Spin-flip configuration interaction: an electronic structure model that is both variational and size-consistent

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Abstract

A new formulation of the configuration interaction (CI) method is presented. It is based on the recently introduced spin-flip (SF) approach. SF-CI target states are described as spin-flipping excitations from the reference Hartree–Fock high-spin, e.g., $M_s = 1$ ($|\alpha\alpha\rangle$), determinant. The resulting model is both variational and size-consistent. Moreover, the SF-CI model can describe within a single-reference formalism some inherently multi-reference situations, such as single bond-breaking and diradicals. Initial benchmarks for the SF-CI model with single and double substitutions (SF-CISD) are presented. © 2001 Published by Elsevier Science B.V.

1. Introduction

Wavefunctions which are variational, size-consistent, and exact for two electrons are held in high esteem within ab initio community [1]. Besides aesthetic reasons, the failure of an approximate model to satisfy one of the above criteria has serious practical consequences. For example, wavefunctions which are not size-consistent cannot be applied to study systematic changes within series of homologically similar compounds, since the quality of such a description degrades with increase in molecular size. It is also well recognized that the above properties are extremely difficult to simultaneously satisfy within a single computationally feasible scheme. Historically, common

wisdom evolved from assigning primary importance to variational properties of the model towards sacrificing the latter for the sake of size-consistency, i.e., from configuration interaction (CI) to coupled-cluster (CC) methods (for comprehensive reviews, see [2–4]). While giving the identical exact result in the limit of full CI (FCI), the performance of the two approaches differs dramatically at any truncated level. For example, CC with singles and doubles (CCSD) and the corresponding excited state theory, i.e., equation-of-motion (EOM) CCSD, are capable of very accurate predictions of molecular properties and excitation energies (at equilibrium geometries and for well-behaved molecules) [5–7]. However, the corresponding CI model, CISD, has less satisfactory performance in the context of chemical applications. The recent study of Olsen [8] has demonstrated, that for small molecules the accuracy of CC is *at least* one level of excitations ahead

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of the corresponding CI, e.g., the accuracy of CCSD may be achieved by CISDT, the gap increasing rapidly with the molecular size increase. On the other hand, the variational property, the linearity of corresponding equations, and the conceptual simplicity of CI approach make it a very attractive electronic structure model.

The recently introduced spin-flip (SF) approach [9,10] allows one to formulate and implement *any truncated CI scheme* such that the resulting SF-CI energies are both *variational* and *size-consistent*. SF-CI is also exact for two electrons (when double or higher excitations are included). Below we introduce the SF-CI method, analyze the conditions under which it is size-consistent, and present initial benchmarks of SF-CISD model for several systems: the ground and excited states of Be atom, bond-breaking, and diradical transition states.

2. Theory

As in the corresponding CC model, the SF-CI method employs a high-spin triplet state, e.g., $M_s = 1$ ($|\alpha\alpha\rangle$) component, as the *reference*. The target ($M_s = 0$) states are described by spin-flipping excitations [9,10]:

$$|\Psi\rangle = \hat{U}|\Psi_0\rangle, \tag{1}$$

where $|\Psi_0\rangle$ refers to the reference wavefunction and $\hat{U}$ is the spin-flipping excitation operator. By employing models of increasing complexity for the reference, a hierarchy of SF models is introduced. We have presented and benchmarked the following SF models [9,10]: (i) SF-SCF or SF-CIS model which uses an SCF wavefunction for the reference and describes target states as a superposition of singly excited determinants which involve SF of an electron; (ii) SF-MP2 or SF-CIS(D) model which corrects SF-SCF energies by perturbation theory; and (iii) SF optimized-orbitals CC doubles (SF-OOCCD or SF-OD) model which employs an OO-CCD wavefunction for the reference and describes final states as single and double excitations which flip the spin of one electron. Models (i)–(iii) employ $M_s = 1$ component of the triplet state, and thus the operator $\hat{U}$ flips the spin of one electron only. The (i)–(iii) equations in spin-orbital form

are identical to the traditional (non-SF) CIS [11–13], CIS(D) [14], and EOM-OD [15] equations, but they are solved in a different (i.e., spin-flipping) subspace of excited determinants. As explained in [9,10], the SF approach allows one to describe *multi-reference* wavefunctions within a *single-reference* formalism and, therefore, it extends the accuracy of single-reference models for bond-breaking and diradicals.

One may consider another set of SF models by employing higher spin, e.g., quintet $|\alpha\alpha\alpha\alpha\rangle$, states as the reference. In this case, the operator $\hat{U}$ flips the spins of two electrons. Thus, no singly excited determinants are present in the quintet reference SF wavefunctions, and the counterpart of the model (i) is SF-CID.

Here we present a new model, SF-CISD, which is not only suitable for bond-breaking, but also represents a significant improvement over traditional CISD because, as we show below, the SF-CISD method is size-consistent. SF-CISD target states are described as single and double excitations (which flip the spin of one electron) from the reference Hartree–Fock $M_s = 1$ ($|\alpha\alpha\rangle$) determinant (see [9, Fig. 2]). Thus, the SF-CISD energies and wavefunctions are found by diagonalizing the Hamiltonian matrix in the basis of so generated determinants. The programmable equations (in spin-orbital form) can be derived from the EOM-OD equations [15] by zeroing out all the terms which involve contractions with ground state CC amplitudes. Even though the scaling of the SF-CISD model with system size is identical to that of CCSD or OO-CCD models (N^6), the computational cost is less due to the linear and Hermitian nature of the problem. Moreover, unlike SF-CC method, the reference state CC equations need not to be solved.

There is no consensus concerning the definition of size-consistency and size-extensivity. We adhere to the terminology used in [16] and use the term size-consistency to refer to the additive separability of the energy in the limit of non-interacting fragments:

$$E_{AB} = E_A + E_B, \tag{2}$$

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. For SF-CI or SF-CC models, total energy of a target state consists of the reference energy and the corresponding transition energy. Thus, Eq. (2) 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. The condition (i) is satisfied by SF-CI model due to size-consistency of the Hartree–Fock model. Below, we are going to prove that the transition energy for the 'excitation' localized on fragment A in the supermolecule 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.

Our proof of size-consistency of the SF-CI model follows the the presentation of Koch et al. [6] and Stanton [16]. We start by classifying 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 high-spin, i.e., $\alpha\alpha$ ($M_s = 1$) component of the reference triplet state. Without loss of generality, we assume that the two unpaired α-electrons are localized on fragment A. 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. Determinants (ii)–(iv) are generated by spin-flipping excitations and thus describe the $M_s = 0$ components of the target singlet and triplet states. Later in the discussion, we use $|0\rangle$ and $|p\rangle$ to refer to (i) and (ii)–(iv) determinants, respectively.

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

$$\hat{H} = \hat{H}_A + \hat{H}_B. \tag{3}$$

In the basis outlined above, the matrix of the Hamiltonian (3) assumes the block-diagonal form:

$$H = \begin{pmatrix} H_{00} & \mathbf{0} & \mathbf{0} & \mathbf{0} \\ \mathbf{0} & H_{AA} & 0 & \tilde{0} \\ \mathbf{0} & 0 & H_{BB} & \tilde{0} \\ \mathbf{0} & \tilde{0} & \tilde{0} & H_{AB} \end{pmatrix}, \tag{4}$$

where the shorthand notation $H_{PQ} \equiv \langle P|H|Q \rangle$ has been used. The boldface zeros in the above equation appear due to the fact that the determinants describing the target states in SF-CI do not interact with the reference across the Hamiltonian since they describe states with different number of α and β electrons, i.e., different values of M_s:

$$\langle 0|H|p \rangle = \langle p|H|0 \rangle = 0. \tag{5}$$

The H_{AB} and H_{BA} blocks involve only matrix elements of the Hamiltonian which couple subsystems A and B and vanish in the separated limit [16]:

$$\begin{aligned} H_{AB} &= \langle \Phi_A \cdot 0_B | \hat{H}_A + \hat{H}_B | 0_A \cdot \Phi_B \rangle \\ &= \langle \Phi_A \cdot 0_B | \hat{H}_A | 0_A \cdot \Phi_B \rangle + \langle \Phi_A \cdot 0_B | \hat{H}_B | 0_A \cdot \Phi_B \rangle \\ &= \langle 0_B | \Phi_B \rangle \cdot \langle \Phi_A | \hat{H}_A | 0_A \rangle + \langle 0_A | \Phi_A \rangle \cdot \langle \Phi_B | \hat{H}_B | 0_B \rangle \\ &= 0 \cdot \langle \Phi_A | \hat{H}_A | 0_A \rangle + 0 \cdot \langle \Phi_B | \hat{H}_B | 0_B \rangle = 0. \end{aligned} \tag{6}$$

The tilded zeros, i.e., $\tilde{0}$ from Eq. (4) require additional attention. The $H_{B,AB}$ block of the Hamiltonian matrix is zero due to the reasons similar to Eqs. (5) and (6):

$$\begin{aligned} H_{B,AB} &= \langle 0_A \cdot \Phi_B | \hat{H}_A + \hat{H}_B | \Phi_A \cdot \Phi'_B \rangle \\ &= \langle 0_A \cdot \Phi_B | \hat{H}_A | \Phi_A \cdot \Phi'_B \rangle \\ &\quad + \langle 0_A \cdot \Phi_B | \hat{H}_B | \Phi_A \cdot \Phi'_B \rangle \\ &= \langle \Phi_B | \Phi'_B \rangle \cdot \langle 0_A | \hat{H}_A | \Phi_A \rangle + \langle 0_A | \Phi_A \rangle \\ &\quad \cdot \langle \Phi_B | \hat{H}_B | \Phi'_B \rangle \\ &= \langle \Phi_B | \Phi'_B \rangle \cdot 0 + 0 \cdot \langle \Phi_B | \hat{H}_B | \Phi'_B \rangle = 0. \end{aligned} \tag{7}$$

By following a similar procedure, the $H_{A,AB}$ matrix element reduces to

$$H_{A,AB} = \langle \Phi_A \cdot 0_B | \hat{H}_A + \hat{H}_B | \Phi'_A \cdot \Phi_B \rangle$$
$$= \langle \Phi_A | \Phi'_A \rangle \cdot \langle 0_B | \hat{H}_B | \Phi_B \rangle. \tag{8}$$

The above presentation is independent of the levels of excitation included in the CI expansion and the multiplicity of the reference (as long as it is a high-spin state). However, in order to analyze the term (8), we have to consider specific models. In case of the SF-CISD model employing a triplet reference, the CI expansion includes single and double 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 is necessarily restricted to a single substitution. Thus, the term $\langle \Phi_B | \hat{H}_B | 0_B \rangle$ zeros out because of the Brillouin's theorem (if one employs unrestricted Hartree–Fock orbitals for the reference determinant). It immediately follows that inclusion of higher excitations into the CI expansion will cause non-zero $H_{A,AB}$ terms to appear. Thus, SF-CISDT and models with higher excitation levels will not be size-consistent *unless* appropriate higher multiplicity states are used for the reference. Applying a similar analysis, it is easy to show that problematic, i.e., $H_{A,AB}$ terms, will be zero for SF-CISDT employing the quintet state for the reference, and so on.

The target states are found by diagonalization of matrix (4), and thus are defined by the following secular equation:

$$\begin{pmatrix} H_{00} - \omega \mathbf{I} & 0 & 0 & 0 \\ 0 & H_{AA} - \omega \mathbf{I} & 0 & 0 \\ 0 & 0 & H_{BB} - \omega \mathbf{I} & 0 \\ 0 & 0 & 0 & H_{AB} - \omega \mathbf{I} \end{pmatrix}$$
$$= 0, \tag{9}$$

where $\mathbf{I}$ stands for the unit matrix and ω is the corresponding eigenenergy. The condition (9) is satisfied when

$$|H_{00} - \omega \mathbf{I}| \times |H_{AA} - \omega \mathbf{I}| \times |H_{BB} - \omega \mathbf{I}| \times |H_{AB} - \omega \mathbf{I}|$$
$$= 0 \tag{10}$$

which means that eigenvalues of the two subsystems are also eigenvalues of the combined system. We have thus proven the size-consistency of the transition energies in SF-CI model, subject to the provisions mentioned in the preceeding paragraph. The total energies, which are the sum of the reference energy and the corresponding transition energy, are thus also size-consistent due to size-consistency of the Hartree–Fock model.

Note that Eq. (10) has solutions corresponding to the simultaneous excitations of both fragments, or to the charge transfer states. The interpretation of these roots requires caution as described in [16, footnote 22]. For example, due to the truncated nature of the operator $\hat{U}$ from the Eq. (1), the EOM models fail to describe situations when both fragments are excited with the same accuracy as the excitations on individual fragments. Due to similar considerations, the Eq. (2) does not mean that for two non-interacting fragments, the total SF energy of the composite system equals to 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. Therefore, the accuracy of SF-CISD description of the bond-breaking localized at a reaction center in a large molecule would not be affected by molecular size. However, SF-CISD would fail to describe simultaneous breaking of two bonds, even in case of non-interacting bonds.

3. Results and discussion

In this section we consider two examples of theoretically challenging situations: bond dissociation in diatomics (the σ-bond in HF and F_2) 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-CISD models with the traditional CISD model, and with previously introduced SF models, i.e., SF-CIS, SF-CIS(D), and SF-OD, as well as with multi-reference CI and the valence OO-CCD(2) [VOO-CCD(2), or VOD(2)] model [17,18]. In the cases of Be and HF, comparison with FCI is possible. The comparison between SF-CISD and SF-OD is particularly interesting, since both models are size-consistent and both include up to double excitations and,

Table 1
Total (hartree) and excitation (eV) energies for beryllium atom, 6-31G basis set

State	FCI [9]	SF-SCF [9]	SD-CIS(D)	SF-OD [9]	SF-CISD	OO-CCD [9]	CISD
^1S ($1s^2 2s^2$)	−14.613 545	−14.584 111	−14.597 209	−14.613 578	−14.613 056	−14.613 518	−14.613 493
^3P ($1s^2 2s 2p$)	2.862	2.111	2.432	2.862	2.861	2.863	2.877
^1P ($1s^2 2s 2p$)	6.577	6.036	6.254	6.578	6.578	6.581	6.598
^3P ($1s^2 2p^2$)	7.669			7.676	7.671	7.675	7.696
^1D ($1s^2 2p^2$)	8.624	8.946	9.038	8.629	8.624	8.630	8.637

therefore, one may investigate the relative importance of variational properties (CISD) vs. effects of higher excitations present in the OD due to the exponential ansatz employed by the latter.

For all SF calculations, a spin-unrestricted Hartree–Fock reference is used. Calculations of Be and HF are performed using the split-valence 6-31G basis set [19]. The calculations of ethylene employs a double-ζ plus polarization (DZP) basis set of contracted Gaussian functions, comprised of the standard Huzinaga–Dunning [20,21] 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 [$\alpha_p(H) = 0.75$]. For F_2, we employ DZP + basis set from [22], derived from the standard Huzinaga–Dunning [20,21] double-ζ (DZ) basis set by uncontracting the most diffuse p-function and augmenting it by a set of six Cartesian d-functions [$\alpha_d(F) = 1.580$].

Calculations are performed using two ab initio packages, Q-Chem [23] and PSI [24], to which programs for (V)OO-CCD, and SF calculations are linked.

3.1. Beryllium atom

Table 1 compares the FCI total and excitation energies of Be with those calculated by SF-CIS, SF-CIS(D), SF-OD, SF-CISD, OD, and CISD methods. Even for this simple system with only two valence electrons, the CISD excitation energies exhibit an order of magnitude larger errors that EOM-OD ones. This is how the size-inconsistency of CISD manifests itself. When size-consistency is restored (in SF-CISD), the corresponding energies agree better with FCI than the SF-OD ones. Thus, in this numerical example

the variational nature of SF-CISD turns out to be more important than the effect of higher excitations (i.e., simultaneous excitations of two pairs of electrons) which are present in CC wavefunction.

We also use this simple example to numerically demonstrate the size-consistency of SF-CISD. Table 2 presents total and transition energies for Be and Ne atom separated by 100 Å. The SF-CISD ground state energy of the combined system is exactly the sum of the SF-CISD energy of the ground state (X^1S) of Be and the SCF energy of Ne (X^1S), and the corresponding excitation energies are exactly equal to the excitation energies of beryllium, i.e., are not in any way affected by the presence of Ne atom. The CISD ground state energy of the composed system is neither the sum of the CISD energies of two fragments, nor the sum of CISD energy of Be and SCF energy of Ne. The errors in CISD transition energies increase dramatically in the composed system due to the non-size-consistent nature of CISD.

3.2. HF

In this section, we discuss single bond-breaking in HF. The comparison of the SF models with the

Table 2
Total (hartree) and excitation (eV) energies for beryllium and neon atoms separated by 100 Å, 6-31G basis set

State	SF-CISD	CISD
Be (^1S) Ne (^1S)[a]	−143.086 933	−143.190 023
Be (^3P) Ne (^1S)	2.861	5.671
Be (^1P) Ne (^1S)	6.578	9.391
Be (^3P) Ne (^1S)	7.671	10.475
Be (^1D) Ne (^1S)	8.624	11.430

[a] SCF and CISD ground state energies of Ne atom are −128.473 876 and −128.586 270 hartrees, respectively.

Table 3
Total energies (hartree) for HF dissociation, 6-31G basis set

R_{HF} (Å)	FCI [9]	SF-SCF [9]	SF-CIS(D) [10]	SF-OD [9]	SF-CISD
0.7	−100.005 489	−99.837 26	−99.990 79	−100.006 18	−99.942 34
0.8	−100.087 139	−99.929 34	−100.071 70	−100.087 50	−100.022 14
0.9	−100.114 251	−99.968 11	−100.098 79	−100.114 47	−100.048 17
0.95	−100.116 698	−99.975 88	−100.101 53	−100.116 92	−100.050 29
1.0	−100.114 621	−99.978 53	−100.099 88	−100.114 88	−100.047 97
1.1	−100.102 115	−99.973 78	−100.088 32	−100.102 46	−100.035 09
1.2	−100.083 938	−99.961 64	−100.070 97	−100.084 35	−100.016 56
1.2764	−100.068 708	−99.950 30	−100.056 26	−100.069 14	−100.001 05
1.4	−100.044 285	−99.931 42	−100.032 52	−100.044 67	−99.976 14
1.6	−100.009 752	−99.904 71	−99.998 97	−100.009 95	−99.940 91
1.8	−99.984 078	−99.885 55	−99.974 37	−99.984 02	−99.915 04
2.0	−99.967 201	−99.873 48	−99.958 50	−99.966 92	−99.898 97
2.1	−99.961 487	−99.869 48	−99.953 20	−99.961 11	−99.894 08
2.2	−99.957 183	−99.866 50	−99.949 23	−99.956 73	−99.890 80
2.4	−99.951 656	−99.862 71	−99.944 17	−99.951 11	−99.887 39
2.6	−99.948 741	−99.860 74	−99.941 53	−99.948 14	−99.886 08
2.8	−99.947 238	−99.859 79	−99.940 25	−99.946 60	−99.885 54
3.0	−99.946 465	−99.859 39	−99.939 68	−99.945 82	−99.885 29
3.2	−99.946 065	−99.859 23	−99.939 45	−99.945 41	−99.885 16
3.4	−99.945 857	−99.859 16	−99.939 36	−99.945 20	−99.885 08

All SF calculations employ a $^3\Sigma$ reference state.

corresponding single-reference approaches can be found in [9,10]. At each level of theoretical sophistication, SF models perform better than corresponding traditional spin-restricted or spin-unrestricted methods. Total energies for the ground state potential energy curve of HF are shown in Table 3, and the errors of SF models against FCI are visualized in Fig. 1. The SF-CISD model represents a considerable improvement over less correlated SF-CIS, and exhibits a performance that is similar to SF-OD.

3.3. F_2

Bond-breaking in F_2 is a rather challenging example due to anomalously strong correlation effects (see [10] for the discussion). Total energies for the ground state potential energy curve of F_2 are shown in Table 4, and are visualized in Fig. 2. For this molecule, the difference between different models is very large. The straightforward comparison of calculated D_e [10] implies that the VOD(2) model is capable of describing F–F bond-breaking in the most accurate fashion: the corresponding D_e of 1.51 eV agrees better with the

experimental value of 1.66 than that of other models (for example, MR-CISD value [22] is 1.22 eV). The curvature of the potential around equilibrium is also better reproduced by VOD(2): around equilibrium, the VOD(2) curve follows closely the CCSD and the OD ones [22,25],
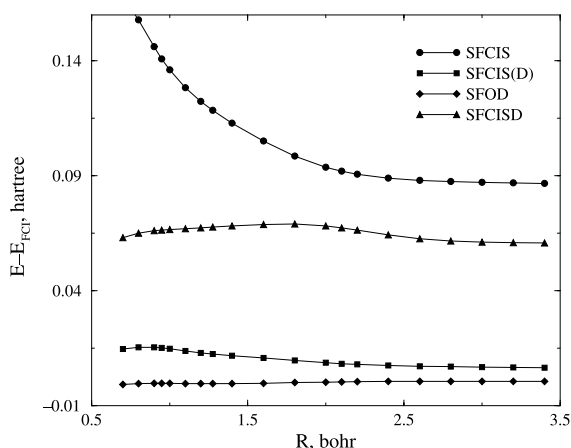

Fig. 1. HF, 6-31G basis. The errors against FCI for SF-SCF, SF-CIS(D), SF-CISD, and SF-OD models. All SF calculations employ a $^3\Sigma$ reference state.

Table 4
F_2, DZP + basis set

R_{FF} (bohr)	SF-CISD	SF-OD [10]
2.0	−198.731 86	−199.040 83
2.2	−198.848 27	−199.153 37
2.4	−198.899 76	−199.203 68
2.5	−198.911 36	−199.215 32
2.6	−198.916 89	−199.221 23
2.7	−198.918 17	−199.223 13
2.8	−198.916 57	−199.222 37
2.9	−198.913 12	−199.219 92
3.0	−198.908 60	−199.216 49
3.2	−198.898 34	−199.208 56
3.5	−198.884 06	−199.197 51
5.0	−198.868 38	−199.178 10
6.0	−198.868 89	−199.178 02

Total energies, hartree, for the ground $X^1\Sigma_g$ state of F_2 calculated by SF models. SF models employ a $^3\Pi_g$ reference.

whereas the MRCI curve yields a more shallow potential. The CCSD harmonic frequency of 945 cm^{-1} better agrees with the experimental value of 917 cm^{-1} than that of MRCI (i.e., 821 cm^{-1}) [22]. Note that for this molecule there is only one valence unoccupied orbital, and the VOO-CCD model is equivalent to the full valence CASSCF and therefore the VOD(2) provides a fully balanced description. This together with fully size-extensive nature of VOD(2) suggests that the
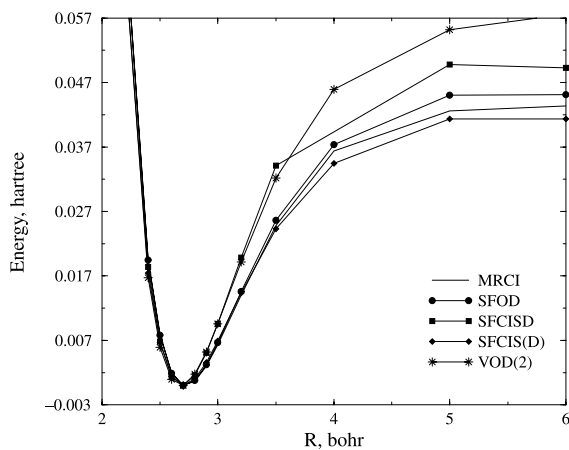

Fig. 2. F_2, DZP + basis. All curves are shifted such that their respective energy minima are zero. The SF-CIS(D) and SF-OD curves are very close to MRCI one. SF-CISD follows closely VOD(2).

VOD(2) curve is more credible than that of the size-inconsistent MRCI. As shown in [10], the SF-OD and SF-CIS(D) curves follow the MRCI curve very closely; the former giving a slightly larger D_e of 1.24 eV. However, the limitations of the basis employed are not known. Thus, it is not clear whether VOD(2) or MR-CISD is closer to the limiting value of D_e in this basis set. As can be seen from Fig. 2, the SF-CISD curve follows VOD(2) very closely, as opposed to SF-OD curve which follows MR-CISD one. Thus we conclude that, similarly to the previous case, the SF-CISD performs better than the SF-OD model. However, a definite conclusion can be made only after more extensive benchmarks of both models are performed.

3.4. Ethylene torsion

Ethylene at a twisted (D_{2d}) geometry is a generic example of a diradical transition state. Due to the orbital degeneracy between π and π^* orbitals (in a valence-bond picture) at the barrier, single-reference methods overestimate the barrier height and produce potential energy curves with unphysical cusps. The balanced description of the torsion potential can be achieved by employing multi-reference wavefunctions, e.g., two-configurational SCF, further corrected for dynamical correlation (TC-CISD). Alternatively, accurate curves can be obtained by the VOD(2) method. As shown in [10], there is small difference between the two models, and (as in the previous example) it is unclear which is closer to the exact value. The SF models also produce cuspless curves [9,10]. They employ $|\pi\alpha\pi^*\alpha\rangle$ triplet state as the reference.

Table 5 shows total energies along the torsional coordinate calculated by CISD, TC-CISD, SF-CISD, and SF-OD methods, as well as unoptimized barrier heights. Corresponding potential energy curves are shown in Fig. 3, which also shows SF-CIS, SF-CIS(D), and VOD(2) results. As in the previous example, the SF-OD curve closely follows the TC-CISD one, the frozen barrier height being 3.23 and 3.27 eV, respectively. The SF-CISD curve however is closer to the VOD(2) one, the corresponding barrier values being identical (3.43 eV).

Table 5
Ethylene torsion, DZP basis

Angle (degrees)	SF-CISD	SF-OD [9]	TCSCF-CISD [10]	CISD
0	−78.145 39	−78.388 38	−78.365 89	−78.356 70
15	−78.140 96	−78.383 93	−78.361 43	−78.352 06
30	−78.127 67	−78.370 69	−78.348 12	−78.338 13
45	−78.105 68	−78.349 08	−78.326 34	−78.315 01
60	−78.075 82	−78.320 31	−78.297 24	−78.283 03
75	−78.041 25	−78.288 27	−78.264 71	−78.242 88
80	−78.030 59	−78.278 95	−78.255 22	−78.227 88
85	−78.022 47	−78.272 18	−78.248 33	−78.212 18
90	−78.019 29	−78.269 64	−78.245 74	−78.195 90
ΔE (eV)	3.43	3.23	3.27	4.38

Total energies (hartree) for TC-SCF, SF-CISD, and SF-OD methods. Unoptimized barrier height, $\Delta E = E(90°) - E(0°)$, is also shown. ($\Delta E$ for RHF, OD, and VOD(2) methods are 4.76, 3.91, and 3.43 eV, respectively [25]. ΔE for SF-CIS and SF-CIS(D) is 2.92 and 3.19 eV, respectively [9,10].) Geometry used: $r_{CC} = 1.330$ Å, $r_{CH} = 1.076$ Å, $\alpha_{HCH} = 116.6°$.
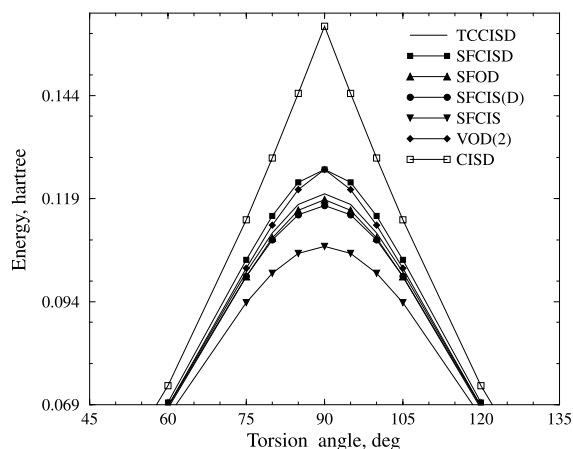

Fig. 3. Ethylene torsion, DZP basis. All curves are shifted such that the energy at 0° is zero.

The CISD curve exhibits a sharp cusp and overestimates the barrier height by more than 1 eV.

4. Conclusions

We have presented a new CI method based on the recently introduced SF approach [9]. Similar to the traditional formulation, the energies and wavefunctions are found by diagonalizing the matrix of the Hamiltonian in the basis of the determinants truncated at a certain excitation level, e.g., up to double excitations in CISD. In the SF formulation, the above determinants are generated by n-electron excitations which flip the spin of one electron from the reference Hartree–Fock $M_s = 1$ ($|\alpha\alpha\rangle$) determinant. The resulting model is both variational and size-consistent. Moreover, SF-CI model can describe within a single-reference formalism inherently multi-reference situations, such as bond-breaking and diradicals. Initial benchmarks for the SF-CISD model are presented and compared with a CC based method, SF-OD. For all test cases considered, the SF-CISD model performs slightly better than SF-OD, thus suggesting that the variational properties of the former are more important than the presence of higher excitations (i.e., simultaneous excitations of pairs of electrons) in the latter. However, a definite conclusion can be made only after more extensive benchmarks of both models are performed.

Acknowledgements

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