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A spin-complete version of the spin-flip approach to bond breaking: What is the impact of obtaining spin eigenfunctions?

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Spin-complete versions of the spin-flip configuration-interaction-singles (SF-CIS) approach have been investigated to determine the impact of making the wave function an eigenfunction of $\hat{S}^2$. The method has been implemented within an extended restricted active space configuration interaction formalism. Spin-complete results are presented for excitation energies, equilibrium geometries, and potential energy curves for dissociation of a single bond in several small molecules. The effect of different orbital choices has also been investigated. The spin-complete results are compared both to results using the original spin-flip method and to more computationally expensive benchmarks. Using spin eigenfunctions dramatically improves upon the accuracy of the SF-CIS approach. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1568735]

I. INTRODUCTION

The rapid advances in *ab initio* methods and computer hardware have made accessible highly accurate electronic structure calculations.[1–3] However, current methods are still unable to efficiently describe many chemically important processes, including bond breaking. In Hartree–Fock theory, the "independent particle" model neglects the fact that electrons instantaneously respond to the position of the other electrons, i.e., that the motion of electrons is correlated. Thus, correlated methods such as many-body perturbation theory and coupled-cluster theory are required to obtain accurate results.[4] As bonds are broken, electrons become separated, and one would expect that the correlation energy (defined as the difference between the Hartree–Fock energy and the exact nonrelativistic energy) should decrease. One observes, however, that the correlation energy actually increases as bonds are broken. This happens because the correlation energy at the dissociation limit is dominated not by the short-range *dynamical correlation* of the electrons, but rather by contributions from near-degeneracies of electronic configurations, termed *nondynamical correlation*. The Hartree–Fock model and post Hartree–Fock single reference theories assume that the electronic wave function of the system can be adequately described by a single determinant. However, when this is not the case then the correlation energy also includes the error due to this single-reference approximation. While being valid for many molecules at their equilibrium geometries, this assumption breaks down at the dissociation limit. For breaking a single bond described by orbital ϕ_B the system is typically well described by a single reference near equilibrium, i.e., $|\Psi_D \phi_B \alpha \phi_B \beta\rangle$, where Ψ_D

represents those orbitals which remain doubly occupied throughout the dissociation. However, near the dissociation limit the method must take into account at least two degenerate or nearly degenerate configurations, i.e., $|\Psi_D \phi_B \alpha \phi_B \beta\rangle$ and $|\Psi_D \phi_B^* \alpha \phi_B^* \beta\rangle$.

Several solutions to the nondynamical correlation problem have been suggested. For example, a zeroth-order wave function which is appropriate for bond breaking can be obtained by optimizing orbitals for a linear combination of near-degenerate Slater determinants, as in multiconfigurational self-consistent-field (MCSCF) and complete active space SCF (CASSCF) methods[5–7] (for an alternative coupled-cluster based active space approach see Ref. 8). To achieve quantitative accuracy, such zeroth-order wave functions should be augmented by corrections for dynamical electron correlation. Unfortunately, the flexibility of the above-mentioned methods and their ability to achieve high accuracy come together with high computational costs and rather complex underlying formalisms. Moreover, many of these models are not size-consistent.

Recently, Krylov has introduced an alternative solution to the nondynamical correlation problem, the spin-flip (SF) approach.[9–12] The SF method is formulated within an equation of motion (EOM) formalism in which the $|\phi_B \alpha \phi_B^* \alpha\rangle$ component of the triplet state is used as a reference, for which effects due to dynamical and nondynamical correlation are much smaller.[9] The final wave functions are then sought in the basis of determinants conserving the number of electrons but exerting an $\alpha \rightarrow \beta$ spin-flip on one electron. The SF method thus describes the *multireference* nature of the wave function using a single-reference formalism. Other attractive features of this approach include its multistate nature (i.e., SF is capable of describing several states in one

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calculation), and unlike traditional configuration interaction singles and doubles (CISD), the method is size-consistent in that excitation energies on one fragment are not affected by the presence of other, noninteracting fragments.[10] However, the SF solutions are not pure spin eigenfunctions. By arbitrarily choosing an $\alpha\alpha$ reference from the three degenerate components of the triplet state, a slight imbalance occurs in the treatment of degenerate spin configurations in the final wave function. Since all the leading determinants are present in the SF subspace together with their spin-coupled counterparts, the resulting spin contamination of target wave functions is rather small (although it can be large for excited states—see the following). In other words, the spin contamination of the SF wave functions is due to the spin polarization of the SF wave functions, rather than spin-symmetry breaking which single-reference methods often exhibit when a single-determinantal description is not appropriate.[13] Despite the above-mentioned imbalance, the simplest SF method, the SF configuration-interaction-singles (SF-CIS) approach (also referred to as SF-SCF) performed well on several test cases[9] and was greatly improved once augmented with perturbative corrections to include dynamical correlation as in SF-CIS(D),[11] or when all double excitations were explicitly included as in SF-CISD.[10] The success of the SF approach leads to questions concerning the improvement that might be obtained by using spin-complete wave functions. This work presents a spin-complete variant of the SF-CIS model, denoted SC-SF-CIS. Section II discusses the theoretical approach and describes the implementation. Results for excitation energies, equilibrium geometries, and potential energy curves for dissociation of a single bond in several small molecules are given in Sec. III and our concluding remarks are given in Sec. IV.

II. THEORETICAL APPROACH

A. Spin-completeness of the SF-CIS wave functions: Theory and implementation

For open-shell electron configurations, several determinants are required to form an eigenfunction of $\hat{S}^2$. For a simple example, consider the case of two electrons in two orbitals. Of the four $M_s = 0$ determinants, two are of a closed shell type, i.e., $|\phi_1\alpha\phi_1\beta\rangle$ and $|\phi_2\alpha\phi_2\beta\rangle$. When the same set of spatial orbitals is employed for the α and β spin-orbitals, the closed-shell determinants are spin pure, i.e., they are eigenfunctions of both the $\hat{S}_z$ and the $\hat{S}^2$ operators. The open-shell determinants, $|\phi_1\alpha\phi_2\beta\rangle$ and $|\phi_1\beta\phi_2\alpha\rangle$, are not eigenfunctions of $\hat{S}^2$. However, they do form what we will call a spin-coupled set, and singlet and triplet $\hat{S}^2$ eigenfunctions are obtained by the appropriate linear combination of these determinants, i.e., $2^{-1/2}(|\phi_1\alpha\phi_2\beta\rangle \pm |\phi_1\beta\phi_2\alpha\rangle)$. Thus, a CI wave function that includes one of these determinants must also include the other if the total wave function is to be a spin eigenfunction.

Turning back to the SF approach, consider the simple case of four electrons in four spatial orbitals, as in Fig. 1. Configurations (b) through (j) result from single SF excitations from the reference (a). Configurations (b) and (c) are of a closed-shell type (i.e., contain no unpaired electrons) and

FIG. 1. System consisting of four electrons in four orbitals. Configuration (a) is the triplet reference. Configurations (b)–(j) are produced by single spin-flipping electronic excitations. Note that (b) and (c) are spin eigenfunctions and that (d) and (e) form a "spin-coupled" set. However, configurations (f)–(j) are all missing one or more complementary spin configurations.

are thus spin eigenfunctions. Open-shell configurations (d) and (e) include singly occupied spatial orbitals and are thus not spin eigenfunctions of the system, but do form a "spin-coupled" set and thus can be combined to obtain an eigenfunction of $\hat{S}^2$. Configurations (f)–(j) are not spin eigenfunctions, and their "spin-complements" cannot be obtained by a single SF excitation from (a). Thus, a linear combination of (b)–(j), i.e., the SF-CIS wave function for this particular system, is not a spin eigenfunction. The missing spin-complements of (f)–(j) are shown in Fig. 2. These nine determinants should be added to the nine SF-CIS determinants from Fig. 1 to achieve spin-completeness. For the case of six

FIG. 2. Determinants (f)–(j) from Fig. 1 and the corresponding "spin-complements."

electrons in six spatial orbitals, the SF-CIS space consists of 16 determinants. To form the SC-SF-CIS wave function, 28 additional determinants are required.

In order to estimate the total number of determinants in the SF-CIS and the SC-SF-CIS subspaces, let us partition the *molecular* orbital space into three subspaces; (i) a subspace of O doubly occupied orbitals denoted by **O**; (ii) a subspace of X singly occupied orbitals denoted by **X** (for the triplet reference, **X** contains only two molecular orbitals); and (iii) a subspace of V unoccupied orbitals denoted by **V**. The choice of the partitioning is defined by the appropriate high-spin reference. The total number of electrons is thus equal to $2O+X$. If there are no symmetry imposed restrictions, the target SF-CIS subspace contains $2(O+V+2)+OV$ determinants: four $X \rightarrow X$ excitations [determinants (b)–(e) from Fig. 1]; $2O$ and $2V$ excitations of the $O \rightarrow X$ and $X \rightarrow V$ types, respectively, since $X=2$ for the SF reference [determinants (h),(i) and (f), (g)]; and OV determinants of the $O \rightarrow V$ type [determinant (j)]. The spin-complements from Fig. 2 are formally a restricted subset of double and triple spin-orbital excitations relative to the high-spin triplet reference. The (f′) and (g′) type determinants are $X \rightarrow X, X \rightarrow V$ doubles (there are $2V$ of these). Likewise, the (h′) and (i′) type determinants are $X \rightarrow X, O \rightarrow X$ doubles (there are $2O$ of these). The (j′₁), (j′₂), (j′₄), and (j′₅) type determinants are $X \rightarrow X, O \rightarrow V$ doubles ($4OV$ total). Finally, there are OV triple $X \rightarrow X, X \rightarrow X, O \rightarrow V$ excitations of the (j′₃) type. To summarize, the total number of determinants in the SC-SF-CIS is $4(O+V+1)+6OV$. Thus, the number of determinants included in either method is $\mathcal{O}(OV)$. For a specific example, the HF molecule in a 6-31G basis, taking symmetry restrictions into account and with the $1s$ orbital on fluorine frozen, requires 17 determinants for SF-CIS and 50 determinants for SC-SF-CIS.

We have implemented the SC-SF-CIS model by modifying the restricted active space configuration interaction (RAS-CI) program, DETCI, of C.D.S.[14] In the RAS-CI method,[15,16] determinants are selected by partitioning of the molecular orbitals into several subspaces and then choosing determinants according to the number of electrons allowed in each subspace. As described by Sherrill and Schaefer,[16] we divide the active (nonfrozen) orbitals into four subspaces, labeled I, II, III, and IV. The orbital partitioning is determined by the specific bond to be broken. The bonding orbital ϕ_B defines the RAS II subspace, and all other active occupied orbitals are placed in RAS I. RAS III contains the corresponding antibonding orbital ϕ_B^*, and all remaining virtual orbitals are placed in RAS IV. In terms of the **O**, **V**, and **X** subspaces introduced earlier, RAS I and RAS IV correspond to the **O** and **V** subspaces, respectively, while RAS II and RAS III form together the **X** subspace.

Once the orbitals have been distributed among these RAS subspaces, the determinants for the SC-SF-CIS are chosen as follows. A maximum of one excitation is allowed from RAS I, a maximum of two electrons are allowed in RAS III (which contains only a single orbital anyway), and a maximum of one electron is allowed in RAS IV. A maximum of two electrons are allowed simultaneously in RAS III and RAS IV. Finally, if an electron is in RAS IV, then there must

be at least one hole in RAS II. These rather complex rules are necessary to generate exactly the SC-SF-CIS determinantal subspace, and are different from the usual RAS-CI procedures.[15,16]

The above-mentioned scheme for selecting determinants can be used with any type of molecular orbitals, allowing us to investigate the effect of different orbital choices in addition to testing the importance of spin-completeness. The EOM formulation of the SF models suggests that one employ orbitals obtained for the high spin reference state [either unrestricted Hartree–Fock (UHF) or restricted open shell Hartree–Fock (ROHF) or Brueckner-type, as in spin-flip optimized orbital coupled-cluster doubles (SF-OD)]. Previous SF-CIS benchmarks employed (UHF) orbitals for the high-spin triplet of the appropriate symmetry. In the present work, we also use high-spin triplet Hartree–Fock orbitals, but they are obtained in the ROHF procedure (for rigorous spin-completeness, it is necessary to use the same spatial molecular orbitals for α and β spin-orbitals). We have also tested the performance of the restricted Hartree–Fock (RHF) orbitals obtained for the closed-shell singlet wave function, as well as two-configuration self-consistent-field (TCSCF) orbitals.

Although our CI space is generated in the RAS-CI scheme as described earlier, for simplicity we will speak as though the space is generated from a triplet ''reference'' as in the original SF-CIS procedure. Results were generated using the lowest triplet state of the given symmetry as a reference. For the bond breaking examples, this reference becomes $|\Psi_D \phi_B \alpha \phi_B^* \alpha\rangle$ as the bond is stretched.

B. Size-consistency of the SC-SF-CIS method

In this section, we discuss the size-consistency of the SC-SF-CIS model, closely following the presentation from Ref. 10. We adhere to the terminology used in Refs. 10 and 17 and use the term size-consistency to refer to the additive separability of the energy in the limit of noninteracting fragments:

$$E_{AB}=E_A+E_B, \tag{1}$$

where E_{AB} is the energy of a system composed of two non-interacting fragments, **A** and **B**, at infinite separation; and E_A, E_B are energies of the corresponding fragments. Here, we restrict ourselves to the case when **A** and **B** are closed shell systems. In the following we will show that SC-SF-CIS, using an UHF triplet reference, is size-consistent in the sense that the total SF energy is equal to the sum of the SF energy of fragment **A** and the HF energy of fragment **B**. Therefore, the accuracy of the SF-CI description of the bond breaking localized at a reaction center in a large molecule would not be affected by molecular size. However, SF-CI would fail to describe simultaneous breaking of two bonds, even in case of noninteracting bonds.

For excited states described by the SF-CI or SF-CC models, the total energy of a target state consists of the reference energy and the corresponding transition energy. Thus, Eq. (1) is satisfied if (i) the reference energy of the composite system is the sum of the reference energies for fragments, and (ii) the transition energy is additive. Condition (i) is satisfied by any SF-CI model due to size-consistency of the

Hartree–Fock model given that the orbitals are obtained from the Hartree–Fock calculation for the SF reference determinant. In the following, we prove that the transition energy for the "excitation" localized on fragment **A** in the super-molecule is the same as the transition energy for the fragment **A**, i.e., that energies of target states on the fragment **A** are not affected by the presence (at infinite distance) of the fragment **B**. Thus, the quality of SF-CI description would not degrade with the increase of molecular size. However, the SF-CI correlation energy is not additive.

We start by dividing all the determinants into four groups; (i) the reference determinant, $|0_A \cdot 0_B\rangle$ or simply $|0\rangle$; (ii) determinants involving excitations localized on fragment **A**, $|\Phi_A \cdot 0_B\rangle$ or $|A\rangle$; (iii) determinants involving excitations localized on fragment **B**, $|0_A \cdot \Phi_B\rangle$ or $|B\rangle$; (iv) determinants that involve excitations of electrons on both fragments, $|\Phi_A \cdot \Phi_B\rangle$ or $|AB\rangle$ (i.e., those which describe simultaneous excitation of both subsystems or electron transfer between them).

In the SF implementation employing a triplet reference, the reference determinant is the Hartree–Fock determinant describing the $\alpha\alpha$ component of the reference triplet state. We assume that the two unpaired α electrons are localized on fragment **A**.[18] Thus, $|0_A\rangle$ is the Hartree–Fock determinant for fragment **A** in the *triplet* state, and $|0_B\rangle$ is the Hartree–Fock determinant for fragment **B** in the *singlet* state. Later in the discussion, we use $|0\rangle$ and $|\mathbf{p}\rangle$ to refer to (i) and (ii)–(iv) determinants, respectively. While $|0\rangle$ is the $M_s = 1$ determinant, all $|\mathbf{p}\rangle$ have $M_s = 0$, since they are generated by spin-flipping excitations from $|0\rangle$.

In the separated limit, the Hamiltonian operator of the composite system is the sum of those for the individual fragments:

$$\hat{H} = \hat{H}_A + \hat{H}_B. \tag{2}$$

As pointed out by Koch *et al.*,[19] the sufficient condition for size-consistency is a block-diagonal structure of the matrix of the Hamiltonian (2) in the above-described many-electron basis,[20] which the rest of this section proves.

First, all the $\langle 0|H|\mathbf{p}\rangle$ and $\langle \mathbf{p}|H|0\rangle$ blocks are zero, because the determinants $|0\rangle$ and $|\mathbf{p}\rangle$ describe states with different number of α and β electrons and, therefore, they do not interact across the (nonrelativistic) Hamiltonian. Using shorthand notation $H_{PQ} \equiv \langle P|H|Q\rangle$, other nondiagonal blocks of the matrix of the Hamiltonian (2) are

$$H_{AB} = \langle 0_B|\Phi_B\rangle \cdot \langle \Phi_A|\hat{H}_A|0_A\rangle + \langle 0_A|\Phi_A\rangle \cdot \langle \Phi_B|\hat{H}_B|0_B\rangle, \tag{3}$$

$$H_{BA} = \langle 0_A|\Phi_A\rangle \cdot \langle \Phi_B|\hat{H}_B|0_B\rangle + \langle \Phi_B|0_B\rangle \cdot \langle 0_A|\hat{H}_A|\Phi_A\rangle, \tag{4}$$

$$H_{B,AB} = \langle \Phi_B|\Phi_B'\rangle \cdot \langle 0_A|\hat{H}_A|\Phi_A\rangle + \langle 0_A|\Phi_A\rangle \cdot \langle \Phi_B|\hat{H}_B|\Phi_B'\rangle, \tag{5}$$

$$H_{A,AB} = \langle 0_B|\Phi_B\rangle \cdot \langle \Phi_A|\hat{H}_A|\Phi_A'\rangle + \langle \Phi_A|\Phi_A'\rangle \cdot \langle 0_B|\hat{H}_B|\Phi_B\rangle. \tag{6}$$

Due to the orthogonality, all the $\langle 0_A|\Phi_A\rangle$ and $\langle 0_B|\Phi_B\rangle$ terms are zero. Moreover, the $\langle 0_A|\hat{H}_A|\Phi_A\rangle$ matrix elements are also zero, since $|0_A\rangle$ and $|\Phi_A\rangle$ have different number of α and β electrons. However, $\langle 0_B|\hat{H}_B|\Phi_B\rangle$ is not necessarily

zero, since the fragment **B** is in the singlet state. Thus, H_{AB}, H_{BA}, and $H_{B,AB}$ blocks are always zero, regardless of the levels of excitation included in the CI expansion, molecular orbitals used, and the multiplicity of the reference (as long as $|0\rangle$ and $|\mathbf{p}\rangle$ are of different M_s). However, the $H_{A,AB}$ term is zero only in the particular circumstances. This term reduces to $\langle \Phi_A|\Phi_A'\rangle \cdot \langle 0_B|\hat{H}_B|\Phi_B\rangle$. In case of the SF-CI model employing a triplet reference and including up to M-tuple excited determinants, the CI expansion includes excitations which flip the spin of one electron. Thus, since the determinant Φ_A includes *at least* one electron excitation, the excitation level in the determinant Φ_B does not exceed $M-1$ substitutions. Therefore, term (6) does not exist for single excitations. Moreover, for any double excitations the term $\langle \Phi_B|\hat{H}_B|0_B\rangle$ zeros out because of the Brillouin theorem (if one employs *unrestricted Hartree–Fock triplet orbitals* for the reference determinant). If the SF-CI expansion includes higher excitations, nonzero $H_{A,AB}$ terms may appear and violate size-consistency.

As discussed in Sec. II A, spin-completeness of the SF-CIS method requires adding a selected subset of doubly and triply excited determinants. As shown earlier, for any double excitations, the $H_{A,AB}$ terms are zero. Therefore, we should consider only triply excited determinants from the SC-SF-CIS determinantal subspace, i.e., the $X \rightarrow X, X \rightarrow X, O \rightarrow V$ excitations. Since such triple excitations include excitations of two electrons within the open-shell subspace **X**, the corresponding Φ_A includes *at least* double electron excitation, and the excitation level in Φ_B is thus restricted to a single substitutions. Thus, for the restricted triple excitations of the $X \rightarrow X, X \rightarrow X, O \rightarrow V$ type, the $H_{A,AB}$ term is zero. Therefore, size-consistency of the SF-CIS model is not impacted by adding the selected subset of doubly and triply excited determinants as required by spin-completeness. However, all of the SF-CI models include terms violating size-consistency when the Brillouin theorem is not satisfied, i.e., in case when *restricted* triplet or singlet orbitals are used. In the following, we present a numerical example which demonstrates the effect of different orbital choices on the size-consistency of excitation energies.

III. RESULTS AND DISCUSSION

We present SC-SF-CIS results for several benchmark molecules and compare the results to the spin-incomplete SF-CIS approach. Using ROHF triplet orbitals allows a clear comparison of the effects of obtaining spin eigenfunctions, while SC-SF-CIS results using other orbitals facilitate the analysis of the importance of triplet orbitals to the success of the method.

A. Be

A clear example of the advantages of using spin-complete wave functions is given by the excited states of Be atom, which have already been investigated using the SF-CIS and spin-flip configuration interaction singles and doubles (SF-CISD) methods.[9,10] The total and excitation energies for low-lying states of Be calculated in a 6-31G basis by different SF models, traditional CISD, and full CI are

TABLE I. Ground state total energies (hartree) and excitation energies (eV) for Be atom using a 6-31G basis set.[a]

State	SC-SF-CIS (singlet orbs)	SC-SF-CIS (triplet orbs)	SF-CIS[b]	SF-CIS(D)[c]	SF-CISD[c]	CISD[c]	FCI[b]
$^1S(1s^22s^2)$	−14.584 255	−14.584 904	−14.584 111	−14.597 209	−14.613 056	−14.613 493	−14.613 545
$^3P(1s^22s2p_z)$	2.102	2.131	2.111	2.432	2.861	2.877	2.862
$^3P(1s^22s2p_{x,y})$	2.129	2.132	4.087	4.144	2.867	2.877	2.862
$^1P(1s^22s2p_z)$	5.938	5.973	6.036	6.254	6.578	6.598	6.577
$^1P(1s^22s2p_{x,y})$	5.988	5.977	7.481	7.743	6.586	6.598	6.577
$^3P(1s^22p_z2p_{x,y})$	7.327	6.982			7.671	7.696	7.669
$^1D(1s^22p_z^2)$	8.815	8.925	8.94	9.038	8.624	8.637	8.624

[a]SF methods employ a $^3P(1s^22s2p_z)$ reference.
[b]Reference 9.
[c]Reference 10.

presented in Table I. If the SF-CIS method is based upon a $^3P(1s^22s2p_z)$ reference, then the $(1s^22s2p_x)$ or $(1s^22s2p_y)$ components of excited ^3P or ^1P states cannot be described properly, because the $|1s^22s\beta 2p_{x,y}\alpha\rangle$ determinants are missing. The same holds for the $(1s^22p_z2p_x)$ and $(1s^22p_z2p_y)$ components because the $|1s^22p_z\beta 2p_{x,y}\alpha\rangle$ determinants are missing. The SF-CIS roots corresponding to these states are heavily spin-contaminated and yield greatly overestimated excitation energies.[9] When all double excitations are explicitly present in the wave function (as in the SF-CISD model), the description of these states significantly improves: both spin-contamination and artificial energy splittings are considerably reduced at the SF-CISD or SF-OD level. As expected, the perturbative account of doubles in the SF-CIS(D) method is not capable of restoring the balance. The SC-SF-CIS model explicitly includes the missing determinants and provides reasonable predictions of the excitation energies of these components of the lowest-lying ^1P and ^3P states, as demonstrated in Table I. In fact, the artificial splittings in the SC-SF-CIS are smaller than those in a more expensive SF-CISD model. The errors against full CI are fairly large (about 0.7 eV) but are about what should be expected for a method containing primarily single excitations (errors of 1 eV or more are common for CIS).[21] The $(1s^22s2p_{x,y})$ and $(1s^22s2p_z)$ components of the lowest ^1P and ^3P states are not strictly degenerate, because even the spin-complete SC-SF-CIS approach fails to treat the three p orbitals on an equal footing when it singles out one of them (here, $2p_z$) to constitute RAS II. The SC-SF-CIS calculation with closed-shell singlet orbitals which have identical energies for all three of the $2p$ orbitals confirms that the failure to reproduce the exact degeneracy is due to the CI space, rather than the orbitals. In fact, singlet orbitals yield slightly larger splittings than triplet orbitals. Overall, the components which should be exactly degenerate are artificially split by no more than 0.05 and 0.004 eV with singlet and triplet orbitals, respectively. Similar to the lowest ^3P state, the description of the $(1s^22p_z2p_{x,y})$ components of the next-higher ^3P state is also considerably improved by the SC-SF-CIS method. To summarize, although the SC-SF-CIS approach is a considerable improvement in that it describes excited states which are not accessible by SF-CIS, unfortunately it does not significantly improve vertical excitation energies of the states present in SF-CIS.

As discussed earlier, the SC-SF-CIS excitation energies

are rigorously size-consistent only when UHF triplet orbitals are employed, due to the applicability of Brillouin's theorem. In this case, the quality of SC-SF-CIS is independent of molecular size, i.e., excitation energies of Be would not be affected by a Ne atom located 100 Å away. We use this example to investigate the numerical consequences of using ROHF triplet or RHF singlet orbitals in the SC-SF-CIS calculations. The ground state and excitation energies for Be with a Ne atom 100 Å away calculated using the same 6-31G basis set are given in Table II. Both RHF orbitals of the ground state, Be(^1S)Ne(^1S), and ROHF orbitals of the lowest triplet state, Be(^3P)Ne(^1S), have been tested. The excitation energies for Be–Ne are identical to those for Be in most cases. For the states where the Be–Ne excitation energy differs from that of Be, the difference is always less than 0.001 eV. These results imply that the size-consistency of the SC-SF-CIS model is not considerably affected by using orbitals other than triplet UHF ones. Therefore, the quality of SC-SF-CIS should be only slightly impacted by molecular size when using the restricted orbitals. The use of the restricted orbitals is important to ensure that the final wave function is an eigenfunction of $\hat{S}^2$.

B. H_2O

Although the spin-flip approach is designed for bond breaking problems, it is important to verify its performance for well-behaved molecules at their equilibrium geometries. Somewhat surprisingly, in previous work SF-CIS had diffi-

TABLE II. SC-SF-CIS ground state total energies (hartree) and excitation energies (eV) for Be atom with and without a Ne atom 100 Å away, using a 6-31G basis set.[a]

State	Be (singlet orbs)	Be (triplet orbs)	Be–Ne (singlet orbs)	Be–Ne (triplet orbs)
$^1S(1s^22s^2)$	−14.584 255	−14.584 904	−143.058 132	−143.058 781
$^3P(1s^22s2p_z)$	2.102	2.131	2.103	2.132
$^3P(1s^22s2p_{x,y})$	2.129	2.132	2.129	2.132
$^1P(1s^22s2p_z)$	5.938	5.973	5.938	5.973
$^1P(1s^22s2p_{x,y})$	5.988	5.977	5.989	5.977
$^3P(1s^22p_z2p_{x,y})$	7.327	6.982	7.327	6.982
$^1D(1s^22p_z^2)$	8.815	8.925	8.815	8.926

[a]SF methods employ a $^3P(1s^22s2p_z)$ reference.

TABLE III. Total energies and equilibrium geometries for H_2O using a DZP basis set.[a]

Method	Energy	r_e	θ_e
SC-SF-CIS(singlet orbs)/($^3B_1$)	$-76.055\ 171$	0.9511	106.14
SC-SF-CIS(triplet orbs)/($^3B_1$)	$-76.042\ 001$	0.9572	106.56
SC-SF-CIS(singlet orbs)/($^3A_1$)	$-76.059\ 521$	0.9629	104.56
SC-SF-CIS(triplet orbs)/($^3A_1$)	$-76.045\ 076$	0.9799	103.92
SF-CIS/($^3B_1$)[b]	$-76.005\ 093$	0.9517	107.70
SF-CIS(D)/($^3B_1$)[b]	$-76.240\ 017$	0.9564	105.58
SF-OD/($^3B_1$)[b]	$-76.268\ 212$	0.9610	104.95
SCF[a]	$-76.047\ 009$	0.9437	106.63
MP2[b]	$-76.258\ 560$	0.9616	104.48
CCSD[b]	$-76.267\ 869$	0.9610	104.63
CCSD(T)[b]	$-76.270\ 965$	0.9618	104.49
Expt.		0.9578	104.5

[a]Total energies in hartree, bond lengths in angstroms, and bond angles in degrees.
[b]Reference 11.

TABLE IV. Total energies (hartree) for HF dissociation using a 6-31G basis set.[a]

R_{HF} (Å)	SC-SF-CIS (singlet orbs)	SC-SF-CIS (triplet orbs)	SF-CIS[b]	FCI[b]
0.7	$-99.892\ 219$	$-99.869\ 146$	$-99.837\ 26$	$-100.005\ 489$
0.8	$-99.973\ 916$	$-99.960\ 823$	$-99.929\ 34$	$-100.087\ 139$
0.9	$-100.003\ 583$	$-99.999\ 269$	$-99.968\ 11$	$-100.114\ 251$
0.95	$-100.008\ 009$	$-100.006\ 798$	$-99.975\ 88$	$-100.116\ 698$
1.0	$-100.008\ 182$	$-100.009\ 077$	$-99.978\ 53$	$-100.114\ 621$
1.1	$-100.000\ 391$	$-100.003\ 006$	$-99.973\ 78$	$-100.102\ 115$
1.2	$-99.986\ 493$	$-99.988\ 806$	$-99.961\ 64$	$-100.083\ 938$
1.2764	$-99.973\ 972$	$-99.975\ 479$	$-99.950\ 30$	$-100.068\ 708$
1.4	$-99.952\ 807$	$-99.952\ 850$	$-99.931\ 42$	$-100.044\ 285$
1.6	$-99.921\ 562$	$-99.919\ 569$	$-99.904\ 71$	$-100.009\ 752$
1.8	$-99.897\ 433$	$-99.894\ 624$	$-99.885\ 55$	$-99.984\ 078$
2.0	$-99.881\ 084$	$-99.878\ 602$	$-99.873\ 48$	$-99.967\ 201$
2.1	$-99.875\ 386$	$-99.873\ 358$	$-99.869\ 48$	$-99.961\ 487$
2.2	$-99.870\ 987$	$-99.869\ 509$	$-99.866\ 50$	$-99.957\ 183$
2.4	$-99.865\ 079$	$-99.864\ 751$	$-99.862\ 71$	$-99.951\ 656$
2.6	$-99.861\ 685$	$-99.862\ 361$	$-99.860\ 74$	$-99.948\ 741$
2.8	$-99.859\ 712$	$-99.861\ 174$	$-99.859\ 79$	$-99.947\ 238$
3.0	$-99.858\ 528$	$-99.860\ 578$	$-99.859\ 39$	$-99.946\ 465$
3.2	$-99.857\ 792$	$-99.860\ 272$	$-99.859\ 23$	$-99.946\ 065$
3.4	$-99.857\ 331$	$-99.860\ 111$	$-99.859\ 16$	$-99.945\ 857$

[a]SF models employ a $^3\Sigma$ reference.
[b]Reference 9.

culty in accurately predicting the equilibrium geometry of H_2O when the lowest-lying triplet state, $^3B_1$, was used as a reference,[11] while SF calculations using a higher $^3B_2$ reference yielded accurate results. The origin of these problems has been attributed to near-instabilities found for the $^3B_1$ Hartree–Fock wave function. Table III presents our SC-SF-CIS values for H_2O using the standard Huzinaga–Dunning[22,23] polarized double-ζ (DZP) basis set. We have employed the $^3B_1$ reference (to compare to previous work) and a $^3A_1$ reference which would be more appropriate for breaking the O–H bonds.

SF-CIS using the $^3B_1$ reference greatly overestimates the bond angle (107.7° versus 104.5° experimentally). The SC-SF-CIS method reduces this error, giving bond angles of 106.1° and 106.6° using singlet and triplet orbitals, respectively. If one employs the $^3A_1$ reference, which is more appropriate for the type of bond breaking reactions targeted by the SF approach, then much more reasonable bond angles are obtained (104.6° and 103.9°), although now the bond length is somewhat overestimated (by 0.005 or 0.022 Å). The SC-SF-CIS wave function for this case requires 78 determinants, compared to 24 determinants for SF-CIS; both of these CI spaces are very small. More complete SF models such as SF-CIS(D) and SF-OD yield results for the $^3B_1$ reference which are in good agreement with experiment or with conventional correlated single-reference methods such as second-order Møller–Plesset perturbation theory (MP2) or coupled-cluster singles and doubles (CCSD).

C. HF

The spin-flip approach seeks to address bond breaking processes. We have considered bond breaking in the HF molecule using a 6-31G basis, for which an exact treatment of electron correlation is readily accessible via full CI and for which previous SF results have been reported.[9] Total electronic energies at various bond lengths are provided in Table IV, and potential energy curves are displayed in Fig. 3. For HF, both the bonding and anti-bonding orbitals are of σ sym-

metry, so we have used a $^3\Sigma$ reference (in the SF language) as in previous SF studies.[9–11] We note that this is the lowest-lying triplet state only at stretched geometries, and not at equilibrium, where the lowest triplet is of $^3\Pi$ symmetry.

Figure 3 makes it clear that the spin-complete SC-SF-CIS is a dramatic improvement over SF-CIS; the error in the well depth compared to full CI is reduced by more than 2/3. Figure 4 displays errors versus full CI as a function of bond length. A perfectly flat error curve would indicate a potential energy curve parallel to the full CI curve, and molecular properties predicted from such a curve would be identical to the full CI results. The errors for SC-SF-CIS are generally flat past about 1.5 Å, but become larger at shorter distances. This reflects the increased importance of dynamical electron correlation—almost totally absent in SF-CIS or SC-SF-CIS—when the nuclei are closer together. As expected, triplet orbitals yield slightly lower SC-SF-CIS energies at large distances, while singlet orbitals perform better around equilibrium. Overall, the singlet orbitals give a potential energy curve which is more parallel to full CI.

As seen in the figures, the SF-CIS(D) method eliminates the vast majority of the error in SF-CIS by including an approximate, perturbative treatment of dynamical correlation. The SF-CIS(D) error curve in Fig. 4 is nearly flat. Since SC-SF-CIS is a much better wave function than SF-CIS, we anticipate that perturbative corrections for dynamical correlation as in SF-CIS(D) should provide excellent results across the entire potential energy surface at modest computational cost.

D. F_2

F_2 is a particularly challenging problem for electronic structure theory due to strong dynamical and nondynamical
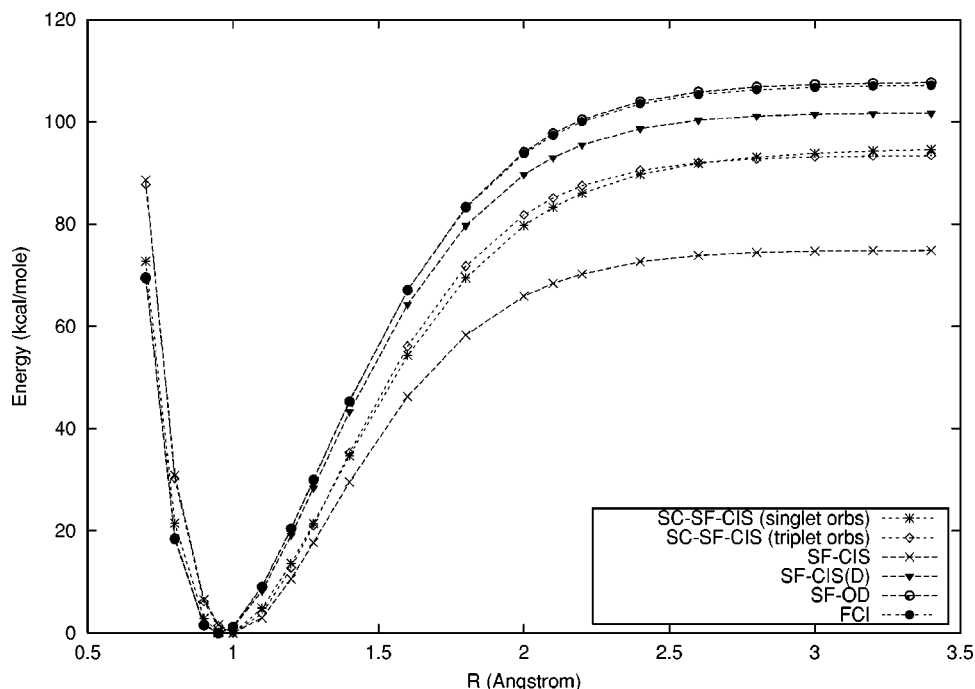
FIG. 3. Potential energy curves for HF using a 6-31G basis set. The minimum energy at each level of theory has been set to zero.

correlation effects. Indeed, it is unbound at the UHF level of theory. Here we examine bond breaking in F_2 using the DZP+ basis set of Ref. 24, which is the standard Huzinaga–Dunning[22,23] double-ζ set with the most diffuse p function uncontracted and augmented by six Cartesian d functions [$\alpha_d(F)=1.580$]. Potential energy curves for SF-CIS and SC-SF-CIS are displayed in Fig. 5 and compared to previously published curves using SF-CIS(D),[11] CASSCF[24] (which is identical to valence optimized orbital coupled-cluster doubles, or VOO-CCD, in this particular case), multireference CISD (MRCISD),[24] and VOO-CCD(2).[13] Table V

presents total energies, equilibrium geometries, dissociation energies, and harmonic vibrational frequencies for F_2 predicted by several theoretical methods.

We observe that even the full valence CASSCF, which should properly describe nondynamical correlation, underestimates the more reliable VOO-CCD(2) dissociation energy by more than a factor of 2. Likewise, SF-CIS provides rather poor results for this case, obtaining just 17% of the experimental dissociation energy and just 19% of the VOO-CCD(2) result, which is probably the most reliable of the theoretical values considered here. Just by adding the miss-
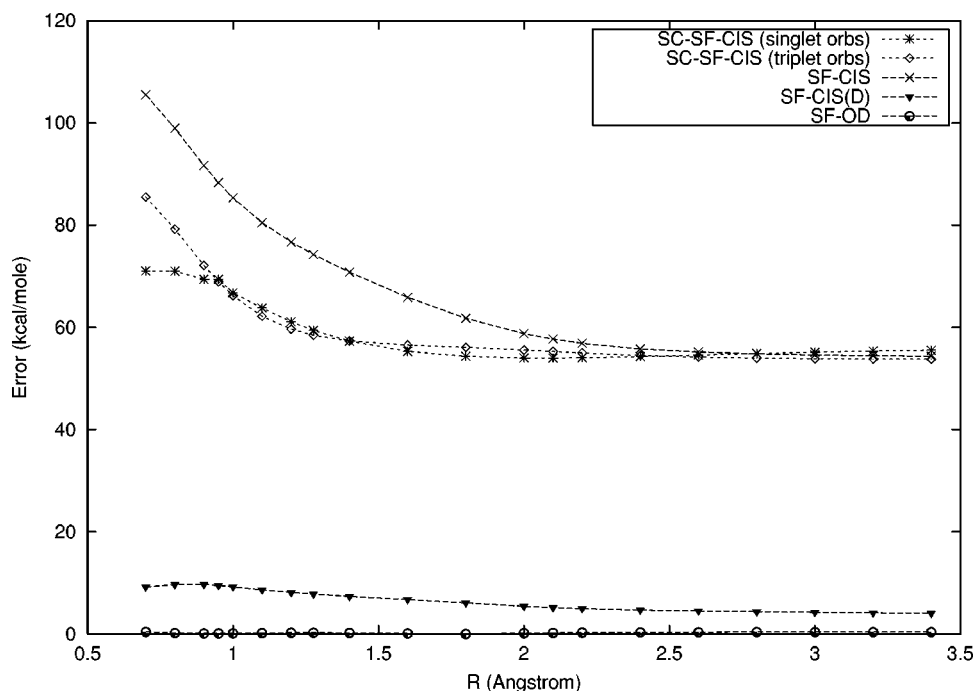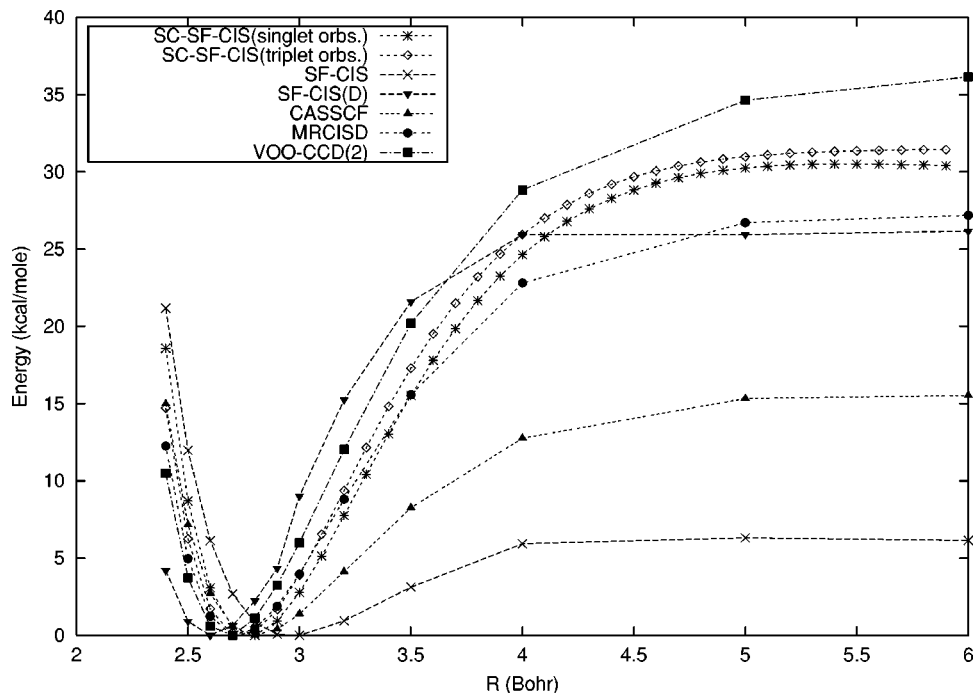

FIG. 4. Error vs FCI for HF using a 6-31G basis set.

FIG. 5. Potential energy curves for F_2 using a DZP+ basis set. The minimum energy at each level of theory has been set to zero.

ing spin complements, SC-SF-CIS comes much closer to matching the VOO-CCD(2) curve and obtains 83% of the experimental dissociation energy and 91% of the VOO-CCD(2) predicted dissociation energy. Singlet and triplet orbitals perform similarly, the latter being slightly closer to VOO-CCD(2) at large distances. The SF-CIS(D) method, while greatly improving upon SF-CIS, nevertheless gives a curve rather different than VOO-CCD(2). Given that SC-SF-CIS is a much better starting point, we expect that SC-SF-CIS(D) results would agree well with VOO-CCD(2).

The very large error in the SF-CIS bond length (more than 0.15 Å) is reduced to less than 0.06 Å in SC-SF-CIS.

TABLE V. Equilibrium distances, dissociation energies, and harmonic vibrational frequencies for F_2 molecule using a DZP+ basis set.[a]

Method	R_e	D_e	ω_e	E_{tot}
SC-SF-CIS(singlet orbs)	1.469	1.29	826.44	−198.851 06
SC-SF-CIS(triplet orbs)	1.448	1.37	855.94	−198.858 07
SF-CIS[b]	1.567	0.28	468	−198.801 57
SF-CIS(D)[b]	1.429	1.14	824	−199.195 42
SF-OD[b]	1.437	1.24	831	−199.223 16
RHF[c]	1.332	10.69	1254	
RHF-CCSD[c]	1.410	2.36	945	
UHF-CCSD[c]	1.410	0.95	1006[e]	
VOO-CCD(2)[d]	1.417	1.51	899[e]	−199.205 71
MR-CISD[c]	1.435	1.22	821	
Expt.	1.412	1.66	916.64	

[a]SF models employ a $^3\Sigma_u$ reference. Total energies are in hartree, dissociation energies are in eV, bond lengths are in Å , and vibrational frequencies are in cm^{-1}. D_e was computed as the total energy difference at R_e and $R_{\text{FF}} = 100$ bohr.
[b]Reference 11.
[c]Reference 24.
[d]Reference 13.
[e]This work.

Likewise, the dissociation energy of 0.28 eV predicted by SF-CIS is greatly improved by SC-SF-CIS (1.3-1.4 eV depending on orbital choice) when compared to the VOO-CCD(2) result of 1.51 eV or the experimental value of 1.66 eV. Note that similar improvement is achieved in frequencies. The SF-CIS underestimates experimental frequencies [or accurate theoretical frequencies, such as the RHF-CCSD or VOO-CCD(2) ones] by almost a factor of 2. The SC-SF-CIS frequencies are much better, and are surprisingly close to the SF-CIS(D) and the SF-OD ones. It is also surprising that, when comparing to the experimental frequency, only the RHF-CCSD model outperforms the vibrational frequencies computed by the SC-SF-CIS model with triplet orbitals for this unusually challenging case. Furthermore, note that the simple SC-SF-CIS method gives better dissociation energies than even coupled-cluster singles and doubles, CCSD, using either a RHF or UHF reference. Only SF or multireference methods which include dynamical correlation [i.e., SF-CIS(D), SF-OD, VOO-CCD(2), or MRCISD] approach the quality of the simple SC-SF-CIS predictions of the dissociation energy, and for this basis set only VOO-CCD(2) is closer to experiment.

E. C_2H_4

For a different type of bond breaking, we consider the rotation about the C–C bond in ethylene, which requires the breaking of a π bond. This is a challenging test case for theory, since traditional single-reference methods yield an unphysical cusp in the torsional potential at 90°. The torsional potential has been calculated by freezing all degrees of freedom except the torsional angle, and the DZP basis and geometrical parameters used here match those in previous work.[8] Total energies are presented in Table VI, and Fig. 6 plots the torsional potentials at each level of theory. Figure 7

TABLE VI. Total energies (hartree) for ethylene torsional potential using a DZP basis. Unoptimized barrier height, $\Delta E = E(90°) - E(0°)$, is also shown.[a]

Angle (deg)	SC-SF-CIS (singlet orbs)	SC-SF-CIS (triplet orbs)	SC-SF-CIS (TCSCF orbs)	SF-CIS[b]	SF-CIS(D)[b]	SF-OD[b]	TCSCF-CISD[b]
0	−78.097 12	−78.105 83	−78.113 87	−78.068 70	−78.346 37	−78.388 38	−78.365 89
15	−78.091 95	−78.100 87	−78.109 09	−78.064 26	−78.341 98	−78.383 93	−78.361 43
30	−78.077 25	−78.086 36	−78.094 85	−78.051 09	−78.328 77	−78.370 69	−78.348 12
45	−78.054 42	−78.063 22	−78.071 49	−78.029 85	−78.306 99	−78.349 08	−78.326 34
60	−78.025 26	−78.033 14	−78.039 95	−78.002 60	−78.277 90	−78.320 31	−78.297 24
75	−77.994 50	−78.000 65	−78.003 90	−77.974 93	−78.246 19	−78.288 27	−78.264 71
80	−77.986 11	−77.991 50	−77.993 22	−77.967 81	−78.237 41	−78.278 95	−78.255 22
85	−77.980 29	−77.984 99	−77.985 46	−77.963 01	−78.231 29	−78.272 18	−78.248 33
90	−77.978 21	−77.982 17	−77.982 55	−77.961 31	−78.229 07	−78.269 64	−78.245 74
ΔE (eV)	3.24	3.36	3.57	2.92	3.19	3.23	3.27

[a]Geometry used: $r_{CC} = 1.330$ Å, $r_{CH} = 1.076$ Å, $\alpha_{HCH} = 116.6°$. ΔE for RHF, OD, VOD(2), and CASSCF methods are 4.76, 3.91, 3.43, and 3.40 eV, respectively (Ref. 13).
[b]Reference 9.

displays these potentials near the barrier. We compare SC-SF-CIS with three different choices of orbitals (singlet, triplet, and TCSCF orbitals) to SF-CIS, CASSCF, SF-CIS(D), SF-OD, and TCSCF-CISD. The most reliable results currently available are from the TCSCF-CISD method, which generates all single and double excitations out of the two determinants $[(\pi)^2$ and $(\pi^*)^2]$ in the TCSCF reference. However, since SC-SF-CIS does not include substantial dynamical correlation, we cannot hope to match the TCSCF-CISD results. Instead, a more direct comparison is to a method with a reliable treatment of nondynamical correlation, such as CASSCF.

The choice of orbitals in the SC-SF-CIS procedure is clearly important; we observe large differences (several kcal mol^{-1}) in energies depending on which orbitals are used. For mimicking the behavior of CASSCF, SC-SF-CIS with triplet orbitals is best, with very small differences from CASSCF (the difference in the barrier height is just

0.8 kcal mol^{-1}). SC-SF-CIS with singlet orbitals underestimates the CASSCF barrier height by about 3.7 kcal mol^{-1}, and SC-SF-CIS with TCSCF orbitals overestimates the barrier hight by about the same amount (4.1 kcal mol^{-1}). The use of singlet orbitals makes SC-SF-CIS fortuitously close to the much more complete TCSCF-CISD treatment. It is perhaps surprising that the TCSCF orbitals, which are optimal for both of the important configurations at 90°, do not give better results. However, Table VI makes it clear that the overestimation of the barrier height is actually due to an improved treatment of the untwisted ethylene at 0°; it appears that the TCSCF orbitals allow SC-SF-CIS to recover a small part of the dynamic correlation near 0°, while they are about the same as triplet orbitals in describing the nondynamical correlation at 90°. Whether singlet, triplet, or TCSCF orbitals are used, the SC-SF-CIS results are significantly improved over SF-CIS in matching the CASSCF curve.
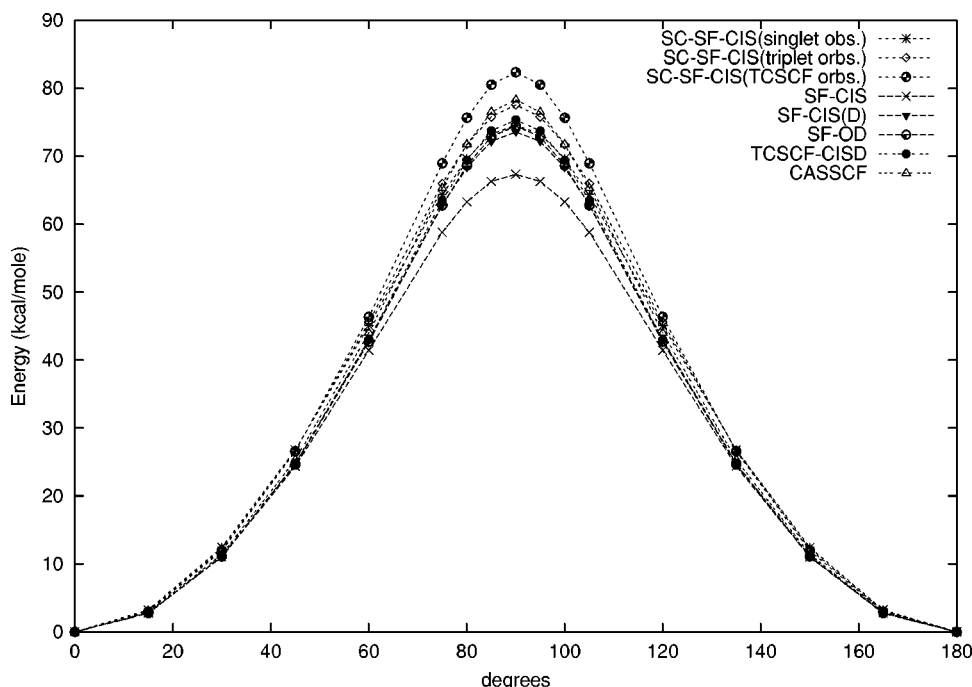

FIG. 6. Potential energy curves for ethylene using a DZP basis set. The minimum energy at each level of theory has been set to zero.
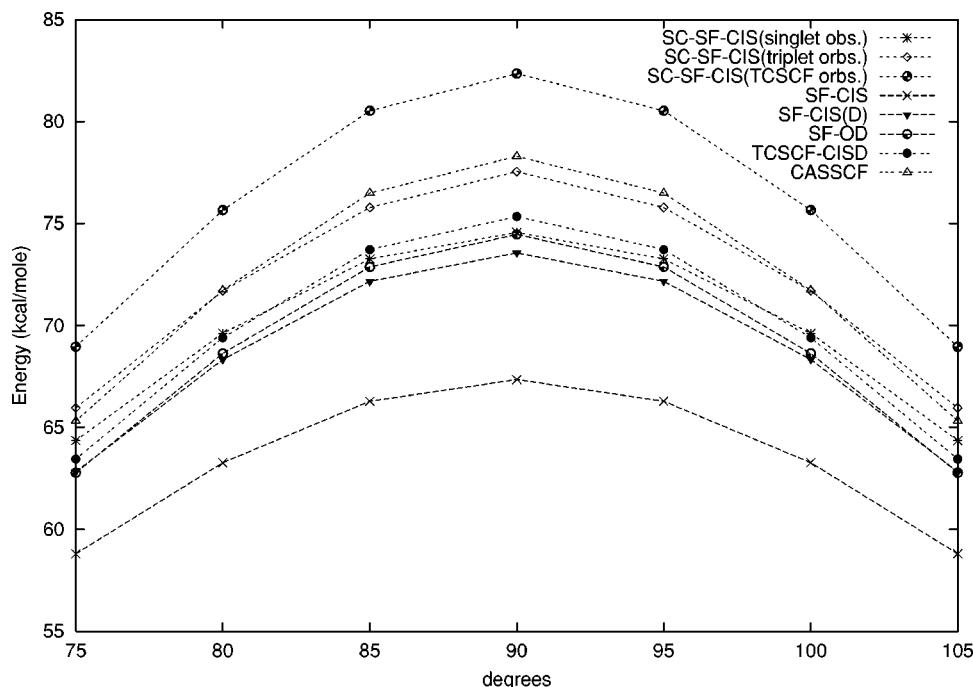
FIG. 7. Potential energy curves for ethylene using a DZP basis set near 90°. The minimum energy at each level of theory has been set to zero.

F. Trimethylenemethane (TMM)

A molecule with a broken bond has two unpaired electrons and can be loosely called a diradical.[25] More rigorously, Salem defines diradicals as molecules in which two electrons occupy two (near)-degenerate orbitals.[25] Due to large nondynamical correlation effects, this is a difficult situation which is well described by the SF approach due to the balanced treatment of the four nearly degenerate configurations needed to describe low-lying diradical states.[26]

To investigate this application of the SF method, SC-SF-CIS has been used to predict the lowest energy levels of TMM. The planar ground state ($^3A_2'$) of TMM is of D_{3h} symmetry. The largest Abelian subgroup of D_{3h} (C_{2v}) is used for computational purposes. The $^3B_2$ (C_{2v} symmetry label) reference is used in the conventional SF terminology. The SC-SF-CI ground state total energy and vertical excitation energies for the lowest excited states have been obtained in the same geometry and DZP basis set used in previous studies[26] (see Table VII, which employs the C_{2v} symmetry labels for excited states). The SC-SF-CIS results are compared to a hierarchy of traditional SF methods.

The most accurate vertical excitation energies are those calculated by SF-OD. Unexpectedly, the SC-SF-CIS actually does worse than SF-CIS for the lowest singlet states. This is probably due to the surprisingly good performance of SF-CIS for these states. The SF-CIS error for these states is 0.044 eV. A maximum error of 0.753 eV is obtained for these states using the SC-SF method. As previously mentioned, errors of an electron volt or more are common for CIS. Thus, these results are surprisingly good for a method that contains primarily single excitations. The benefits of the SC-SF-CIS method become noticeable, however, when one considers the higher excited states of TMM. Errors in the vertical excitation energies range from 1.5 to 2.6 eV for conventional SF-CIS, while the errors in SC-SF-CIS never exceed 1.7 eV and are typically around 0.5 eV for all states except the second A_1 state. Apparently, the SC-SF approach offers a more balanced treatment of all of the low-lying excited states.

As for other test cases, the perturbative corrections to SF as in SF-CIS(D) greatly correct the errors of SF-CIS. Indeed, SF-CIS(D) reduces the errors in vertical excitation energies to less than 0.492 eV for TMM. We anticipate that SC-SF-CIS(D) will offer even better results for such systems.

IV. CONCLUSIONS

Employing spin eigenfunctions significantly improves the quality of the SF-CIS results for the single bond breaking processes and excited states. Indeed, the SC-SF-CIS method

TABLE VII. Ground state total energies (hartree) and excitation energies (eV) for TMM using a DZP basis set.[a]

Method	$^3A_2'$	$^1A_1$	$^1B_2$	$2\,^1A_1$	$^3A_1$	$^3B_2$	$^5B_2$
SC-SF-CIS (singlet orbs)	−154.937 82	1.951	1.529	5.651	6.475	5.899	7.750
SC-SF-CIS (triplet orbs)	−154.937 03	1.376	1.372	5.263	6.105	5.123	6.889
SF-CIS[b]	−154.905 53	1.154	1.154	6.627	8.428	8.428	5.712
SF-CIS(D)[b]	−155.435 85	1.160	1.160	3.821	6.018	6.018	6.729
SF-OD[b]	−155.514 14	1.198	1.198	4.000	5.941	5.941	7.221

[a]SF-DFT/6-31G* optimized geometries (see Ref. 26).
[b]Reference 26.

eliminates spin-contamination and recovers over 50% of the error in the SF-CIS dissociation energies. Formally, spin-completeness is achieved by adding a selected subset of doubly and triply spin-orbital excited (with respect to the SF reference) determinants. Although the number of determinants increases, the scaling of the number of determinants comprising the SC-SF-CIS determinantal space is the same as in SF-CIS, i.e., $\mathcal{O}(OV)$ as opposed to the $\mathcal{O}(O^2V^2)$ scaling of the size of the SF-CISD subspace.

Results are not dramatically different for different choices of orbitals. This implies that the excellent performance of the SF approach is due to the determinants included in the wave function and not the orbital choice. The determinants that represent single SF excitations from the triplet reference, including their spin complements, are important in describing the changes that take place when bonds are stretched from equilibrium. Further investigations into the importance of various classes of determinants for describing stretched geometries are under way.

In cases where the SF-CIS method works only qualitatively (e.g., F_2), the SF-CIS(D) approach was very close to the more computationally expensive benchmark results. It is anticipated that perturbative correction to the improved zeroth-order reference will offer even better results than SF-CIS(D) at equivalent computational costs.

[1] J. R. Thomas, B. J. DeLeeuw, G. Vacek, T. D. Crawford, Y. Yamaguchi, and H. F. Schaefer, J. Chem. Phys. **99**, 403 (1993).

[2] T. Helgaker, J. Gauss, P. Jørgensen, and J. Olsen, J. Chem. Phys. **106**, 6430 (1997).

[3] D. Feller and K. A. Peterson, J. Chem. Phys. **108**, 154 (1998).

[4] R. J. Bartlett and J. F. Stanton, in *Computational Chemistry*, edited by K. B. Lipkowitz and D. B. Boyd (VCH, New York, 1994), Vol. 5, pp. 65–169.

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

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

[7] M. Schmidt and M. Gordon, Annu. Rev. Phys. Chem. **49**, 233 (1998).

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

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

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

[11] A. I. Krylov and C. D. Sherrill, J. Chem. Phys. **116**, 3194 (2002).

[12] Y. Shao, M. Head-Gordon, and A. Krylov, J. Chem. Phys. **118**, 4807 (2003).

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

[14] C. D. Sherrill and H. F. Schaefer, *The Configuration Interaction Method: Advances in Highly Correlated Approaches*, in Advances in Quantum Chemistry, Vol. 34, edited by P.-O. Löwdin (Academic, New York, 1999), pp. 143–269.

[15] J. Olsen, B. O. Roos, P. Jørgensen, and H. J. Aa. Jensen, J. Chem. Phys. **89**, 2185 (1988).

[16] C. D. Sherrill and H. F. Schaefer, J. Phys. Chem. **100**, 6069 (1996).

[17] J. Stanton, J. Chem. Phys. **101**, 8928 (1994).

[18] In case of two nonequivalent fragments, such as Be and Ne, or two H_2 molecules with one of the bonds being stretched, the lowest energy Hartree–Fock triplet state is naturally localized on Be or on the stretched H_2 molecule, respectively. However, in case of two identical fragments in a symmetric configuration, the lowest triplet state cannot be described by a single Slater determinant using symmetry-adapted orbitals. Therefore, it is necessary to use a symmetry-broken Hartree–Fock wave function to describe localization in the case of symmetrically arranged, noninteracting equivalent fragments.

[19] H. Koch, H. Jørgen Aa. Jensen, and P. Jørgensen, J. Chem. Phys. **93**, 3345 (1990).

[20] Since the target states are found by diagonalization of the Hamiltonian matrix, the block-diagonal structure of the latter ensures that the eigenvalues of the subsystems **A** and **B** are also eigenvalues of the combined system **AB**. The total SF energies, which are the sum of the high-spin reference energy and the corresponding transition energy, are thus also size-consistent due to size-consistency of the Hartree–Fock model. Note that the matrix of the Hamiltonian (2) has eigenvalues corresponding to the simultaneous excitations of both fragments, or to the charge transfer states, i.e., those from the $H_{AB,AB}$ block. The interpretation of these roots requires caution as described in footnote 22 of Ref. 17. For example, due to the truncated nature of the excitation operators, the EOM and CI models fail to describe situations when both fragments are excited with the same accuracy as the excitations on individual fragments. Due to similar considerations, Eq. (1) does not mean that for two noninteracting fragments, the total SF energy of the composite system equals the sum of total SF energy of individual fragments; rather, the total SF energy is equal to the sum of SF energy of fragment **A** and Hartree–Fock energy for the fragment **B**.

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

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

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

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

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

[26] L. Slipchenko and A. Krylov, J. Chem. Phys. **117**, 4694 (2002).