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Size-consistent wave functions for bond-breaking: the equation-of-motion spin-flip model

Anna I. Krylov *

Department of Chemistry, University of Southern California, Los Angeles, CA 90089, USA

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Abstract

A new approach to the bond-breaking problem is proposed. Both closed and open shell singlet states are described within a single reference formalism as spin-flipping, e.g., $\alpha \rightarrow \beta$, excitations from a triplet ($M_s = 1$) reference state for which both dynamical and non-dynamical correlation effects are much smaller than for the corresponding singlet state. Formally, the new theory can be viewed as an equation-of-motion (EOM) model where excited states are sought in the basis of determinants conserving the total number of electrons but changing the number of α and β electrons. The results for two simplest members of the proposed hierarchy of approximations are presented. © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

The methodological difficulties associated with bond-breaking originate from the multi-reference character of the wave function at the dissociation limit. For example, in order to describe bond-breaking in H_2 , the appropriate ground state ($^1\Sigma_g^+$) wave function must: (i) include two configurations which are degenerate at the dissociation limit, i.e., $(\sigma)^2$ and $(\sigma^*)^2$; and (ii) treat these configurations on an equal footing, i.e., the importance of the $(\sigma)^2$ configuration should not be overemphasized. The latter is associated with the mean-field self-consistent field (SCF) wave function usually used as a *reference* (i.e., zero-order wave function) in correlated models. While (i) is easily achieved by including double excitations (in a size-extensive

fashion) into the theoretical model, e.g., as in the coupled-cluster singles and doubles (CCSD) model [1], (ii) is much more difficult to satisfy within a single-reference formalism for any system with more than two electrons (for a detailed discussion, see [2,3]).

On the other hand, the wave function of the $M_s = 1$ component of the $^3\Sigma_u^+$ state remains essentially single reference *at all nuclear separations*, the leading configuration being $|\sigma\alpha\sigma^*\alpha\rangle$. Therefore, the $M_s = \pm 1$ components of a triplet state can be described with a uniform accuracy by a single-reference model along the bond-breaking coordinate. Indeed, since there is no chemical bond formed by two α electrons, there is no conceptual problem in breaking one!

Moreover, the *absolute value* of the correlation energy (defined as the difference between the full configuration interaction (FCI) and SCF energies) is about order of magnitude smaller for a pair of two electrons with the same spins than for a pair of

* Fax: +1-213-740-3972.

E-mail address: krylov@chem1.usc.edu (A.I. Krylov).

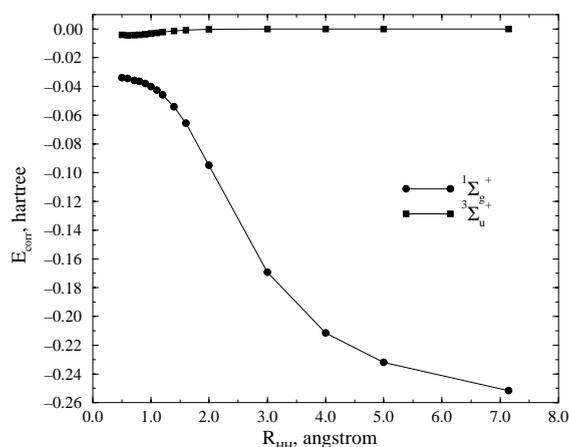


Fig. 1. Correlation energy for the lowest $^1\Sigma_g^+$ and $^3\Sigma_u^+$ states of H_2 , 6-311G(*,*) basis. At equilibrium geometry, the correlation energy of the triplet state is almost an order of magnitude smaller than that of the singlet state. At the dissociation limit, the former is zero, and the latter becomes very large (≈ -0.25 hartree).

electrons with opposite spins, as demonstrated in Fig. 1 and Table 1. This is because the Pauli hole partially compensates for the poor description of the Coulomb hole by the mean-field Hartree–Fock (HF) model. The Pauli exclusion principle, which keeps electrons with the same spin away from each other, is correctly described by the mean-field HF model by employing an antisymmetric ansatz for the wave function (Slater determinants). Thus, the absolute error in the mean-field description of electron–electron repulsion is smaller for a pair of electrons with the same spin, simply because the probability of finding both at the same point in space is zero. Therefore, for a given level of theoretical sophistication, the $M_s = \pm 1$ component of a triplet state is better described than the corresponding singlet state.

Another well recognized phenomenon is that the *quality of transition energies*, calculated for a

given approximate ground state wave function by using linear response (LR) or equation-of-motion (EOM) techniques, is closely related to the *quality of the ground state wave function*. For example, the EOM-CCSD (or CCSDLR) models [4,5] can describe singly excited states at the equilibrium geometry with remarkable accuracy (0.1–0.3 eV error), but break down when CCSD becomes qualitatively incorrect, e.g., as in diradicals (see [6] for numerical examples).

We propose to model both closed and open shell singlet states as spin-flipping, e.g., $\alpha \rightarrow \beta$, excitations from a triplet ($M_s = 1$) reference state for which both dynamical and non-dynamical correlation effects are much smaller than for the corresponding singlet state. Formally, the new theory can be viewed as an EOM model where final states are sought in the basis of determinants, conserving the total number of electrons but changing the number of α and β electrons. This new approach is termed the EOM spin-flip (EOM-SF or SF) method.

It should be mentioned that performing calculations for a state other than the ground state of the system of interest with a subsequent treatment of the target state as an excited state with respect to this reference state is a well known method. For example, to avoid the notorious symmetry breaking in doublet radicals, ionized states EOM CCSD methods have been successfully applied [7,8]. In this approach, the ground state CC equations are solved for a *closed shell* cation or anion, and the ground state of the corresponding doublet radical is sought in the basis of determinants which do not conserve the number of electrons, e.g., either in $N - 1$ (EOM ionization potential CC (EOMIP-CC)), or in $N + 1$ (EOM electron affinity CC (EOMEA-CC)) electron basis [9–12].

Table 1
Total and correlation energies (hartree) for H_2 at $r_e = 0.7146 \text{ \AA}$ and $10r_e$, 6-311G(*,*) basis

| State | r_{HH} | E_{HF} | E_{FCI} | E_{corr} |
|----------------|----------|-----------|-----------|------------|
| $^1\Sigma_g^+$ | r_e | -1.132464 | -1.168338 | -0.035874 |
| $^1\Sigma_g^+$ | $10r_e$ | -0.748027 | -0.999620 | -0.251593 |
| $^3\Sigma_u^+$ | r_e | -0.758522 | -0.762900 | -0.004378 |
| $^3\Sigma_u^+$ | $10r_e$ | -0.999620 | -0.999620 | -0.000000 |

2. Theory

The EOM-SF model employs the $M_s = 1$ ($\alpha\alpha$) component of the triplet state as a reference configuration. The final (singlet and triplet $M_s = 0$) states are described as spin-flipping excitations from the reference state. Note that for the $M_s = \pm 1$ reference, the only excitations which may produce $M_s = 0$ configurations are those that flip the spin of one electron. By employing theoretical models of increasing complexity for the reference wave function, the description of the final states can be systematically improved.

The simplest member in the proposed hierarchy of approximations is based on Hartree–Fock wave function for the reference state. When applied to the SCF model, the EOM method (along with the Tamm–Dancoff approximation [13,14]) results in the configuration interaction singles (CIS) model [15,16]. In this method, the Hamiltonian is diagonalized in the basis of all single excitations from the reference configuration. Thus, the simplest spin-flip model is defined by exactly the same set of equations (in the spin–orbital form) as the CIS model [15,16], the only difference being that only

$\alpha \rightarrow \beta$ excitations are considered (as opposed to $\alpha \rightarrow \alpha$ and $\beta \rightarrow \beta$ excitations in the traditional implementations of CIS). We will refer to this model as spin-flip self-consistent field (SF-SCF).

The left panel of Fig. 2 shows the reference configuration and the spin-flipping single excitations for two electrons in three orbitals system. Configuration (b) corresponds to a ground state closed shell singlet. Configurations (c)–(e) are those which become degenerate with (b) at the dissociation limit. It is easy to see that (b)–(e) are treated on an *equal footing*. Configurations (d) and (e) describe also the $M_s = 0$ component of the reference triplet state. Configurations (f) and (g) are single excitations from (c), (e) and (b), (d) configurations, respectively. Alternatively, they can be described as double excitations from the (b), (d) and (c), (e) configurations. Even though not all single excitations from the (c) and (b) configurations are present in the SF-SCF model, i.e., the spin-flipping counterparts of (f) and (g) are omitted, the important feature is that (f) and (g) *do not introduce imbalance in treating* (b)–(e).

The computational cost of SF-SCF, which is that of the cost of Hartree–Fock and CIS

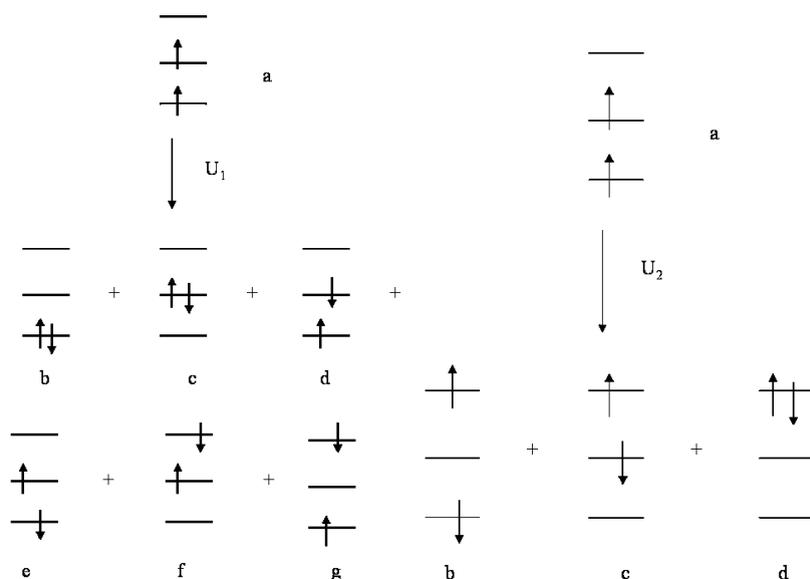


Fig. 2. Two electrons in three orbitals system. Configuration (a) is the reference configuration. Single electron excitations with spin-flip produce configurations (b)–(f) (left panel). Two-electron excitations with the single spin-flip produce configurations (b)–(d) (right panel). Note that non-spin-flipping excitations or excitations that flip the spin of two electrons produce $M_s = \pm 1$ configurations, which do not interact through the Hamiltonian with the final $M_s = 0$ states, and thus are not present in the model.

calculations, is very low. Our current implementation is based on a spin-orbital formulation and thus scales as N^5 due to the integral transformation. This scaling can be reduced to approximately N^2 by implementing the direct algorithm for the CIS procedure, and efficient Hartree-Fock computational schemes [17]. The SF-SCF model is fully variational and size-extensive. The similarity between the CIS and SF-SCF models suggests that the latter can be easily augmented by perturbative corrections [18]. This work is currently in progress.

The next model we present is based on the optimized orbitals CCD (OO-CCD, or OD) description of the reference state [1,19,20]. Excited states are described by single and double spin-flipping excitations. The resulting equations (in spin-orbital form) are identical to the EOM excitation energies (EE) OD (EOMEE-OD) equations [6]. The scaling of the resulting EOMSF-OO-CCD, or SF-OD, model is N^6 , the computational cost being identical to that of the EOMEE-OD model [6].

Similarly, one may employ the CCSD model for the ground state description [1]. In this case, the equations of the EOMSF-CCSD model will be identical to those of EOMEE-CCSD [5]. Based on the very similar performance of the EOMEE-OD and EOMEE-CCSD models [6], the accuracy of the SF-OD and SF-CCSD models is expected to be very close.

The right panel of Fig. 2 shows the reference and the double spin-flipping excitations for two electrons in three orbitals system. Configurations (b) and (c) are complementary to configurations (f) and (g) from the left panel of Fig. 2. Configuration (d) is the double excitation with respect to the configurations (b)–(e) from the left panel of Fig. 2.

SF-OD and SF-CCSD models are size-extensive and exact for two-electron systems. However, in cases of bond-breaking in many-electron molecules the SF models describe the ground singlet state in a more balanced way than when using the closed shell reference OO-CCD or CCSD methods.

The coding of the SF-SCF and SF-OD models required very minor modifications of the EOM-OD codes employing our C++ tensor library [21], which supports multi-dimensional tensors with an arbitrary type of zero-block structure. Specifically, the procedure of the guess vector generation for

the iterative diagonalization procedure [22,23] has been modified to generate spin-flipping excitations instead of those which conserve the total number of α and β electrons. The current version of the code allows energy calculations and approximate calculations of transition and excited state properties, e.g., $\langle S^2 \rangle$, by using non-relaxed density matrices from [6].

The extension of the SF model to the challenging case of multiple-bond-breaking is also possible. For example, to break a double bond, one should start from a quintet ($M_s = 2$) reference and describe the final ($M_s = 0$) states as excitations that flip the spins of two electrons. In this case, the counterpart of the SF-SCF model describes the target states as double excitations which flip the spins of two electrons. Note that no single excitations interact with the target state, and thus are not present in the model. This work is in progress.

3. Results and discussion

In this section, we consider two examples of chemically important situations: bond dissociation in diatomics (the σ -bond in HF) and polyatomics (the π -bond in ethylene), and diradical transition states (ethylene torsion). We also report results for the singly and doubly excited states of beryllium.

We compare the SF models with the spin-restricted and spin-unrestricted Hartree-Fock (RHF and UHF), and the OD (R-OD and U-OD) models. In the cases of Be and HF, comparison with FCI is possible. In the case of ethylene, we benchmark the SF theories against valence OO-CCD(2) [VOO-CCD(2), or VOD(2)] model [2,24]. For all SF calculations, the UHF reference is used. All electrons are active in the FCI and OD calculations. The VOD(2) calculations are performed in the full active valence space.

In addition to benchmarks vs more accurate methods, i.e., FCI or VOD(2), we also investigate two naturally appearing diagnostics for the SF method. The first one is spin-contamination of the reference and the final states. Large spin-contamination signals that the employed model is not appropriate for the particular system [3]. The attractive feature of the SF model is that the spin-

Table 2
Total (hartree) and excitation (eV) energies for beryllium atom, 6-31G basis set

| State | FCI | SCF/CIS | OO-CCD | SF-SCF | SF-OD |
|--------------------|------------|------------|------------|------------|------------|
| $^1S (1s^2 2s^2)$ | -14.613545 | -14.566764 | -14.613518 | -14.584111 | -14.613578 |
| $^3P (1s^2 2s 2p)$ | 2.862 | 1.653 | 2.863 | 2.111 | 2.862 |
| $^1P (1s^2 2s 2p)$ | 6.577 | 5.502 | 6.581 | 6.036 | 6.578 |
| $^3P (1s^2 2p^2)$ | 7.669 | | 7.675 | | 7.676 |
| $^1D (1s^2 2p^2)$ | 8.624 | | 8.630 | 8.946 | 8.629 |

contaminated solutions arise naturally, without cumbersome procedures of searching for spin-symmetry broken UHF solutions for the singlet reference state. The second diagnostic is the artificial energy splitting between the reference ($M_s = 1$) and the corresponding excited ($M_s = 0$) triplet state components. For the exact model, e.g., H_2 , these two components should be degenerate. Large splitting suggests that the model is not well balanced. We will refer to this diagnostic as the self-splitting diagnostic.

Calculations of Be and HF are performed using the split-valence 6-31G basis set [25]. Results for H_2 are obtained in the 6-311G(*,*) basis [26]. The calculations of ethylene employs a double- ζ plus polarization (DZP) basis set of contracted Gaussian functions, comprised of the standard Huzinaga–Dunning [27,28] double- ζ basis augmented by six d-type polarization functions for first-row atoms [$\alpha_d(C) = 0.75$] and three p-type polarization functions for hydrogen [$\alpha_p(H) = 0.75$].

Calculations are performed using two ab initio packages, Q-Chem [17] and PSI [29], to which our programs for (V)OO-CCD, SF-SCF, and SF-OD calculations are linked. Additional results are obtained using ACES II ab initio program [30]. Some basis sets used in this work are obtained from the EMSL database ¹.

¹ 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, Washington 99352, USA, and funded by the US Department of Energy. The Pacific Northwest Laboratory is a multi-program laboratory operated by Battelle Memorial Institute for the US Department of Energy under contract DE-AC06-76RLO 1830. Contact David Feller or Karen Schuchardt for further information.

3.1. Be

As discussed in Section 1, the SF-OD (or SF-CCSD) method is exact for two-electron systems. The Be atom, which has two core and two valence electrons, is thus the simplest system for which SF-OD is not exact.

Table 2 compares FCI total and excitation energies of Be with those calculated by CIS, OD/EOM-OD, SF-SCF, and SF-OD methods. OD/EOM-OD reproduces the total and excitation energies very well, even for two doubly excited states (singlet and triplet $1s^2 2p^2$). The reason for this good performance is that in Be excitations of more than two electrons necessarily involve core electrons, and thus are less important than excitations involving only valence-shell electrons. The CIS model cannot describe these doubly excited states. Moreover, it performs rather poorly for singly excited states (more than 1 eV error). The SF-SCF model: (i) gives a lower energy for the ground state and thus is better in a variational sense; (ii) describes the singly excited states better, i.e., errors of about 0.7 eV; and (iii) provides a reasonable estimation for one of the doubly excited singlet states (error of about 0.4 eV). The SF-OD model gives a very accurate estimation of the total ground state energy, and the excitation energies of singly and doubly excited states. The two $1s^2 2p^2$ states, which are double excitations with respect to the singlet closed shell reference, become formally single excitations in the SF model, with the weight of double excitations being 50% and 33%, respectively, as opposed to 100% in the EOM-OD wave function. Therefore, we expect the SF-OD model to perform better than the EOM-OD model for doubly excited states.

In the case of the Be atom, where the lowest triplet state (reference for SF calculations) has

three degenerate spatial components, i.e., $1s^22s2p_x$, $1s^22s2p_y$, and $1s^22s2p_z$, there is an imbalance in the description of the corresponding components of the degenerate excited states. If the triplet reference is chosen to be $1s^22s\alpha2p_x\alpha$, then the spin-flipping single excitations produce two configurations, i.e., $1s^22s\alpha2p_x\beta$ and $1s^22s\beta2p_x\alpha$, which are necessary to describe the singlet and triplet $1s^22s2p_x$ states. However, the corresponding $1s^22s2p_y$ and $1s^22s2p_z$ components cannot be described well by the SF-SCF model, because the configurations $1s^22s\beta2p_{y,z}\alpha$ are formally double excitations with respect to the triplet reference. The situation is expected to improve in the SF-OD model, which does include the corresponding double excitations.

This artificial splitting of the spatially degenerate excited states is very large in the SF-SCF model: in addition to the relatively spin-pure states ($|\langle S^2_{\text{exact}} \rangle - \langle S^2 \rangle| < 10^{-2}$) from Table 2, the SF-SCF method produces two degenerate pairs of heavily spin-contaminated states ($\langle S^2 \rangle = 1$), with excitation energies of 4.087 and 7.481 eV. The amplitude analysis confirms that the first and the second pairs of states consist of the two other components of the singlet and triplet $1s^22s2p$ states, respectively. The inclusion of double excitations in the SF-OD model restores the degeneracy almost completely: the energies of these unbalanced components become 2.868 and 6.586 eV, with the values of $\langle S^2 \rangle$ equal to 2.0000 and 0.0000, respectively. The appearance of such unphysical solutions is expected in systems with (spatially) degenerate lowest triplet states. The heavy spin-contamination of these SF-SCF states provides a straightforward diagnostic.

The self-splitting diagnostic for Be is excellent: the energy splitting between the $M_s = 1$ and $M_s = 0$ components is smaller than 10^{-6} hartree for both the SF-SCF and SF-OD methods.

3.2. Ethylene torsion

The torsional potential in ethylene is one of the most challenging problems for ab initio theory [2,3]. The unbalanced treatment (within a single reference framework) of $(\pi)^2$ and $(\pi^*)^2$ configurations results in unphysical shapes of the PES, i.e., a cusp at 90° and large errors in barrier heights. The

spin-unrestricted PESs are smooth; however, the barrier height is usually grossly underestimated, even by highly correlated methods [3].

Fig. 3 shows the torsional potential calculated by the SF-SCF and SF-OD methods, as well as the restricted and unrestricted PESs for the HF and OD methods [3]. The total energies and $\langle \hat{S}^2 \rangle$ values are given in Table 3. VOD(2), HF, and OD energies are from [3]. Both SF-SCF and SF-OD models produce smooth PESs. Quantitatively, SF-SCF represents a definite advantage over both the RHF and UHF results. Similarly, the SF-OD curve is closer to our reference VOD(2) curve than either R-OD or U-OD.

As can be seen from Table 3, the spin-contamination in the SF-SCF and SF-OD states is small and almost constant along the torsional coordinate. This confirms that, unlike in the closed shell single reference models, our wave function is qualitatively correct at all angles. Tables 4 and 5 show the SF-SCF and SF-OD energies for the $M_s = 1$ (reference) and $M_s = 0$ (excited state) components of the $\pi\pi^*$ triplet state. The important trends are: (i) the spin-contamination is small for both components; (ii) the artificial energy splitting is small and almost constant; (iii) the correlated SF-OD model exhibits smaller contamination and splitting; and

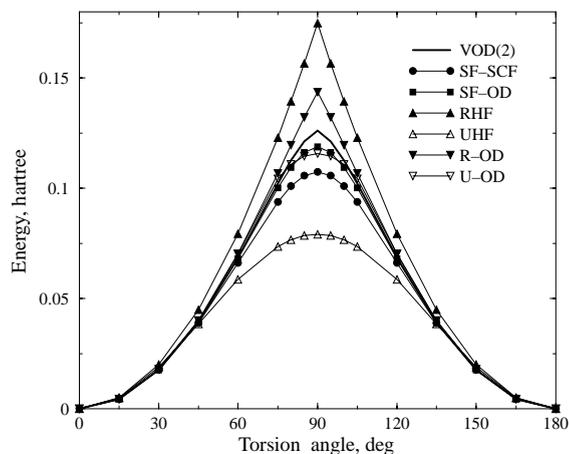


Fig. 3. Ethylene torsion, DZP basis. All curves are shifted such that the energy at 0° is zero. The spin-flip curves do not exhibit an unphysical cusp and are closer to the VOD(2) curve than the corresponding spin-restricted and spin-unrestricted models.

Table 3
Ethylene torsion, DZP basis^a

| Angle (degree) | SF-SCF | $\langle S^2 \rangle$ | SF-OD | $\langle S^2 \rangle$ |
|-----------------|-----------|-----------------------|-----------|-----------------------|
| 0 | -78.06870 | 0.0312 | -78.38838 | 0.0003 |
| 15 | -78.06426 | 0.0314 | -78.38393 | 0.0003 |
| 30 | -78.05109 | 0.0320 | -78.37069 | 0.0004 |
| 45 | -78.02985 | 0.0332 | -78.34908 | 0.0005 |
| 60 | -78.00260 | 0.0341 | -78.32031 | 0.0005 |
| 75 | -77.97493 | 0.0332 | -78.28827 | 0.0002 |
| 80 | -77.96781 | 0.0322 | -78.27895 | -0.0001 |
| 85 | -77.96301 | 0.0313 | -78.27218 | -0.0004 |
| 90 | -77.96131 | 0.0308 | -78.26964 | -0.0006 |
| ΔE (eV) | 2.92 | | 3.23 | |

^aTotal energies (hartree) and $\langle S^2 \rangle$ for SF-SCF and SF-OD methods. Unoptimized barrier height, $\Delta E = E(90^\circ) - E(0^\circ)$, is also shown. ΔE for RHF, OD, and VOD(2) methods are 4.76, 3.91, and 3.43 eV, respectively [3]. Geometry used: $r_{CC} = 1.330$ Å, $r_{CH} = 1.076$ Å, $\alpha_{HCH} = 116.6^\circ$.

Table 4
Ethylene torsion by SF-SCF method, DZP basis^a

| Angle (degree) | $E, M_s = 1$ | $\langle S^2 \rangle, M_s = 1$ | $E, M_s = 0$ | $\langle S^2 \rangle, M_s = 0$ | ΔE (eV) |
|----------------|--------------|--------------------------------|--------------|--------------------------------|-----------------|
| 0 | -77.924806 | 2.0173 | -77.91735 | 2.0472 | 0.203 |
| 15 | -77.927879 | 2.0163 | -77.92074 | 2.0446 | 0.194 |
| 30 | -77.935990 | 2.0141 | -77.92952 | 2.0390 | 0.176 |
| 45 | -77.946441 | 2.0122 | -77.94058 | 2.0341 | 0.159 |
| 60 | -77.956235 | 2.0110 | -77.95075 | 2.0312 | 0.149 |
| 75 | -77.963031 | 2.0104 | -77.95772 | 2.0299 | 0.145 |
| 80 | -77.964363 | 2.0103 | -77.95908 | 2.0297 | 0.144 |
| 85 | -77.965173 | 2.0103 | -77.95990 | 2.0296 | 0.143 |
| 90 | -77.965445 | 2.0103 | -77.96018 | 2.0296 | 0.143 |

^aTotal energies (hartree) and $\langle S^2 \rangle$ for the triplet ($\pi\pi^*$) state of ethylene. Total energies (hartree) for the $M_s = 1$ (reference) and $M_s = 0$ (excited) components are given.

Table 5
Ethylene torsion by SF-OD method, DZP basis^a

| Angle (degree) | $E, M_s = 1$ | $\langle S^2 \rangle, M_s = 1$ | $E, M_s = 0$ | $\langle S^2 \rangle, M_s = 0$ | ΔE (eV) |
|----------------|--------------|--------------------------------|--------------|--------------------------------|-----------------|
| 0 | -78.220062 | 2.0003 | -78.21968 | 2.0015 | 0.010 |
| 15 | -78.223892 | 2.0003 | -78.22354 | 2.0013 | 0.010 |
| 30 | -78.233728 | 2.0003 | -78.23343 | 2.0011 | 0.008 |
| 45 | -78.245923 | 2.0003 | -78.24565 | 2.0011 | 0.007 |
| 60 | -78.256977 | 2.0003 | -78.25672 | 2.0011 | 0.007 |
| 75 | -78.264478 | 2.0004 | -78.26423 | 2.0011 | 0.007 |
| 80 | -78.265934 | 2.0004 | -78.26568 | 2.0011 | 0.007 |
| 85 | -78.266818 | 2.0004 | -78.26657 | 2.0011 | 0.007 |
| 90 | -78.267114 | 2.0004 | -78.26686 | 2.0011 | 0.007 |

^aTotal energies (hartree) and $\langle S^2 \rangle$ for the triplet ($\pi\pi^*$) state of ethylene. Total energies (hartree) for the $M_s = 1$ (reference) and $M_s = 0$ (excited) components are given.

(iv) both diagnostics are in good agreement with each other: the energy splitting is larger for more spin-contaminated wave functions. This suggests

that the spin-flipping models are well balanced and that both the spin-contamination and the self-splitting may be used as a reliable diagnostic

of the methods' stability. The small spin-contamination also suggests that, unlike the single-reference spin-unrestricted models, the quality of the PESs can be improved by perturbative corrections for the SF-SCF or SF-OD models.

3.3. HF

The last example is σ bond-breaking in the HF molecule. The errors against FCI in the SF-SCF, RHF, and UHF methods are shown in Fig. 4 (the

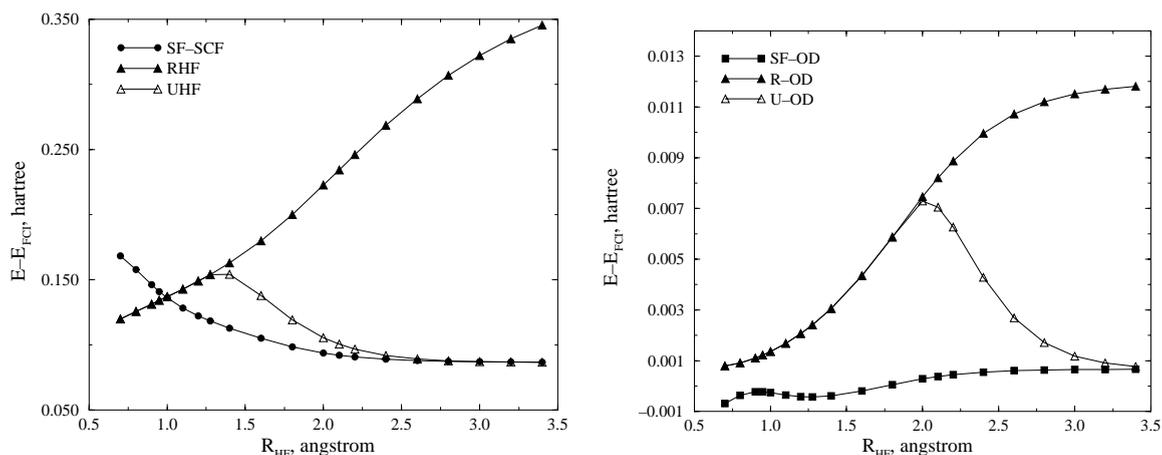


Fig. 4. HF, 6-31G basis. SF-SCF model (left panel) describes accurately both the asymptotic limit and the so-called intermediate region. The SF-OD model (right panel) describes the PES for the ground state much more accurately than either the R-OD or U-OD methods.

Table 6
Total energies (hartree) for HF dissociation, 6-31G basis set

| R_{HF} (Å) | FCI | SF-SCF ^a | SF-OD ^a | R-OD | U-OD |
|---------------------|-------------|---------------------|--------------------|-------------|------------|
| 0.7 | -100.005489 | -99.83726 | -100.00618 | -100.004693 | |
| 0.8 | -100.087139 | -99.92934 | -100.08750 | -100.086228 | |
| 0.9 | -100.114251 | -99.96811 | -100.11447 | -100.113153 | |
| 0.95 | -100.116698 | -99.97588 | -100.11692 | -100.115479 | |
| 1.0 | -100.114621 | -99.97853 | -100.11488 | -100.113266 | |
| 1.1 | -100.102115 | -99.97378 | -100.10246 | -100.100437 | |
| 1.2 | -100.083938 | -99.96164 | -100.08435 | -100.081871 | |
| 1.2764 | -100.068708 | -99.95030 | -100.06914 | -100.066298 | |
| 1.4 | -100.044285 | -99.93142 | -100.04467 | -100.041228 | |
| 1.6 | -100.009752 | -99.90471 | -100.00995 | -100.005406 | |
| 1.8 | -99.984078 | -99.88555 | -99.98402 | -99.978205 | |
| 2.0 | -99.967201 | -99.87348 | -99.96692 | -99.959742 | -99.959910 |
| 2.1 | -99.961487 | -99.86948 | -99.96111 | -99.953288 | -99.954446 |
| 2.2 | -99.957183 | -99.86650 | -99.95673 | -99.948312 | -99.950921 |
| 2.4 | -99.951656 | -99.86271 | -99.95111 | -99.941695 | -99.947373 |
| 2.6 | -99.948741 | -99.86074 | -99.94814 | -99.938025 | -99.946050 |
| 2.8 | -99.947238 | -99.85979 | -99.94660 | -99.936034 | -99.945526 |
| 3.0 | -99.946465 | -99.85939 | -99.94582 | -99.934957 | -99.945286 |
| 3.2 | -99.946065 | -99.85923 | -99.94541 | -99.934369 | -99.945160 |
| 3.4 | -99.945857 | -99.85916 | -99.94520 | -99.934043 | -9.945088 |

^a $^3\Sigma$ state is used as the reference in SF calculations.

left panel). The right panel of Fig. 4 displays errors for SF-OD, R-OD, and U-OD models. Selected total energies are given in Table 6. Fig. 4 demonstrates that the spin-flipping model describes single bond dissociation in HF with higher accuracy than the corresponding spin-unrestricted single reference models. In the case of the SF-OD model, the maximum relative error is smaller than 0.5 mhartree. Moreover, the spin-contamination of the SF-OD wave function is small for all nuclear separations, and does not exceed 3×10^{-3} .

The error in the self-splitting ($M_s = 0$ component of the reference triplet state) is smaller than 0.001 eV. The spin-contamination in the SF-SCF curve is also rather small ($< 2 \times 10^{-2}$), except for the three last points which are heavily contaminated ($\langle S^2 \rangle \approx 1$). The maximum error in the self-splitting for the SF-SCF model is 0.058 eV. It has been found that HF molecule in its triplet state exhibits symmetry-breaking. The results presented in this work are obtained for a symmetry-pure (${}^3\Sigma$) reference.

4. Conclusions

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

The simplest member of the proposed hierarchy of approximations, SF-SCF, is based on the Hartree-Fock description of the reference state. SF-SCF equations are *identical* to those of the CIS model, but they are solved in a different, i.e., spin-flipping, subspace of single excitations. The SF-SCF model is variational and size-extensive. Its

computational cost scales as N^5 (for the integral transformation) in the spin-orbital formulation, and can be reduced to N^2 by using atomic orbital implementation. The initial benchmarks of this inexpensive method are very encouraging: the performance of SF-SCF is superior to that of UHF for PESs, and to that of CIS for excited states.

We have also introduced the SF-OD method, which employs the correlated OD wave function for the reference state. The computational cost (N^6) and equations of SF-OD are identical to those of the EOM-OD method. The SF-OD method is size-extensive and exact for two-electron systems. Initial benchmarks demonstrate excellent performance of SF-OD for single-bond-breaking.

The stable behavior and small spin-contamination of the SF models suggest that perturbative treatment of higher order effects would uniformly improve the quality of the PESs. Further development of the model is in progress and includes more detailed benchmarks for diradicals and excited states, as well as extensions to multiple-bond-breaking, and applications to DFT.

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