturbative corrections to a recently introduced spin–flip self-consistent field (SF-SCF) wave function. The spin–flip model describes both closed and open shell singlet states 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 nondynamical correlation effects are much smaller than for the corresponding singlet state. The simplest spin–flip model employs a SCF wave function for the reference state, and the resulting equations for target states are therefore identical to configuration interaction singles (in spin–orbital form). While being a qualitatively correct zero-order wave function, SF-SCF should be augmented by dynamical correlation corrections to achieve a quantitative accuracy. The results demonstrate that the second-order approximation to the more theoretically complete spin–flip coupled-cluster model (truncated at double substitutions) represents a systematic improvement over the SF-SCF model. © 2002 American Institute of Physics. [DOI: 10.1063/1.1445116]

I. INTRODUCTION

$Ab\ iniio$ modeling of bond-breaking and diradicals, which are of central importance in chemistry, remains challenging, even though several elegant approaches have been suggested.1–18 This is because the inherent multireference character of the electronic state is difficult to reconcile (within a single computationally feasible scheme) with factors such as the size-consistency of the model, uniform accuracy of the approximations, unambiguous selection of important configurations, and a balanced treatment of dynamical and nondynamical correlations. Several recent theoretical strategies16–20 address these issues in ways that are not application-dependent and thus can be defined as theoretical model chemistries.21 This work presents further development of a new approach to the bond-breaking problem formulated in a single-reference formalism, i.e., the equation-of-motion spin–flip (EOM-SF or SF) model.19,20

The SF model describes closed and open shell singlet states 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 nondynamical correlation effects are much smaller than for the corresponding singlet state.19,22 By employing theoretical models of increasing complexity for the reference wave function, the description of the final states can be systematically improved. Thus, the SF model enables one to extend the well developed hierarchy of single-reference approximations to the exact wave function (see, for example, Refs. 23 and 24 for review) to treat challenging multireference cases of bond-breaking and diradicals.

It should be mentioned that, similarly to the traditional methods, the SF models may fail in cases when the Hartree–Fock reference wave function exhibits orbital (near)-instabilities. The stability analysis of the reference triplet wave function can be used to detect such situations. Unlike doublet radicals (see, for example, Ref. 25), the orbital instabilities in triplet states are less common. Moreover, in the cases when the singlet Hartree–Fock reference exhibits (near)-instabilities in connection with the mixing of one or more occupied orbital with low-lying LUMO (as in diradicals, e.g., $p$-benzylene26), the corresponding triplet state is less likely to be plagued by instabilities since the singlet’s LUMO is occupied in the triplet reference.

The simplest member of the proposed hierarchy of approximations is based on the self-consistent field (SCF) description of the reference state and treats target states as single spin–flipping excitations. The resulting equations in spin–orbital form are identical to those of the configuration interaction singles (CIS) model27–30 but they are solved in a different (i.e., spin–flipping) subspace of single excitations. Initial benchmarks19 have demonstrated that this model, i.e., SF-SCF or SF-CIS, represents a systematic improvement over both spin-restricted or spin-unrestricted Hartree–Fock models for the single bond-breaking, and that the corresponding wave function is qualitatively correct and remains well balanced along the bond-breaking coordinate. To achieve quantitative accuracy, however, one has to augment this zero-order wave function by a dynamical correlation. This can be done by employing correlated, e.g., coupled-cluster (CC),31,32 wave functions for the reference state, and by treating the target states within EOM formalism.33
corresponding SF models extend high accuracy of the CC methods for the regions away from equilibrium geometry. They also inherit a computational cost of the traditional CC methods. For example, the SF optimized-orbitals coupled-cluster doubles (SF-OOCCD or SF-OD) model\(^{19}\) produces accurate potential energy curves, with the computational cost of \(N^6\) being identical to that of OO-CCD (Refs. 34, 35, 32) and EOM-OD (Ref. 18) models. While this polynomial scaling represents a definite advantage over the factorial scaling of multireference models, it still limits the scope of applications to moderate-size molecules. Therefore, the approximations of CC-based models which allow to reduce computational cost are of the considerable practical interest.

For the traditional, i.e., non-spin–flip, ground state calculations, the simplest recipe for including dynamical correlation is by second-order Møller–Plesset perturbation theory (MP2).\(^{30}\) The noniterative nature of the MP2 corrections and the computational cost which scales as the fifth power of molecular size enable applications to larger systems than those accessible by more theoretically complete CC models. Inspired by the success of MP2 theory, efforts have been made to develop the perturbative corrections to excited and/or ionized states theories.\(^{37–40}\) A second order approximation to EOM-CCSD is given by the so-called CIS(D) model\(^{37}\) which uses a CIS wave function as the zero-order wave function. While representing a systematic improvement for vertical excitation energies,\(^{37}\) the method fails for excited states’ equilibrium properties.\(^{40}\) The reason for this failure has been correctly attributed to the rapidly degrading quality of a single-determinant representation of the ground state wave function as one moves away from the ground state equilibrium geometry.\(^{39,40}\) The balanced nature of the SF-SCF wave function suggests that perturbative corrections performed in the CIS(D) (Ref. 37) fashion would considerably improve SF-SCF potential energy surfaces.

This work introduces the SF-CIS(D) model, and presents detailed benchmarks of three SF methods, i.e., SF-SCF, SF-CIS(D), and SF-OD. The structure of the paper is as follows: the next section introduces the SF-CIS(D) theory, Sec. III presents numerical examples for (i) equilibrium properties of closed-shell and diradical species, and (ii) potential energy curves along bond-breaking coordinates; and Sec. IV gives our concluding remarks.

II. THEORY

The SF-SCF wave function is:

\[
|\Psi^{\text{CIS}}\rangle = R_1 |\Phi_0\rangle,
\]

where \(\Phi_0\) is a Slater determinant describing the reference state which in the present work is chosen to be the \(\alpha\alpha\) component of a triplet state (as has been mentioned in Refs. 19,20, alternative choices of the reference, i.e., higher multiplicity states, promise certain advantages), and \(R_1\) is the single excitation operator which flips the spin of an electron,

\[
R_1 = \sum_{ia} r_i^a a^+_i.
\]

Here, and throughout the paper, we follow the convention that \(i,j,k,\ldots\) represents spin–orbitals that are occupied in the reference determinant \(\Phi_0\), \(a,b,c,\ldots\) correspond to virtual orbitals, and the indices \(p,q,r,s,\ldots\) are reserved for the general case, i.e., when an orbital may be either occupied or unoccupied in the reference. Orbitals satisfy the SCF equations for the reference \(\Phi_0\), while amplitudes \(r_i^a\) are found by a diagonalization of the Hamiltonian in the basis of singly excited determinants involving a spin–flip. The spin–orbital form of programmable equations is identical to that of the CIS model.\(^{28,30}\)

CIS(D) is a rigorous second-order approximation to the EOM-CCSD eigenvalue problem,\(^{37,40}\) which, most importantly, preserves size-extensivity of the CIS model. Here, we omit the derivation of the CIS(D) correction, and refer the reader to the excellent presentation of the CIS(D) energy and gradient derivation given in the Ref. 40. The final expression is:

\[
E^{\text{CIS(D)}} = \langle \Psi^{\text{CIS}} | V | U_2 \Phi_0 \rangle + \langle \Psi^{\text{CIS}} | V | U_1 T_2 \Phi_0 \rangle,
\]

where \(V\) is the fluctuation potential, i.e., the difference between the Hamiltonian and Fock operator, and amplitudes of excitation operators \(T_2\), \(U_1\), and \(U_2\) are defined by perturbation theory.\(^{37,40}\)

The qualitative analysis of Eq. (3) including its relation to ground state perturbation theory is given in the original paper;\(^{37}\) the first term in Eq. (3) is approximately accounting for the orbital relaxation since it can be viewed as single excitations from \(\Psi^{\text{CIS}}\), whereas the second term which corresponds to the double excitations from \(\Psi^{\text{CIS}}\) represents correlation of an excited state, such that the correlation of inactive, i.e., unaffected by excitation, electrons is described by the ground state double substitution operator \(T_2\) (calculated by MP2). Thus, the performance of the CIS(D) correction depends not only on the quality of the Hartree–Fock description of the reference wave function, but also on the quality of the MP2 treatment of correlation in the reference state. With this in mind, it is not surprising that the CIS(D) model fails to represent a systematic improvement over the CIS for excited state stationary points. In our case, however, since the MP2 description of triplet states is more uniformly accurate, we expect the SF-CIS(D) theory to improve SF-CIS energies not only around equilibrium, but for the wider range of nuclear distortions, e.g., along bond-breaking coordinate.

The programmable expressions for the CIS(D) correction, \(\Delta E^{\text{CIS(D)}}\), are:\(^{37}\)

\[
\Delta E^{\text{CIS(D)}} = -\frac{1}{4} \sum_{ijab} \frac{(u_{ijab}^a)^2}{\Delta_{ij} - \omega} + \sum_{ia} r_i^a v_i^a,
\]

\[
u_{ijab} = \sum_{r} (\langle ic||ab ||j \rangle - (jc||ab ||i) + \sum_{k} (\langle ij||ka ||r \rangle).
\]

\[
v_i^a = \frac{1}{2} \sum_{jkbc} \langle jk ||bc ||r \rangle (r_i^a r_j^c + 2 r_i^a r_j^b + 2 r_i^b r_j^c).
\]

\[
\Delta_{ij} = \epsilon_a + \epsilon_b - \epsilon_i - \epsilon_j.
\]
where $\omega$ is the CIS excitation energy for the given state, and $\epsilon_p$ is a diagonal value of the Fock matrix (canonical orbitals are assumed). The scaling of the noniterative correction defined by Eq. (4) is $N^5$, and the computational cost is roughly equivalent to that of the MP2 calculations. The only difference in the SF-CIS(D) implementation vs the traditional one is that the SF-CIS amplitudes $r_{ij}^\text{sf}$ are those which flip spin of an electron, as opposed to the $\alpha\rightarrow\alpha$ and $\beta\rightarrow\beta$ amplitudes which are allowed in non-SF-CIS.

### III. RESULTS AND DISCUSSION

In this section, we present detailed benchmarks of SF-SCF, SF-CIS(D), and SF-OD models. SF approach targets systems with a significant diradical character, i.e., those with large nondynamical correlation derived from a single HOMO-LUMO pair (e.g., $\pi$ and $\pi^*$ in twisted ethylene). In such situations, SF models provide a more balanced description than the corresponding traditional single-reference methods which overemphasize the importance of the closed-shell Hartree–Fock configuration, ($\pi^2$). Moreover, SF models are capable of describing other two low-lying diradical singlet states, e.g., the doubly excited ($[\pi\pi^*]^2$) Z-state and open-shell ($[\pi\pi^*]v$)-state of ethylene. Singlet methylene ($\tilde{a}^1A_1$, $\tilde{b}^1B_1$, and $\tilde{c}^1A_1$ states), ozone, singlet oxygen, and ethylene torsional potential ($N$, $V$, and $Z$-states) fell in this category. For these molecules, the choice of the reference triplet state is straightforward and usually is the lowest triplet (which can even be the true ground state of the system as in the case of methylene or oxygen).

However, it is also very important to test how new methods perform in case of a well-behaved closed-shell molecule. To investigate this, we apply the SF method to calculate equilibrium properties of the well behaved molecule, e.g., H$_2$O. We also discuss how sensitive SF results are to the choice of the reference state (for water molecule, the choice of the triplet reference is no longer dictated by simple qualitative considerations as for most diradicals). We also present results for the single bond breaking in HF, BH, and F$_2$. It should be mentioned, that for nondiradical molecules (e.g., water or diatomics at small internuclear separations) the lowest triplet state is not necessarily the valence $\sigma\pi^*$ state, but may be a Rydberg state. At large distance, this state will adiabatically change into the valence state. As such change occurs, the SF curve may exhibit a discontinuity. The simple remedy for this problem is not to include diffuse functions into the basis set. Fortunately, diffuse functions usually are not necessary for the accurate ground state description. However, if the SF model is to be used to calculate both ground and excited state potential energy curves, the diffuse functions must be included into the basis, and the changes of the lowest triplet state from Rydberg to valence may cause problems. We will address this issue when benchmarking performance of the SF for excited states.

In order to eliminate uncertainties due to basis set effects and anharmonicities, we benchmark SF models not only against experimental results, but also against full configuration interaction (FCI) (methylene, HF, and BH), multireference configuration interaction (MRCI) (F$_2$ and ethylene), or CCSD(T) (equilibrium properties of H$_2$O).

Calculations are performed using two ab initio packages, Q-CHEM and PSI, to which our programs for (V)OO-CCD, SF-SCF, SF-CIS(D), and SF-OD calculations are linked. Additional results are obtained using ACES II ab initio program. Some basis sets used in this work are obtained from the EMSL database.

### A. H$_2$O

We start our study by comparing the performance of the spin–flip models to the corresponding traditional approaches for a well-behaved problem, the equilibrium properties of the water molecule. Calculations are performed using two basis sets: (i) a double-$\zeta$ plus polarization (DZP) basis set of contracted Gaussian functions, comprised of the standard Huzinaga–Dunning double-$\zeta$ basis augmented by six $d$-type polarization functions for oxygen, and three $p$-type polarization functions for hydrogen; and (ii) a triple-$\zeta$ plus two sets of polarization functions (TZ2P) basis set, comprised of the $(11s6p5s4p)$ triple-$\zeta$ basis set of Dunning augmented with two sets of six $d$-type polarization functions for oxygen, and $(5s3p)$ triple-$\zeta$ basis set of Dunning [with exponents scaled by (1.25)$^3$] augmented by two sets of three $p$-type polarization functions for hydrogen.

Calculated total energies, equilibrium geometries, and harmonic frequencies are shown in Table I. For the TZ2P basis set, we present results for the spin–flip models employing two different references, i.e., the $3B_1$ and $3B_2$ states. For both basis sets, the lowest triplet state is the $3B_1$ state (EOM-OD vertical excitation energy is 8.25 eV in DZP basis, and 8.06 eV in TZ2P basis), and the $3B_2$ state is the highest one (EOM-OD excitation energy is 12.62 eV in DZP basis and 12.55 eV in TZ2P basis). The lowest $3A_1$ and $3A_2$ states have very similar excitation energies around 10 eV. As can be seen from Table I, total energies are surprisingly insensitive to the reference employed, e.g., the difference in the SF-SCF total energies (at corresponding optimized geometries) is about 0.4 eV, and the difference decreases (as we proceed to a more correlated models) down to 0.02 eV for SF-CIS(D), and 0.003 eV for SF-OD.

The optimized geometries and frequencies are more sensitive to the reference choice, the sensitivity being rather small for explicitly correlated SF-OD model. The quality of SF-OD optimized geometries is comparable with that of the corresponding traditional models (OD or CCSD). However, calculated harmonic frequencies depend dramatically on the reference state. The least correlated SF-SCF model performs better when using the lowest triplet state, i.e., the $3B_1$ state, as the reference. However, the errors in vibrational frequencies are larger than for the SCF model; the antisymmetric stretch is underestimated by 14% with the TZ2P basis (the symmetric stretch and bending frequencies are described slightly better by the SF-SCF method). Contrary to this behavior, the correlated SF-CIS(D) and SF-OD models produce much more accurate frequencies when using the highest, i.e.,
of the antisymmetric stretch is grossly overestimated by 53% in the small basis set model. The frequency of the antisymmetric stretch is underestimated by 7.5% in the small basis set (DZP) when using the 3$^1$B$_2$ reference. In the TZ2P basis the difference between the SF-OD/3$^1$B$_2$ and SF-OD/3$^2$B$_1$ frequencies is much less, all frequencies being described with an accuracy similar to the results improving slightly in a larger basis set.

B. CH$_2$

The ground state of methylene is a triplet $\bar{X}$$^3$B$_1$ state,

$$\bar{X}$$^3B$_1$ = (1$^1a_1$)$^2$(2$^1a_2$)$^2$(1$^2b_1$)$^2$(3$^1a_1$)(1$^1b_1$).  \hspace{1cm} (5)$$

Following Salem, three low-lying singlet states are diradical states which can be qualitatively described by a two electrons in two orbitals model:

$$\bar{a}^1A_1 = \lambda(1^1a_1)^2(2^1a_2)^2(1^2b_1)^2(3^1a_1)^2$$

$$- \sqrt{1-\lambda^2}(1^1a_1)^2(2^1a_2)^2(1^2b_1)^2(1^1b_1)^2, \hspace{1cm} (6)$$

$$\bar{b}^1B_1 = (1^1a_1)^2(2^1a_2)^2(1^2b_1)^2(3^1a_1)(1^1b_1), \hspace{1cm} (7)$$

$$\bar{c}^1A_1 = (1^1a_1)^2(2^1a_2)^2(1^2b_1)^2(3^1a_1)^2$$

$$+ \sqrt{1-\lambda^2}(1^1a_1)^2(2^1a_2)^2(1^2b_1)^2(1^1b_1)^2. \hspace{1cm} (8)$$

While the $\alpha\alpha$ ($M_s=1$) component of the $\bar{X}$$^3$B$_1$ state (5) is essentially a single-reference wave function, the corresponding singlet $\bar{b}^1B_1$ state (as well as the $M_s=0$ component of the triplet) is a linear combination of two Slater determinants with equal coefficients. Therefore, the $\bar{b}^1B_1$ state cannot be described within a formalism that uses a single Slater determinant reference. The character of the lowest singlet, $\bar{a}^1A_1$, varies from a single-reference ($\lambda \approx 1$) to the two-configurational ($\lambda \approx 1/\sqrt{2}$) wave function. At the equilibrium geometry, the effect of the second configuration is relatively small, and the $\bar{a}^1A_1$ state can be reasonably well described by a single reference model. The second $\bar{A}_1$ state, $\bar{c}^1A_1$, can be described as the doubly excited state with respect to the $\bar{a}^1A_1$. At its equilibrium geometry, the $\bar{c}^1A_1$ state requires the two-configurational wave function. Therefore, it is not possible to describe all three singlet states of methylene by a single-reference model. The spin–flip model, however, describes all three singlet states as spin–flipping excitations from the reference $M_s=1$ triplet $\bar{X}$$^3$B$_1$ state [see Fig. 2(a) in Ref. 19].
For this small system, we compare the performance of different methods against FCI results.\textsuperscript{50–52} Basis sets employed, DZP and TZ2P, are the same as in the corresponding FCI benchmark papers.\textsuperscript{50–52}

Calculated equilibrium geometries and vibrational frequencies for the singlet $\tilde{a}^1A_1$ state of methylene are shown in Table II. Results for the $\tilde{b}^1B_1$ and $\tilde{c}^1A_1$ states are shown in Tables III and IV, respectively. In the case of the $\tilde{a}^1A_1$ state, the equilibrium properties are reproduced well by both traditional and spin–flip models. Spin–flip models describe $\tilde{b}^1B_1$ and $\tilde{c}^1A_1$ states with a similar accuracy. For all three states, SF-CIS(D) represents a qualitative improvement over the SF-CIS. In both basis sets, SF-OD results follow FCI closely.

\begin{table}[h]
\centering
\begin{tabular}{lcccc}
\hline
Method & $E_{\text{tot}}$, & $r_c$ & $\alpha$ & $\omega_1$ & $\omega_2$ & $\omega_3$ \\
& hartree & & (\AA) & (\AA$^{-1}$) & (\AA$^{-1}$) & (\AA$^{-1}$) \\
\hline
FCI/DZP & $-38.985 669$ & $1.0845$ & $140.97$ & $3163$ & $1011$ & $3444$ \\
SF-SCF/DZP & $-38.857 64$ & $1.0768$ & $142.28$ & $3312$ & $1101$ & $3623$ \\
SF-CIS(D)/DZP & $-38.970 40$ & $1.0757$ & $140.95$ & $3234$ & $1096$ & $3552$ \\
SF-OD/DZP & $-38.998 24$ & $1.0823$ & $140.55$ & $3175$ & $1047$ & $3466$ \\
FCI/TZ2P & $-39.010 059$ & $1.0748$ & $141.56$ & $3136$ & $1006$ & $3470$ \\
SF-SCF/TZ2P & $-38.863 87$ & $1.0624$ & $142.38$ & $3311$ & $1103$ & $3611$ \\
SF-CIS(D)/TZ2P & $-38.995 49$ & $1.0652$ & $141.59$ & $3243$ & $1082$ & $3546$ \\
SF-OD/TZ2P & $-39.022 99$ & $1.0716$ & $141.32$ & $3160$ & $1028$ & $3424$ \\
Expt. & $1.105$ & & $140$ & & & \\
Expt. & & & $1.086$ & $139.3$ & & \\
\hline
\end{tabular}
\caption{Total energies, equilibrium geometries, and harmonic vibrational frequencies (cm$^{-1}$) for singlet methylene ($\tilde{b}^1B_1$ state) using DZP and TZ2P basis sets. Spin–flip models employ the $\tilde{X}^1B_1$ ground state as the reference.}
\end{table}

\begin{table}[h]
\centering
\begin{tabular}{lcccccc}
\hline
Method & $E_{\text{tot}}$, & $r_c$ & $\omega_1$ & $\omega_2$ & $\omega_3$ \\
& hartree & & (\AA) & (\AA$^{-1}$) & (\AA$^{-1}$) & (\AA$^{-1}$) \\
\hline
FCI/DZP & $-38.942 663$ & $1.0749$ & $169.68$ & $3246$ & $695$ & $3503$ \\
SF-SCF/DZP & $-38.794 18$ & $1.0553$ & $173.68$ & $3455$ & $295$ & $3826$ \\
SF-CIS(D)/DZP & $-38.920 09$ & $1.0622$ & $170.32$ & $3373$ & $660$ & $3753$ \\
SF-OD/DZP & $-38.954 02$ & $1.0723$ & $168.68$ & $3253$ & $773$ & $3618$ \\
FCI/TZ2P & $-38.968 471$ & $1.0678$ & $170.08$ & $3200$ & $666$ & $3531$ \\
SF-SCF/TZ2P & $-38.800 76$ & $1.0507$ & $174.48$ & $3446$ & $343$ & $3809$ \\
SF-CIS(D)/TZ2P & $-38.947 62$ & $1.0544$ & $173.73$ & $3374$ & $416$ & $3727$ \\
SF-OD/TZ2P & $-38.980 70$ & $1.0639$ & $170.14$ & $3238$ & $672$ & $3555$ \\
\hline
\end{tabular}
\caption{Total energies, equilibrium geometries, and harmonic vibrational frequencies (cm$^{-1}$) for singlet methylene ($\tilde{c}^1A_1$ state) using DZP and TZ2P basis sets. Spin–flip models employ the $\tilde{X}^1B_1$ ground state as the reference.}
\end{table}
TABLE VI. Total energies, equilibrium geometries, and harmonic vibrational frequencies for O₂, ¹Δg state, using DZP and TZ2P+diff basis sets.

<table>
<thead>
<tr>
<th>Method</th>
<th>E_{tot}, hartree</th>
<th>r_e, Å</th>
<th>ωe, cm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>RHF/DZP</td>
<td>−149.573 460</td>
<td>1.1687</td>
<td>1999</td>
</tr>
<tr>
<td>TCSCF/DZP</td>
<td>−149.591 143</td>
<td>1.1666</td>
<td>2015</td>
</tr>
<tr>
<td>MP2/DZP</td>
<td>−149.962 579</td>
<td>1.2787</td>
<td>1206</td>
</tr>
<tr>
<td>CCSD/DZP</td>
<td>−149.962 840</td>
<td>1.2345</td>
<td>1563</td>
</tr>
<tr>
<td>CCSD(T)</td>
<td>−149.977 112</td>
<td>1.2476</td>
<td>1464</td>
</tr>
<tr>
<td>SF-SCF/DZP</td>
<td>−149.586 927</td>
<td>1.1659</td>
<td>2013</td>
</tr>
<tr>
<td>SF-CIS(D)/DZP</td>
<td>−149.950 137</td>
<td>1.2411</td>
<td>1461</td>
</tr>
<tr>
<td>SF-OD/DZP</td>
<td>−149.973 053</td>
<td>1.2296</td>
<td>1600</td>
</tr>
<tr>
<td>SCF/TZ2P+diff</td>
<td>−149.594 491</td>
<td>1.1562</td>
<td>1953</td>
</tr>
<tr>
<td>MP2/TZ2P+diff</td>
<td>−150.057 832</td>
<td>1.2590</td>
<td>1196</td>
</tr>
<tr>
<td>CCSD/TZ2P+diff</td>
<td>−150.054 471</td>
<td>1.2145</td>
<td>1545</td>
</tr>
<tr>
<td>CCSD(T)/TZ2P+diff</td>
<td>−150.075 526</td>
<td>1.2319</td>
<td>1424</td>
</tr>
<tr>
<td>SF-SCF/TZ2P+diff</td>
<td>−149.607 730</td>
<td>1.1532</td>
<td>1969</td>
</tr>
<tr>
<td>SF-CIS(D)/TZ2P+diff</td>
<td>−150.044 678</td>
<td>1.2197</td>
<td>1462</td>
</tr>
<tr>
<td>SF-OD/TZ2P+diff</td>
<td>−150.064 323</td>
<td>1.2096</td>
<td>1583</td>
</tr>
</tbody>
</table>

Expt. 1.2155 1509, a 1483b

aReference 69.
bReference 70.

(11s6p/5s3p) triple-ζ basis set of Dunning augmented with two sets of six d-functions [αd(O) = 1.7, 0.425] and one diffuse s-function [αs(O) = 0.08993] and a set of three diffuse p-functions [αp(O) = 0.0584], TZ2P+diff. Results are compared against experiment53,54 and highly correlated CCSDT (Ref. 55) and CISD[TQ] (Ref. 56) results.

One of the manifestations of the significant diradical character in ozone is that perturbative models which employ single-reference wave functions fail to improve corresponding zero-order results; contrary to the well-behaved molecules, MP2 fails dramatically for the asymmetric stretch, and CCSD(T) behavior is rather unstable, e.g., ω3 exhibits very strong dependence upon the basis set. The large difference between CCSD(T) and complete CCSDT results also points out to the significant multireference character of the wave function,55,57 while CCSD(T) and CCSDT values of ω3 and ω2 differ by no more than 10 cm⁻¹ (in DZP or cc-pVTZ basis set), the CCSD(T) value of ω3 is 60–80 cm⁻¹ lower than the CCSDT value. Finally, even the complete CCSDT method yields much larger errors in equilibrium properties of ozone than for closed-shell molecules.57 Watts and Bartlett pointed out that connected quadruple excitations (i.e., double excitations from the second important configuration) are needed for a quantitatively correct description of ozone.57

The spin–flip model represents a systematic improvement for all frequencies, including the most problematic asymmetric stretch. Note that SF-CIS(D) performs very well, its accuracy being close to the SF-OD model.

D. O₂

The ground state of oxygen molecule is the triplet state, and the lowest singlet state is a diradical ¹Δg state. Table VI shows equilibrium properties for the ¹Δg state of O₂ calculated by using the DZP and TZ2P+diff basis sets (described in the previous subsection).

![FIG. 1. HF. 6-31G basis. The errors against the FCI for SF-SCF, SF-CIS(D), and SF-OD models. Filled symbols are for SF calculations employing the ³Σ reference state, empty symbols—for the ³Π reference state. The errors of the SF-OD model are very small. The perturbative corrections significantly improve the SF-SCF model; the SF-CIS(D) curve is very close to much more expensive SF-OD one. The ³Σ reference gives better results.](image-url)

In this case, SF-CIS(D) achieves a dramatic improvement over MP2. The SF-SCF and SF-OD models perform similarly to the corresponding traditional approaches. It seems surprising that the RHF and two-configuration SCF (TCSCF) properties are so similar for this case, both being close to the SF-SCF, given that the TCSCF description should be much more appropriate for this diradical than RHF. O₂ appears similar to F₂ where both non-dynamical and dynamical correlations are crucial for a qualitatively correct description (see Sec. III.G).

E. HF

In this section, we investigate performance of the spin–flip model for a single bond breaking process. We also present more examples of how the choice of reference state affects the results. Calculations for HF are performed using the split-valence 6-31G basis set.58 Figure 1 compares FCI total energies for the potential energy curve with the spin–flip models employing two different references, i.e., ³Σ and ³Π states.

For the balanced description of σ-bond breaking by the SF model, the triplet ωσ8 reference (i.e., ³Σ) is the most appropriate choice, since single spin–flipping excitations from this reference generates the two most important configurations, (σ)2 and (σ*)2. However, a reasonable description can also be achieved by using the ³Π reference (lowest
TABLE VII. BH, DZP basis set. Total energies, hartree, for the $X^1\Sigma$ state by SF-SCF, SF-CIS(D), and SF-OD methods. The $^3\Pi$ state is used as the reference for spin–flip calculations.

<table>
<thead>
<tr>
<th>$R_{\text{BH}}$, bohr</th>
<th>SF-SCF</th>
<th>SF-CIS(D)</th>
<th>SF-OD</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.8</td>
<td>-25.086 88</td>
<td>-25.151 33</td>
<td>-25.176 11</td>
</tr>
<tr>
<td>2.0</td>
<td>-25.120 95</td>
<td>-25.185 02</td>
<td>-25.209 91</td>
</tr>
<tr>
<td>2.2</td>
<td>-25.134 87</td>
<td>-25.198 73</td>
<td>-25.223 89</td>
</tr>
<tr>
<td>2.4</td>
<td>-25.136 50</td>
<td>-25.200 34</td>
<td>-25.225 98</td>
</tr>
<tr>
<td>2.8</td>
<td>-25.119 87</td>
<td>-25.184 39</td>
<td>-25.212 28</td>
</tr>
<tr>
<td>3.2</td>
<td>-25.088 69</td>
<td>-25.153 04</td>
<td>-25.189 48</td>
</tr>
<tr>
<td>3.6</td>
<td>-25.059 51</td>
<td>-25.118 89</td>
<td>-25.164 91</td>
</tr>
<tr>
<td>4.0</td>
<td>-25.043 25</td>
<td>-25.098 05</td>
<td>-25.142 60</td>
</tr>
<tr>
<td>5.0</td>
<td>-25.030 64</td>
<td>-25.080 94</td>
<td>-25.109 63</td>
</tr>
<tr>
<td>7.0</td>
<td>-25.027 86</td>
<td>-25.076 71</td>
<td>-25.099 65</td>
</tr>
<tr>
<td>8.0</td>
<td>-25.027 67</td>
<td>-25.076 44</td>
<td>-25.099 31</td>
</tr>
<tr>
<td>9.0</td>
<td>-25.027 57</td>
<td>-25.076 32</td>
<td>-25.099 17</td>
</tr>
<tr>
<td>10.0</td>
<td>-25.027 53</td>
<td>-25.076 27</td>
<td>-25.099 12</td>
</tr>
</tbody>
</table>

As shown in Fig. 1, results obtained with the $^3\Sigma$ reference are considerably better than those obtained with the $^3\Pi$ reference. The difference is particularly large for the least correlated SF-SCF model, and becomes rather small for more successful in accounting for the HOMO-LUMO correlation, its very strong dynamical correlation effects, e.g., full valence CASSCF underestimates the dissociation energy by a factor of 2.5 (for more examples, see Ref. 60). For this molecule, we employ the DZP+ basis set from Ref. 61, derived from the standard Huzinaga–Dunning $^{47,48}$ double-$\zeta$ (DZ) basis set by uncontracting the most diffuse $p$-function and augmenting it by a set of six Cartesian $d$-functions [$\alpha_a(F) = 1.580$]. Figure 2 shows potential energy curves calculated by spin–flip models and compares them with (i) the spin-
TABLE VIII. Equilibrium distances and dissociation energies for the F₂ molecule, DZP basis set.

<table>
<thead>
<tr>
<th>Method</th>
<th>R_e , Å</th>
<th>D_e , eV</th>
<th>E_{diss}, hartree</th>
</tr>
</thead>
<tbody>
<tr>
<td>VOO-CCD(2)</td>
<td>1.417</td>
<td>1.51</td>
<td>−199.205 71</td>
</tr>
<tr>
<td>RHF</td>
<td>1.332</td>
<td>10.69</td>
<td></td>
</tr>
<tr>
<td>R-CCSD</td>
<td>1.410</td>
<td>2.36</td>
<td></td>
</tr>
<tr>
<td>U-CCSD</td>
<td>1.410</td>
<td>0.95</td>
<td></td>
</tr>
<tr>
<td>MR-CISD</td>
<td>1.435</td>
<td>1.22</td>
<td></td>
</tr>
<tr>
<td>SF-SCF</td>
<td>1.567</td>
<td>0.28</td>
<td>−198.801 57</td>
</tr>
<tr>
<td>SF-CIS(D)</td>
<td>1.429</td>
<td>1.14</td>
<td>−199.195 42</td>
</tr>
<tr>
<td>SF-OD</td>
<td>1.437</td>
<td>1.24</td>
<td>−199.223 16</td>
</tr>
<tr>
<td>Expt.</td>
<td>1.412</td>
<td>1.66</td>
<td></td>
</tr>
</tbody>
</table>

Notes: a) D_e was computed as total energy difference at R_e and R_e-p=100 bohr. b) Reference 60. c) Reference 61.

restricted and spin-unrestricted OO-CCD; (ii) VOO-CCD(2) (note that in this case VOO-CCD is equivalent to the full valence CASSCF); (iii) MR-CISD (with CASSCF reference defined in the full valence active space).61 Total energies for spin–flip curves are given in Ref. 20. OO-CCD and VOO-CCD(2) results are from Ref. 60, and MRCl results are from Ref. 61. Table VIII shows equilibrium geometries and dissociation energies.

SF-SCF behaves similarly to full valence CASSCF, i.e., it grossly underestimates the dissociation energy. Inclusion of dynamical correlation in SF-CIS(D) improves the results, and the corresponding curve becomes very close to MR-CISD. The SF-OD curve is also quite close to MR-CISD, the corresponding D_e being slightly better. Based on the good performance of the SF-CIS(D) model, we expect that perturbative corrections for the SF-OD wave function would allow one to achieve high accuracy.

We attribute an unusually large error in D_e for MR-CISD to the anomalously strong correlation effects which are probably due to very high electronegativity of fluorine. The latter causes the electron density to be very compact. This tight electron distribution may result in the large local, i.e., dynamical, correlation. This explanation also seems consistent with the singlet oxygen results.

H. Ethylene

Twisted ethylene (at D_{2d} geometry) is a generic example of a diradical transition state. Due to an imbalance in the treatment of degenerate configurations, i.e., (π)^2 and (π*)^2, single-reference models using restricted orbitals overestimate the torsional barrier height and produce an unphysical cusp.15 Corresponding spin-unrestricted models, on the other hand, considerably underestimate the barrier.60,19 The results presented in this section show that the spin–flip models are capable of accurately describing this type of bond-breaking. The present study employs a DZP basis set, comprised of the standard Huzinaga–Dunning27,48 double-ζ basis augmented by six d-type polarization functions for carbon [α_d(C) = 0.75] and three p-type polarization functions [α_p(H) = 0.75] for hydrogen.

Table IX shows total energies along the torsional coordinate calculated by the SF-SCF, SF-CIS(D), and SF-OD models. For comparison, we also report multireference configuration interaction results which include all single and double excitations from the (π)^2 and (π*)^2 configurations. These computations use two-configuration SCF orbitals and are therefore labeled TCSCF-CISD. The TCSCF-CISD method should be fairly reliable for this system since it correlates both of the two most important configurations and does so without bias towards one configuration over the

FIG. 3. Ethylene torsion, DZP basis. All curves are shifted such that the energy at 0° is zero. The perturbative corrections significantly improve the SF-SCF model; the SF-CIS(D) curve almost coincides with the much more expensive SF-OD one.
TABLE X. Optimized geometry in the ethylene, DZP basis.a

<table>
<thead>
<tr>
<th>Method</th>
<th>$r_{CC}$, Å</th>
<th>$r_{CH}$, Å</th>
<th>$\alpha_{HCH}$</th>
<th>$E_{tot}$, hartree</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D_{2h}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SF-SCF</td>
<td>1.3520</td>
<td>1.0774</td>
<td>117.09</td>
<td>-78.069 24</td>
</tr>
<tr>
<td>SF-CIS(D)</td>
<td>1.3449</td>
<td>1.0838</td>
<td>116.93</td>
<td>-78.346 81</td>
</tr>
<tr>
<td>SF-OD</td>
<td>1.3508</td>
<td>1.0883</td>
<td>117.08</td>
<td>-78.389 29</td>
</tr>
</tbody>
</table>

| $D_{2d}$   |             |             |                |                   |
| SF-SCF     | 1.4717      | 1.0796      | 117.34         | -77.978 17        |
| SF-CIS(D)  | 1.4626      | 1.0881      | 116.78         | -78.244 01        |
| SF-OD      | 1.4696      | 1.0925      | 116.79         | -78.286 26        |

aOptimized barrier height is thus 2.48 eV for the SF-SCF, and 2.80 eV for the SF-CIS(D), and for the SF-OD.

other; of course, it will suffer a small error due to its lack of size extensivity. Potential energy curves for each method are shown in Fig. 3. Since the SF-SCF curve is qualitatively correct, the perturbative correction results in a uniform improvement, and the resulting SF-CIS(D) curve is very close to the more computationally expensive SF-OD or TCSCF-CISD ones.

Table X shows optimized geometries for the planar (equilibrium) and twisted (barrier) configurations. For the reference, we consider experimental estimations of 2.8 and 2.59 eV,62–66 and the MR-CISD value of 2.72 eV.67 The SF-SCF value of 2.48 eV can be considered qualitatively correct (especially, if compared with 4.59 or 1.70 eV predicted by spin-restricted and spin-unrestricted SCF models, respectively68). The SF-CIS(D) and SF-OD models yield the same value of 2.80 eV. Unfortunately, due to the uncertainty in experimental values, and the modest basis set used, it is unclear how close this value is to the exact one.

IV. CONCLUSIONS

We present size-consistent noniterative perturbative corrections to the SF-SCF. The model, SF-CIS(D), can be viewed as a second-order approximation to the more theoretically complete SF-CCSD wave function. Unlike the previously reported applications,37,40 of the CIS(D) model to the excited states of closed-shell molecules, SF-CIS(D) represents a systematic improvement over the SF-SCF model at all nuclear distortions along bond-breaking coordinates (given that there is no orbital near-instabilities in the Hartree–Fock reference wave function). The scaling of the SF-CIS(D) model is $N^3$, and the computational cost is roughly equivalent to that of the MP2 calculations.

Detailed benchmarks of SF-SCF, SF-CIS(D), and SF-OD methods demonstrate that the SF model allows us to extend the hierarchy of single-reference approximations to the exact wave function to a challenging situation of bond-breaking and diradicals which traditionally were treated within a framework of multireference formalism. Further developments include the implementation of an analytic gradient for the SF models, and perturbative corrections to the SF-OD wave function.

ACKNOWLEDGMENTS

A.I.K. acknowledges support from the National Science Foundation CAREER Award (Grant No. CHE-0094116), the Camille and Henry Dreyfus New Faculty Awards Program, and the Donors of the Petroleum Research Fund, administered by the American Chemical Society. C.D.S. acknowledges a National Science Foundation CAREER Award (Grant No. CHE-0094088) and a Camille and Henry Dreyfus New Faculty Award. A.I.K. thanks L. V. Slipchenko for her improvements of the iterative diagonalization procedure, and S. V. Levchenko for his help in testing numerical frequencies. The authors thank Professor J. F. Stanton for his suggestion to perform stability analysis, and to Professor M. Nooijen for his critical comments. Dr. Jing Kong is acknowledged for his help with setting up calculations of frequencies using finite differences. The Center for Computational Science and Technology is funded through a Shared University Research (SUR) grant from IBM and by Georgia Tech.
reference wave function—the degeneracy between occupied orbitals is immaterial.

36 C. Møller and M. S. Plesset, Phys. Rev. 46, 618 (1934).
46 Basis sets were obtained from the Extensible Computational Chemistry Environment Basis Set Database, Version, as developed and distributed by the Molecular Science Computing Facility, Environmental and Molecular Sciences Laboratory which is part of the Pacific Northwest Laboratory, P.O. Box 999, Richland, WA 99352, and funded by the U. S. Department of Energy. The Pacific Northwest Laboratory is a multiprogram laboratory operated by Battelle Memorial Institute for the U. S. Department of Energy under Contract No. DE-AC06-76RLO 1830. Contact David Feller or Karen Schuchardt for further information.
68 C. D. Sherrill, A. I. Krylov, and M. Head-Gordon (in preparation).