JOURNAL OF CHEMICAL PHYSICS VOLUME 116, NUMBER 8 22 FEBRUARY 2002

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 initio 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 strategies[16–20] 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*-benzyne[26]), 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) model,[27–30] but they are solved in a different (i.e., spin–flipping) subspace of single excitations. Initial benchmarks[19] 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] The 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).[36] 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:

$$|\Psi^{\mathrm{CIS}}\rangle = R_1|\Phi_0\rangle, \tag{1}$$

where Φ_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,

$$R_1 = \sum_{ia} r_i^a a^+ i. \tag{2}$$

Here, and throughout the paper, we follow the convention that $i,j,k,\ldots$ represents spin–orbitals that are occupied in the reference determinant Φ_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 Φ_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.[29,30]

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:

$$E^{\mathrm{CIS(D)}} = \langle\Psi^{\mathrm{CIS}}|V|U_2\Phi_0\rangle + \langle\Psi^{\mathrm{CIS}}|V|U_1T_2\Phi_0\rangle, \tag{3}$$

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 Ψ^{CIS}, whereas the second term which corresponds to the double excitations from Ψ^{CIS} represents correlation of an excited state, such that the correlation of inactive, i.e., uneffected 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, $\Delta E^{\mathrm{CIS(D)}}$, are[37]:

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

$$u_{ij}^{ab} = \sum_c (\langle ic||ab\rangle r_j^c - \langle jc||ab\rangle r_i^c) + \sum_k (\langle ij||ka\rangle r_k^b - \langle ij||kb\rangle r_k^a),$$

$$v_i^a = \frac{1}{2}\sum_{jkbc}\langle jk||bc\rangle (r_i^b t_{jk}^{ca} + r_j^a t_{ik}^{cb} + 2r_j^b t_{ik}^{ac}),$$

$$\Delta_{ij}^{ab} = \epsilon_a + \epsilon_b - \epsilon_i - \epsilon_j,$$

$$t_{ij}^{ab}=\frac{\langle ij||ab\rangle}{\Delta_{ij}^{ab}}, \tag{4}$$

where ω is the CIS excitation energy for the given state, and ϵ_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,[37] 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_i^a 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., π and π^* 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, $(\pi)^2$.[19] Moreover, SF models are capable of describing other two low-lying diradical singlet states,[41] e.g., the doubly excited $[(\pi^*)^2]$ 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 very 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_2O. 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 $\sigma\sigma^*$ 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.[42] 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_2O).

Calculations are performed using two *ab initio* packages, Q-CHEM[43] and PSI,[44] 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.[45] Some basis sets used in this work are obtained from the EMSL database.[46]

A. H_2O

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-ζ plus polarization (DZP) basis set of contracted Gaussian functions, comprised of the standard Huzinaga–Dunning[47,48] double-ζ basis augmented by six d-type polarization functions for oxygen $[\alpha_d(\mathrm{O})=0.9]$ and three p-type polarization functions $[\alpha_p(\mathrm{H})=1.0]$ for hydrogen; and (ii) a triple-ζ plus two sets of polarization functions (TZ2P) basis set, comprised of the $(11s6p/5s4p)$ triple-ζ basis set of Dunning[49] augmented with two sets of six d functions $[\alpha_d(\mathrm{O})=1.35,0.45]$ for oxygen, and $(5s/3s)$ triple-ζ basis set of Dunning[49] [with exponents scaled by $(1.25)^2$] augmented by two sets of three p-type polarization functions $[\alpha_p(\mathrm{H})=1.5,0.5]$ 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.,

TABLE I. Total energies, equilibrium geometries, and harmonic vibrational frequencies (cm^{-1}) for H_2O using DZP and TZ2P basis sets.

Method	E_{tot}, hartree	r_e, Å	θ_e	$\omega_1(a_1)$	$\omega_2(a_1)$	$\omega_3(b_2)$
SCF/DZP[a]	−76.047 009	0.9437	106.63	4165	1752	4288
MP2/DZP	−76.258 560	0.9616	104.48	3912	1665	4058
CCSD/DZP[a]	−76.267 869	0.9610	104.63	3915	1684	4044
OO-CCD/DZP[a]	−76.267 733	0.9609	104.64	3917	1684	4046
CCSD(T)/DZP	−76.270 965	0.9618	104.49	3899	1678	4030
SF-SCF/DZP/($^3B_1$)	−76.005 093	0.9517	107.70	4025	1719	3641
SF-CIS(D)/DZP/($^3B_1$)	−76.240 017	0.9564	105.58	4041	1728	6020
SF-OD/DZP/($^3B_1$)	−76.268 212	0.9610	104.95	3909	1676	3646
SCF/TZ2P[a]	−76.061 002	0.9403	106.31	4133	1756	4235
MP2/TZ2P	−76.325 833	0.9582	104.48	3858	1641	3984
CCSD/TZ2P[a]	−76.331 905	0.9563	104.74	3879	1668	3987
OO-CCD/TZ2P	−76.331 632	0.9563	104.74	3879	1669	3987
CCSD(T)/TZ2P	−76.338 955	0.9586	104.52	3842	1656	3953
SF-SCF/TZ2P/($^3B_1$)	−76.015 121	0.9503	107.45	3941	1701	3404
SF-CIS(D)/TZ2P/($^3B_1$)	−76.307 315	0.9522	105.71	3991	1713	5292
SF-OD/TZ2P/($^3B_1$)	−76.333 164	0.9560	105.00	3876	1676	4028
SF-SCF/TZ2P/($^3B_2$)	−76.029 473	0.9699	102.17	3789	1786	4809
SF-CIS(D)/TZ2P/($^3B_2$)	−76.306 418	0.9557	104.77	3901	1698	4083
SF-OD/TZ2P/($^3B_2$)	−76.333 267	0.9587	103.97	3817	1668	3955
Expt.		0.9578	104.5	3832	1649	3942

[a] Reference 68.

$^3B_2$ state, as the reference. The accuracy of spin–flip frequencies calculated with the $^3B_2$ reference is roughly comparable to that of the traditional models. However, the SF-CIS(D) model fails when using the lowest, $^3B_1$ state, as the reference (the results improving slightly in a larger basis set): the antisymmetric stretch is grossly overestimated (by 34%–53%). The SF-OD model is less sensitive to the reference, in particular, in a larger basis set. The errors for the symmetric stretch and bending are comparable with those of the CCSD model. The frequency of the antisymmetric stretch is underestimated by 7.5% in the small basis set (DZP) when using the $^3B_1$ reference. In the TZ2P basis the difference between the SF-OD/$^3B_2$ and SF-OD/$^3B_1$ frequencies is much less, all frequencies being described with an accuracy similar to CCSD or OO-CCD.

We have found that the origin of the strong sensitivity of the SF-CIS(D) model to the reference choice is in orbital near-instabilities; for the $^3B_1$ state, the lowest eigenvalue of the stability matrix in b_2 block equals 0.086, whereas the corresponding value for $^3B_2$ state is 0.346. It is not surprising that the perturbative treatment, i.e., SF-CIS(D), fails in case of near-instabilities, whereas the explicitly correlated model, SF-OD, is more stable. We have also found that the $^3B_2$ UHF reference exhibits instabilities in b_1 and a_2 blocks which can effect second-order properties. Thus, stability analysis of the UHF solution for triplet references can be used to detect potentially problematic situations.

B. CH_2

The ground state of methylene is a triplet $\tilde{X}\,^3B_1$ state,

$$\tilde{X}\,^3B_1 \approx (1a_1)^2(2a_1)^2(1b_2)^2(3a_1)(1b_1). \tag{5}$$

Following Salem, three low-lying singlet states are diradical states which can be qualitatively described by a two electrons in two orbitals model:[41]

$$\tilde{a}\,^1A_1 \approx \lambda(1a_1)^2(2a_1)^2(1b_2)^2(3a_1)^2 - \sqrt{1-\lambda^2}(1a_1)^2(2a_1)^2(1b_2)^2(1b_1)^2, \tag{6}$$

$$\tilde{b}\,^1B_1 \approx (1a_1)^2(2a_1)^2(1b_2)^2(3a_1)(1b_1), \tag{7}$$

$$\tilde{c}\,^1A_1 \approx \lambda(1a_1)^2(2a_1)^2(1b_2)^2(3a_1)^2 + \sqrt{1-\lambda^2}(1a_1)^2(2a_1)^2(1b_2)^2(1b_1)^2. \tag{8}$$

While the $\alpha\alpha$ ($M_s=1$) component of the $\tilde{X}\,^3B_1$ state (5) 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, the $\tilde{b}\,^1B_1$ 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 ($\lambda \approx 1/\sqrt{2}$) wave function. At the equilibrium geometry, the effect of the second configuration is relatively small, and the $\tilde{a}\,^1A_1$ state can be reasonably well described by a single reference model. The second $^1A_1$ state, $\tilde{c}\,^1A_1$ can be described as the doubly excited state with respect to the $\tilde{a}\,^1A_1$. At its equilibrium geometry, the $\tilde{c}\,^1A_1$ 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 $\tilde{X}\,^3B_1$ state [see Fig. 2(a) in Ref. 19].

TABLE II. Total energies, equilibrium geometries, and harmonic vibrational frequencies (cm^{-1}) for singlet methylene ($\tilde{a}\,^1A_1$ state) using DZP and TZ2P basis sets. Spin–flip models employ the $\tilde{X}\,^3B_1$ ground state as the reference.

Method	E_{tot}, hartree	r_e, Å	α	ω_1 (a_1)	ω_2 (a_1)	ω_3 (b_2)
FCI/DZP[a]	−39.027 183	1.1167	102.4			
FCI/DZP[b,c]	−39.026 635	1.1199	101.44	2928	1396	3013
SF-SCF/DZP	−38.894 492	1.1007	104.05	3113	1478	3206
SF-CIS(D)/DZP	−39.009 815	1.0901	102.70	3208	1416	3316
SF-OD/DZP	−39.039 014	1.1167	102.07	2958	1426	3030
FCI/TZ2P[d]	−39.048 984	1.1089	101.89	2899	1404	2971
SCF/TZ2P[d]		1.0945	103.73	3105	1503	3169
MP2/TZ2P	−39.034 243	1.1010	102.14	2987	1436	3065
CCSD/TZ2P[b,d]		1.1074	101.73	2919	1428	2988
SF-SCF/TZ2P	−38.900 403	1.0945	104.07	3096	1485	3176
SF-CIS(D)/TZ2P	−39.033 462	1.0974	102.86	3017	1443	3111
SF-OD/TZ2P	−39.061 603	1.1043	102.37	2932	1422	3025
Expt.		1.107	102.4	2805.9	1352.6	2864.5
Expt.				2846	1371.3	

[a] Reference 50.
[b] One frozen core and one deleted virtual orbital.
[c] Reference 51.
[d] Reference 52.

For this small system, we compare the performance of different methods against FCI results.[50–52] Basis sets employed, DZP and TZ2P, are the same as in the corresponding FCI benchmark papers.[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.

TABLE III. 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 $\tilde{X}\,^3B_1$ ground state as the reference.

Method	E_{tot}, hartree	r_e, Å	α	ω_1 (a_1)	ω_2 (a_1)	ω_3 (b_2)
FCI/DZP[a,b]	−38.985 569	1.0845	140.97	3163	1011	3444
SF-SCF/DZP	−38.857 64	1.0678	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[a,c]	−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			

[a] One frozen core and one deleted virtual orbital.
[b] Reference 51.
[c] Reference 52.

TABLE IV. 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 $\tilde{X}\,^3B_1$ ground state as the reference.

Method	E_{tot}, hartree	r_e, Å	α	ω_1 (a_1)	ω_2 (a_1)	ω_3 (b_2)
FCI/DZP[a,b]	−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[a,c]	−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

[a] One frozen core and one deleted virtual orbital.
[b] Reference 51.
[c] Reference 52.

C. O_3

Since the ozone molecule in its ground $^1A_1$ state exhibits stronger diradical character than the singlet ($\tilde{a}\,^1A_1$) methylene, the single-reference methods are less successful in describing its equilibrium properties. Table V shows equilibrium geometries and vibrational frequencies calculated using (i) a double-ζ plus polarization (DZP) basis set, comprised of the standard Huzinaga–Dunning[47,48] double-ζ basis augmented by six d-type polarization functions for oxygen $[\alpha_d(\mathrm{O})=0.85]$; and (ii) a triple-$\zeta$ plus two sets of polarization functions (TZ2P) basis set, comprised of the

TABLE V. Total energies, equilibrium geometries, and harmonic vibrational frequencies (cm^{-1}) for ozone using DZP and TZ2P+diff basis sets. Spin–flip models employ $^3B_2$ state as the reference.

Method	E_{tot}, hartree	r_e, Å	α	ω_1 (a_1)	ω_2 (a_1)	ω_3 (b_2)
SCF/DZP[a]	−224.320 019	1.199	119.2	1547	859	1427
MP2/DZP	−224.966 875	1.3028	116.24	1185	730	2425
CCSD/DZP	−224.943 608	1.2733	117.20	1258	733	1259
CCSD(T)/DZP	−224.976 753	1.2973	116.55	1132	688	995
SF-SCF/DZP	−224.399 21	1.2718	114.11	1158	753	1380
SF-CIS(D)/DZP	−224.912 010	1.2826	115.75	1112	710	1234
SF-OD/DZP	−224.963 062	1.2890	116.03	1165	709	1144
CCSDT/DZP[b]		1.286	116.7	1141	705	1077
CISD[TQ]/DZP[c]		1.281	116.7	1166	716	1138
SCF/TZ2P+diff	−224.355 603	1.1966	119.20	1515	862	1369
MP2/TZ2P+diff	−225.111 175	1.2915	116.64	1135	733	2293
CCSD/TZ2P+diff	−225.080 118	1.2568	117.64	1237	749	1197
CCSD(T)/TZ2P+diff	−225.124 411	1.2849	117.01	1105	697	955
SF-SCF/TZ2P+diff	−224.426 66	1.2636	114.46	1120	759	1327
SF-CIS(D)/TZ2P+diff	−225.055 01	1.2665	116.36	1081	710	1186
Expt.[d]		1.272	116.8	1135	716	1089

[a] Reference 68.
[b] Reference 55.
[c] Reference 56.
[d] References 53 and 54.

TABLE VI. Total energies, equilibrium geometries, and harmonic vibrational frequencies for O_2, $^1\Delta_g$ state, using DZP and TZ2P+diff basis sets.

Method	E_{tot}, hartree	r_e, Å	ω, cm^{-1}
RHF/DZP	−149.573 460	1.1687	1999
TCSCF/DZP	−149.591 143	1.1666	2015
MP2/DZP	−149.962 579	1.2787	1206
CCSD/DZP	−149.962 840	1.2345	1563
CCSD(T)	−149.977 112	1.2476	1464
SF-SCF/DZP	−149.586 927	1.1659	2013
SF-CIS(D)/DZP	−149.950 137	1.2411	1461
SF-OD/DZP	−149.973 053	1.2296	1600
SCF/TZ2P+diff	−149.594 491	1.1562	1953
MP2/TZ2P+diff	−150.057 832	1.2590	1196
CCSD/TZ2P+diff	−150.054 471	1.2145	1545
CCSD(T)/TZ2P+diff	−150.075 526	1.2319	1424
SF-SCF/TZ2P+diff	−149.607 730	1.1532	1969
SF-CIS(D)/TZ2P+diff	−150.044 678	1.2197	1462
SF-OD/TZ2P+diff	−150.064 323	1.2096	1583
Expt.		1.2155	1509,[a] 1483[b]

[a] Reference 69.

[b] Reference 70.

$(11s6p/5s3p)$ triple-ζ basis set of Dunning[49] augmented with two sets of six d-functions $[\alpha_d(\mathrm{O})=1.7,\ 0.425]$ and one diffuse s-function $[\alpha_s(\mathrm{O})=0.08993]$ and a set of three diffuse p-functions $[\alpha_p(\mathrm{O})=0.0584]$, TZ2P+diff. Results are compared against experiment[53,54] 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., ω_3 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 ω_1 and ω_2 differ by no more than 10 cm^{-1} (in DZP or cc-pVTZ basis set), the CCSD(T) value of ω_3 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. O_2

The ground state of oxygen molecule is the triplet state, and the lowest singlet state is a diradical $^1\Delta_g$ state. Table VI shows equilibrium properties for the $^1\Delta_g$ state of O_2 calculated by using the DZP and TZ2P+diff basis sets (described in the previous subsection).

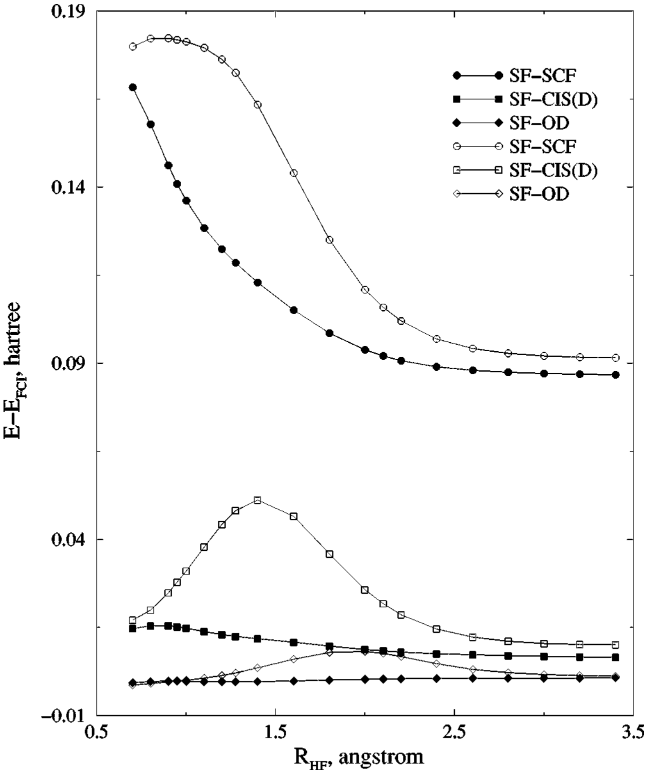

FIG. 1. HF, 6-31G basis. The errors against the FCI for SF-SCF, SF-CIS(D), and SF-OD models. Filled symbols are for SF calculations employing the $^3\Sigma$ reference state, empty symbols—for the $^3\Pi$ reference state. The errors of the SF-OD model are very small. The perturbative corrections significantly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

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. O_2 appears similar to F_2 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 effects 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., $^3\Sigma$ and $^3\Pi$ states.

For the balanced description of σ-bond breaking by the SF model, the triplet $\sigma\sigma^*$ reference (i.e., $^3\Sigma$) is the most appropriate choice, since single spin–flipping excitations from this reference generates the two most important configurations, $(\sigma)^2$ and $(\sigma^*)^2$. However, a reasonable description can also be achieved by using the $^3\Pi$ 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.

R_{BH}, bohr	SF-SCF	SF-CIS(D)	SF-OD
1.8	−25.086 88	−25.151 33	−25.176 11
2.0	−25.120 95	−25.185 02	−25.209 91
2.2	−25.134 87	−25.198 73	−25.223 89
2.4	−25.136 50	−25.200 34	−25.225 98
2.8	−25.119 87	−25.184 39	−25.212 28
3.2	−25.088 69	−25.153 04	−25.189 48
3.6	−25.059 51	−25.118 89	−25.164 91
4.0	−25.043 25	−25.098 05	−25.142 60
5.0	−25.030 64	−25.080 94	−25.109 63
6.0	−25.028 39	−25.077 56	−25.101 11
7.0	−25.027 86	−25.076 71	−25.099 65
8.0	−25.027 67	−25.076 44	−25.099 31
9.0	−25.027 57	−25.076 32	−25.099 17
10.0	−25.027 53	−25.076 27	−25.099 12

triplet state). Both ${}^3\Sigma$ and ${}^3\Pi$ states are purely repulsive and remain single reference along the dissociation coordinate, the correlation energy being smaller for ${}^3\Sigma$.

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 (but not negligible) for the SF-OD. Note that not only *relative* but also *absolute* errors are smaller for the ${}^3\Sigma$ reference. Thus, in case of the variational SF-SCF model, the ${}^3\Sigma$ reference is superior in a variational sense too. It is important that, even when using less appropriate ${}^3\Pi$ reference, the SF describes bond-breaking better than the corresponding single-reference models.

Another important observation is that SF-CIS(D) improves SF-SCF curves considerably. For both references, it yields dissociation energies which are quite close to those of SF-OD, however there are still considerable errors in the intermediate region for the calculations using the ${}^3\Pi$ reference.

F. BH

The present study employs a DZP basis, comprised of the standard Huzinaga–Dunning[47,48] double-ζ basis augmented by six d-type polarization functions for first-row atoms $[\alpha_d(\mathrm{B})=0.5]$ and three p-type polarization functions $[\alpha_p(\mathrm{H})=1.0]$ for hydrogen.[59]

Table VII presents total energies for the ground, $X\ {}^1\Sigma$, state. FCI energies for the $X\ {}^1\Sigma$ state can be found in Ref. 16. Bond-breaking in the BH molecule is more challenging since this molecule exhibits significant nondynamical correlation even at equilibrium geometries. This nondynamical correlation is derived from two π-type LUMOs. Therefore, BH is more difficult to describe by SF models than HF. As in the latter case, it is appropriate to use ${}^3\Sigma$ reference to describe the σ-bond breaking. On the other hand, ${}^3\Pi$ reference would be more successful in accounting for the HOMO-LUMO correlation. However, the SF model which uses ${}^3\Pi$ reference will not describe the two important configurations, i.e., $(\pi_x)^2$ and $(\pi_y)^2$, as being equally important (similar to the Be example from Ref. 19). The imbalance will be smaller for the correlated SF-OD model. An additional complication associated with the ${}^3\Pi$-reference is that, unlike the HF example, the ${}^3\Pi$ state is quite strongly bound, and, therefore, is described less accurately by single reference models. This explains larger errors of spin–flip models in the intermediate region. For example, the errors of SF-OD are slightly larger than those of the spin-unrestricted OD.[60] We expect that spin–flip curves calculated by using repulsive ${}^3\Sigma$ reference will exhibit smaller errors (due to the limitations of our current implementation, we were not able to perform such calculations). The encouraging observation is that SF results are superior to traditional single-reference description, even when the less appropriate ${}^3\Pi$ reference is used.

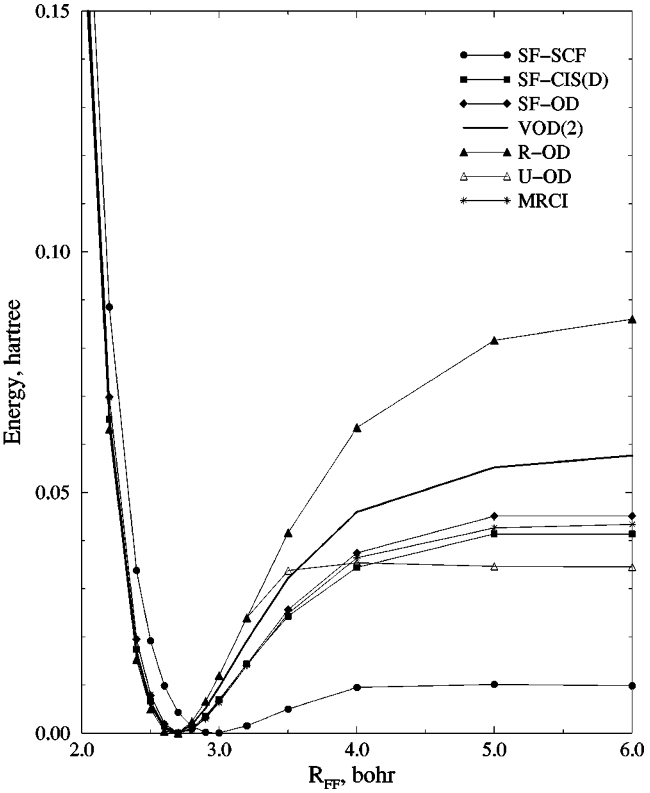

FIG. 2. F_2, DZP+ basis. All curves are shifted such that their respective energy minima are zero. SF-CIS(D) and SF-OD curves are very close to the MRCI one.

G. F_2

F_2 is a very challenging case of bond breaking for very strong nondynamical and dynamical correlation effects. It is known for being unbound at the UHF level of theory, and for 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-ζ (DZ) basis set by uncontracting the most diffuse p-function and augmenting it by a set of six Cartesian d-functions $[\alpha_d(\mathrm{F})=1.580]$.

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 F_2 molecule, DZP+ basis set.[a]

Method	R_e, Å	D_e, eV	E_{tot}, hartree
VOO-CCD(2)[b]	1.417	1.51	−199.205 71
RHF[c]	1.332	10.69	
R-CCSD[c]	1.410	2.36	
U-CCSD[c]	1.410	0.95	
MR-CISD[c]	1.435	1.22	
SF-SCF	1.567	0.28	−198.801 57
SF-CIS(D)	1.429	1.14	−199.195 42
SF-OD	1.437	1.24	−199.223 16
Expt.	1.412	1.66	

[a] D_e was computed as total energy difference at R_e and $R_{\mathrm{F-F}}=100$ 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 MRCI 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., $(\pi)^2$ and $(\pi^*)^2$, single-reference models using restricted orbitals overestimate the torsional barrier height and produce an unphysical cusp.[16] 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–Dunning[47,48] double-ζ basis augmented by six d-type polarization functions for carbon $[\alpha_d(\mathrm{C})=0.75]$ and three p-type polarization functions $[\alpha_p(\mathrm{H})=0.75]$ for hydrogen.

TABLE IX. Ethylene torsion, DZP basis. Total energies (hartree) for SF-SCF, SF-CIS(D), and SF-OD methods. Unoptimized barrier height, $\Delta E=E(90°)-E(0°)$, is also shown.[a] Geometry used: $r_{\mathrm{CC}}=1.330$ Å, $r_{\mathrm{CH}}=1.076$ Å, $\alpha_{\mathrm{HCH}}=116.6°$.

Angle (deg)	SF-SCF[b]	SF-CIS(D)	SF-OD[b]	TCSCF-CISD
0	−78.068 70	−78.346 37	−78.388 38	−78.365 89
15	−78.064 26	−78.341 98	−78.383 93	−78.361 43
30	−78.051 09	−78.328 77	−78.370 69	−78.348 12
45	−78.029 85	−78.306 99	−78.349 08	−78.326 34
60	−78.002 60	−78.277 90	−78.320 31	−78.297 24
75	−77.974 93	−78.246 19	−78.288 27	−78.264 71
80	−77.967 81	−78.237 41	−78.278 95	−78.255 22
85	−77.963 01	−78.231 29	−78.272 18	−78.248 33
90	−77.961 31	−78.229 07	−78.269 64	−78.245 74
ΔE, eV	2.92	3.19	3.23	3.27

[a] ΔE for RHF, OD, and VOD(2) methods are 4.76, 3.91, and 3.43 eV, respectively (Ref. 60).
[b] Reference 19.

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 $(\pi)^2$ and $(\pi^*)^2$ 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

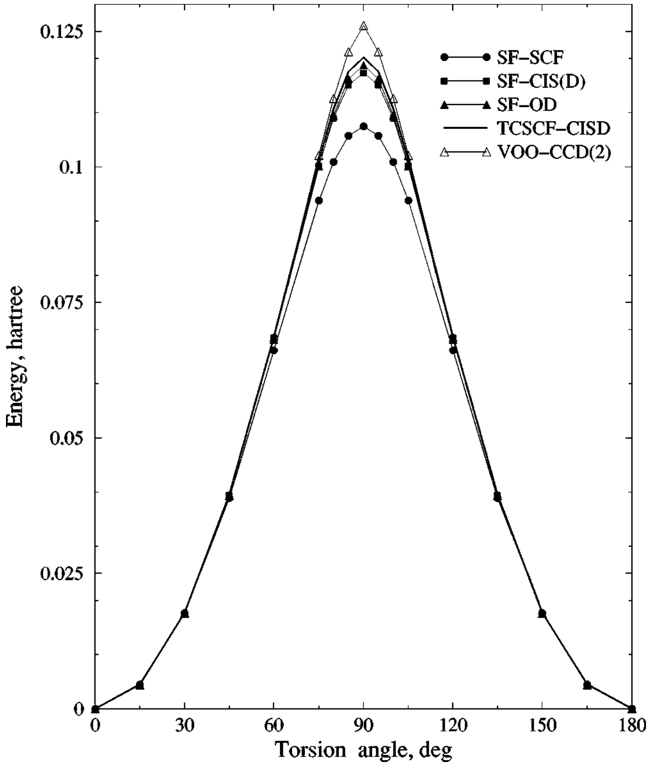

FIG. 3. Ethylene torsion, DZP basis. All curves are shifted such that the energy at 0° is zero. The perturbative corrections significantly improve the SF-SCF model; the SF-CIS(D) curve almost coincides with the much more expensive SF-OD one.

TABLE X. Optimized geometry in the ethylene, DZP basis.[a]

Method	r_{CC}, Å	r_{CH}, Å	α_{HCH}	E_{tot}, hartree
D_{2h}				
SF-SCF	1.3520	1.0774	117.09	−78.069 24
SF-CIS(D)	1.3449	1.0838	116.93	−78.346 81
SF-OD	1.3508	1.0883	117.08	−78.389 29
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

[a] Optimized 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, respectively[68]). 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^5, 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. Sliptchenko 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.

[1] See articles by B. O. Roos; P. Bruna and S. D. Peyerimhoff; R. Shepard; and D. L. Cooper, J. Gerratt, and M. Raimondi, in *Ab Initio Methods in Quantum Chemistry, II* (Wiley, New York, 1987).

[2] B. O. Roos, P. R. Taylor, and P. E. M. Siegbahn, Chem. Phys. **48**, 157 (1980).

[3] K. Ruedenberg, M. W. Schmidt, M. M. Gilbert, and S. T. Elbert, Chem. Phys. **71**, 41 (1982).

[4] K. Andersson, P.-Å. Malmqvist, B. O. Roos, A. J. Sadlej, and K. Wolinski, J. Phys. Chem. **94**, 5483 (1990).

[5] E. A. Carter and W. A. Goddard III, J. Chem. Phys. **88**, 3132 (1988).

[6] J. M. Bofill and P. Pulay, J. Chem. Phys. **90**, 3637 (1989).

[7] P.-Å. Malmqvist, A. Rendell, and B. O. Roos, J. Phys. Chem. **94**, 5477 (1990).

[8] D. Mukherjee and S. Pal, Adv. Quantum Chem. **29**, 291 (1989), and references therein.

[9] U. Kaldor, Theor. Chim. Acta **80**, 427 (1991).

[10] L. Z. Stolarczyk, Chem. Phys. Lett. **217**, 1 (1994).

[11] P. Piecuch, N. Oliphant, and L. Adamowicz, J. Chem. Phys. **99**, 1875 (1993).

[12] V. V. Ivanov and L. Adamowicz, J. Chem. Phys. **112**, 9258 (2000).

[13] X. Li and J. Paldus, J. Chem. Phys. **108**, 637 (1998).

[14] S. Pal, M. Rittby, R. J. Bartlett, D. Sinha, and D. Mukherjee, J. Chem. Phys. **88**, 4357 (1988).

[15] E. Rosta and P. R. Surján, J. Chem. Phys. **116**, 878 (2002).

[16] A. I. Krylov, C. D. Sherrill, E. F. C. Byrd, and M. Head-Gordon, J. Chem. Phys. **109**, 10669 (1998).

[17] S. R. Gwaltney, C. D. Sherrill, M. Head-Gordon, and A. I. Krylov, J. Chem. Phys. **113**, 3548 (2000).

[18] A. I. Krylov, C. D. Sherrill, and M. Head-Gordon, J. Chem. Phys. **113**, 6509 (2000).

[19] A. I. Krylov, Chem. Phys. Lett. **338**, 375 (2001).

[20] A. I. Krylov, Chem. Phys. Lett. **350**, 522 (2001).

[21] J. A. Pople, Theoretical models for chemistry, in *Energy, Structure, and Reactivity: Proceedings of the 1972 Boulder Summer Research Conference on Theoretical Chemistry*, edited by D. W. Smith and W. B. McRae, (Wiley, New York, 1973), pp. 51–61.

[22] Dynamical correlation is smaller in high-spin states because the Pauli exclusion principle keeps electrons with the same spin away from each other thus minimizing errors in the mean-field description of electron–electron repulsion. It is important that the Pauli exclusion principle is correctly described by the Hartree–Fock model by employing an antisymmetric ansatz for the wave function (Slater determinants). Moreover, nondynamical correlation can be less important in high-spin states: when the HOMO-LUMO gap is small (e.g., π and π^* in twisted ethylene), the singlet state is a two-configurational one $[(\pi)^2+(\pi^*)^2]$, whereas the $\alpha\alpha$ component of the corresponding triplet is described well by a single configuration, i.e., $\pi\alpha\pi^*\alpha$. In other words, it is only a degeneracy between occupied and virtual orbitals which effects the quality of a single-

reference wave function—the degeneracy between occupied orbitals is immaterial.

[23] R. J. Bartlett and J. F. Stanton, Rev. Comput. Chem. **5**, 65 (1994).

[24] M. Head-Gordon, J. Phys. Chem. **100**, 13213 (1996).

[25] T. D. Crawford and J. F. Stanton, J. Chem. Phys. **112**, 7873 (2000).

[26] T. D. Crawford, E. Kraka, J. F. Stanton, and D. Cremer, J. Chem. Phys. **114**, 10638 (2001).

[27] I. Tamm, J. Phys. (Moscow) **9**, 449 (1945).

[28] S. R. Dancoff, Phys. Rev. **78**, 382 (1950).

[29] J. A. Pople, Trans. Faraday Soc. **49**, 1375 (1953).

[30] J. B. Foresman, M. Head-Gordon, J. A. Pople, and M. J. Frisch, J. Phys. Chem. **96**, 135 (1992).

[31] J. Cizek, J. Chem. Phys. **45**, 4256 (1966).

[32] G. D. Purvis and R. J. Bartlett, J. Chem. Phys. **76**, 1910 (1982).

[33] J. F. Stanton and R. J. Bartlett, J. Chem. Phys. **98**, 7029 (1993).

[34] C. D. Sherrill, A. I. Krylov, E. F. C. Byrd, and M. Head-Gordon, J. Chem. Phys. **109**, 4171 (1998).

[35] G. E. Scuseria and H. F. Schaefer, Chem. Phys. Lett. **142**, 354 (1987).

[36] C. Møller and M. S. Plesset, Phys. Rev. **46**, 618 (1934).

[37] M. Head-Gordon, R. J. Rico, M. Oumi, and T. J. Lee, Chem. Phys. Lett. **219**, 21 (1994).

[38] M. Nooijen and J. G. Snijders, J. Chem. Phys. **102**, 1681 (1995).

[39] J. F. Stanton and J. Gauss, J. Chem. Phys. **103**, 1064 (1995).

[40] J. F. Stanton, J. Gauss, N. Ishikawa, and M. Head-Gordon, J. Chem. Phys. **103**, 4160 (1995).

[41] L. Salem and C. Rowland, Angew. Chem. Int. Ed. Engl. **11**, 92 (1972).

[42] T. Helgaker, P. Jørgensen, and J. Olsen, *Molecular Electronic Structure Theory* (Wiley, New York, 2000).

[43] J. Kong, C. A. White, A. I. Krylov *et al.*, Q-Chem 2.0: A high performance *ab initio* electronic structure program package, J. Comput. Chem. **21**, 1532 (2000).

[44] T. D. Crawford, C. D. Sherrill, E. F. Valeev *et al.*, PSI 3.0, PSITECH, Inc., Watkinsville, GA 30677, 1999.

[45] J. F. Stanton, J. Gauss, J. D. Watts, W. J. Lauderdale, and R. J. Bartlett, ACES II, 1993. The package also contains modified versions of the MOLECULE Gaussian integral program of J. Almlöf and P. R. Taylor, the ABACUS integral derivative program written by T. U. Helgaker, H. J. Aa. Jensen, P. Jørgensen, and P. R. Taylor, and the PROPS property evaluation integral code of P. R. Taylor.

[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.

[47] S. Huzinaga, J. Chem. Phys. **42**, 1293 (1965).

[48] T. H. Dunning, J. Chem. Phys. **53**, 2823 (1970).

[49] T. H. Dunning, J. Chem. Phys. **55**, 716 (1971).

[50] C. W. Bauschlicher and P. R. Taylor, J. Chem. Phys. **85**, 6510 (1986).

[51] C. D. Sherrill, T. J. Van Huis, Y. Yamaguchi, and H. F. Schaefer III, J. Mol. Struct. **400**, 139 (1997).

[52] C. D. Sherrill, M. L. Leininger, T. J. Van Huis, and H. F. Schaefer III, J. Chem. Phys. **108**, 1040 (1998).

[53] A. Barbe, C. Secroun, and P. Jouve, J. Mol. Spectrosc. **49**, 171 (1974).

[54] T. Tanaka and Y. Morino, J. Mol. Spectrosc. **33**, 538 (1970).

[55] J. D. Watts, J. F. Stanton, and R. J. Bartlett, Chem. Phys. Lett. **178**, 471 (1991).

[56] M. L. Leininger and H. F. Schaefer III, J. Chem. Phys. **107**, 9059 (1997).

[57] J. D. Watts and R. J. Bartlett, J. Chem. Phys. **108**, 2511 (1998).

[58] W. J. Hehre, R. Ditchfield, and J. A. Pople, J. Chem. Phys. **56**, 2257 (1972).

[59] R. J. Harrison and N. C. Handy, Chem. Phys. Lett. **95**, 386 (1983).

[60] A. I. Krylov, J. Chem. Phys. **113**, 6052 (2000).

[61] W. D. Laidig, P. Saxe, and R. J. Bartlett, J. Chem. Phys. **86**, 887 (1987).

[62] J. E. Douglas, B. S. Rabinovitch, and F. S. Looney, J. Chem. Phys. **23**, 315 (1955).

[63] B. S. Rabinovitch and K. W. Michel, J. Am. Chem. Soc. **81**, 5065 (1959).

[64] S. W. Benson and H. E. O'Neal, Natl. Stand. Ref. Data Ser. (U.S., Natl. Bur. Stand.) **21**, 111 (1970).

[65] R. J. Sension, L. Mayne, and B. Hudson, J. Am. Chem. Soc. **109**, 5036 (1987).

[66] R. Wallace, Chem. Phys. Lett. **159**, 35 (1989).

[67] B. Gemein and S. D. Peyerimhoff, J. Phys. Chem. **100**, 19257 (1996).

[68] C. D. Sherrill, A. I. Krylov, and M. Head-Gordon (in preparation).

[69] G. Herzberg, *Molecular Spectra and Molecular Structure: I. Spectra of Diatomic Molecules* (van Nostrand Reinhold, New York, 1950), Vol. I.

[70] K. P. Huber and G. Herzberg, *Constants of Diatomic Molecules* (data prepared by J. W. Gallagher and R. D. Johnson, III), NIST Chemistry WebBook, NIST Standard Reference Database No. 69, edited by P. J. Linstrom and W. G. Mallard, July 2001, National Institute of Standards and Technology, Gaithersburg, MD, 20899 (http://webbook.nist.gov).