PHYSICAL REVIEW A **75**, 012503 (2007)

Combining multiconfigurational wave functions with correlation density functionals: A size-consistent method based on natural orbitals and occupation numbers

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(Received 24 August 2006; published 8 January 2007)

We propose a size-consistent method to combine small active space multiconfigurational self-consistent-field (MCSCF) wave functions with standard correlation energy density functionals. The correlation energy is not evaluated from the standard spin densities but from a pair of alternative densities obtained from the natural orbitals and occupation numbers. The method substantially improves the MCSCF estimates of the spectroscopic constants of a set of 11 diatomics, with an accuracy comparable to that from Becke three-parameter Lee-Yang-Parr (B3LYP) hybrid functional and Becke–Lee-Yang-Parr (BLYP) functional spin-unrestricted Kohn-Sham density functional theory (DFT) calculations. The method also provides estimates in good agreement with multireference coupled-cluster calculations for the diradical-involved automerization barrier of cyclobutadiene, with deviations $\sim 0.3-1.7$ kcal mol^{-1} as compared to deviations $\sim 14-15$ kcal mol^{-1} provided by B3LYP or BLYP spin-restricted Kohn-Sham DFT calculations. It also yields rather good estimates of energy differences between triplet and open-shell singlet states in the helium atom and the methylene molecule.

DOI: 10.1103/PhysRevA.75.012503 PACS number(s): 31.10.+z, 31.15.Ar, 31.25.Qm, 31.15.Rh

I. INTRODUCTION

Every chemical process is characterized by the changes in the electronic structure experienced by the species involved. In bond rearrangements near transition states or dissociation of molecules into open-shell fragments such changes can be quite drastic. There are several methods within quantum chemistry that can be applied to appropriately handle these situations [1]. In particular, multiconfiguration self-consistent-field (MCSCF) [2,3] procedures are well suited to describe the usually multiconfigurational (MC) nature of the complete reaction path. Large configuration spaces, however, are usually required to obtain accurate results so that this method is mostly restricted to small molecules due to the corresponding increase in computational cost. Alternative methods such as MC analogs to perturbation [4], configuration interaction [5], and coupled-cluster theories [6] share the same shortcomings. Therefore, a computationally simpler strategy would be highly desirable.

Kohn-Sham density functional theory (KS DFT) [7,8] is, on the other hand, a much less demanding computational method, but it lacks a procedure to systematically improve the accuracy in a well-defined way. Despite the fact that the standard implementation of KS DFT involves a single-determinant wave function, its unrestricted version (UKS DFT) may implicitly include some nonspecific MC effects. This is connected with the self-interaction error of some exchange functionals [9], and may lead to reasonable potential energy surfaces at the expense of a wrong description of the spin densities [10–12]. Although alternatives to UKS DFT have been proposed and applied over the years (see, e.g., Refs. [10–30]) they are not entirely satisfactory [31].

A different approach tries to combine the accuracy of MC wave functions with the low computational cost typical of DFT. The goal is merging MC wave functions with correlation energy functionals while avoiding the *double-count* problem: some correlation energy is counted twice, as part of the wave function description and as part of the DFT description. In their pioneering work, Lie and Clementi solved this problem by choosing a MCSCF wave function with an active space as small as possible, adding the correlation energy calculated with a reparametrized Gombás functional depending on MC natural orbitals and occupation numbers [32–35]. Probably the simplest approach is that of Kraka [36] who directly adds the energy from a local spin density correlation energy functional to that from a generalized valence bond of the perfect pairing (GVB PP) type wave function [37]. Savin and co-workers propose an explicit splitting of the electron-electron interaction operator into a long-ranged and a short-range part, the effect of each treated by a multireference wave function and by DFT density functionals, respectively [38–43]. Panas follows a similar approach by modifying the two-electron integrals [44,45]. The on-top pair density has also been used as a key ingredient to link MCSCF calculations and correlation energy functionals, as in the works by Colle and Salvetti [46,47], Moscardó and San-Fabián [48], Mielich, Stoll, and Savin [49], Gräfenstein and Cremer [31,50,51], McDouall [52], Takeda, Yamanaka, and Yamaguchi [53], or Gusarov, Malmqvist, and Lindh [54]. Other approaches based on several partitioning techniques that go beyond the simple addition of a (corrected) correlation energy functional to the energy from a MC calculation are those of Wu and Shaik [55], Malcolm and McDouall[56–59], and Stoll [60]. The interested reader can find an account of the achievements and drawbacks of most of the above MC+DFT approaches in Ref. [31].

An important property that every method aimed at describing chemical reactions should have is *size consistency*: if a supersystem A-B is composed of two noninteracting systems A and B, then a method is size consistent if the energy of the supersystem A-B is equal to the sum of the energy of A plus the energy of B taken by themselves $[E(A-B)=E(A)+E(B)]$. Unfortunately, in a MC+DFT approach size

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TABLE I. Correlation energies for the dissociated hydrogen molecule (absolute values, in mhartree). "Exact" values are the difference between the exact total energy and the UHF or two-configuration MCSCF energy. B88 values are computed by applying Becke's correlation functional [63] to the corresponding UHF or MCSCF spin densities, while $B88_{><}$ ones are evaluated by applying the Becke functional [63] to the transformed spin densities $\rho_>$ and $\rho_<$.

	Exact	B88	$B88_{><}$
UHF	0	0	0
MCSCF	0	27	0

consistency problems may arise either from the chosen MC wave function and/or from the way used to evaluate the DFT correction. In this work we use a method recently proposed in the context of UKS DFT calculations [61] to combine MC wave functions with DFT correlation energy functionals in a size-consistent fashion by using information from MC natural orbitals and occupation numbers. The method can be applied to every kind of wave function, it is easy to implement, and it works well for correlation energy density functionals frequently used in KS DFT. Its performance is tested here by evaluating the spectroscopic constants of several diatomic molecules, the automerization barrier of cyclobutadiene, and energy differences between triplet and open-shell singlet states of He and CH_2. These are well-known representatives of problems where important reorganizations of the electronic structure take place.

II. DESCRIPTION OF THE METHOD

For systems where the Hartree-Fock description is reasonably accurate, it is possible [62] to approximate the total energy as

$$E \approx E_{\mathrm{HF}} + E_c[\rho_\alpha,\rho_\beta], \tag{1}$$

where E_{HF} is the Hartree-Fock energy, and $E_c[\rho_\alpha,\rho_\beta]$ is an approximation to the correlation evaluated from the Hartree-Fock spin densities.

In some situations, such as bond dissociation, the Hartree-Fock description is not adequate. A way of dealing with such problems will be to use a better wave function instead of the Hartree-Fock determinant. We could use, for example, a MCSCF wave function that correctly describes the bond dissociation, and then write, in analogy to Eq. (1),

$$E \approx E_{\mathrm{MCSCF}} + E_c[\rho_\alpha,\rho_\beta]. \tag{2}$$

There is a problem with this last approach, as can be seen in Table I. For a dissociated hydrogen molecule, both the exact unrestricted Hartree-Fock and MCSCF correlation energies should be zero (because the system is composed of two isolated hydrogen atoms). A typical correlation energy functional [63] (column B88) shows the correct behavior when applied to Hartree-Fock densities, but fails for MCSCF densities.

Let us analyze this problem in detail. For the H_2 ground state and all along the potential energy curve, the exact spin densities satisfy the relation

$$\rho_\alpha = \rho_\beta = \frac{1}{2}\rho. \tag{3}$$

Near the equilibrium distance, both UHF and MCSCF densities comply with this relation and therefore any correlation energy functional takes the value

$$E_c[\rho/2,\rho/2]. \tag{4}$$

Near the dissociation limit, the MCSCF densities still comply with Eq. (3), but the correlation energy is wrong, as seen in Table I. The behavior for the UHF method is just the opposite: Eq. (3) is no longer satisfied, but the correlation energy is correct. Note that, at dissociation distances, and regarding energies and total densities, the UHF solution for a dissociated system composed of an α hydrogen atom plus a β hydrogen atom is equivalent to that of a system composed of two α hydrogens or two β hydrogens. Therefore, we can express the correlation energy of a dissociated UHF solution as

$$E_c[\rho_\alpha,\rho_\beta] \equiv E_c[\rho,0] \equiv E_c[0,\rho]. \tag{5}$$

We can summarize the results of our analysis for the hydrogen molecule as follows: both for UHF and MCSCF solutions, the correlation energy can be correctly evaluated by

$$E_c[\rho/2,\rho/2] \tag{6}$$

near the equilibrium distance, and by

$$E_c[\rho,0] \equiv E_c[\rho,0] \tag{7}$$

near the dissociation limit. The problem is how to switch from one behavior to the other.

One possible solution will be to use natural orbitals and their occupation numbers as indicators of which alternative should be used. Considering again the H_2 molecule we have that, near the equilibrium distance both the UHF and the MCSCF natural orbitals are mainly composed of a single orbital with an occupation number equal or almost equal to 2. On the other hand, near the dissociation limit, both the UHF and the MCSCF natural orbitals are composed of two natural orbitals (one per hydrogen atom), each with an occupation number equal to 1.

A generalized way of implementing this idea has been proposed recently [61] to improve the results of UHF correlation energies in certain situations. The same method can be applied without any modification to MCSCF calculations. The method splits the total density into two components according to the natural orbitals and their occupation numbers, avoiding the conventional splitting into spin components that does not work for MCSCF densities. A description of the method follows.

Given a density ρ expressed in terms of a set of natural orbitals as

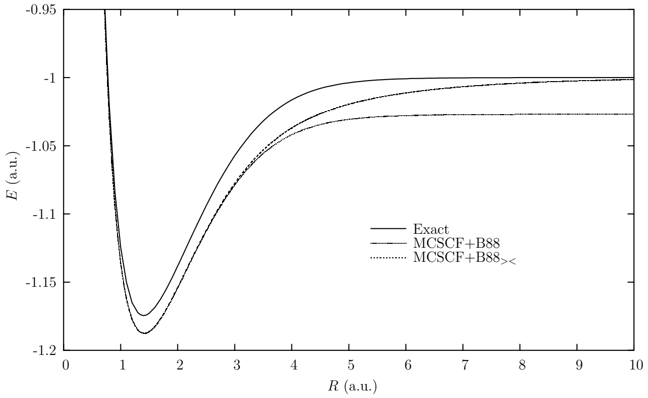

FIG. 1. Potential energy curves for the ground state of the H_2 molecule from two-configuration MCSCF calculations corrected with the B88 correlation energy functional (see text for details). The exact values are those of Kołos and Wolniewicz [96,97].

$$\rho = \sum_{i=1} n_i |\psi_i|^2, \tag{8}$$

where n_i is the occupation number of natural orbital ψ_i, we define the following densities,

$$\rho_> = \sum_{i,n_i \geq 1} (n_i - 1)|\psi_i|^2 \tag{9}$$

$$\rho_< = \rho - \rho_> = \sum_{i,n_i \geq 1} |\psi_i|^2 + \sum_{i,n_i < 1} n_i |\psi_i|^2. \tag{10}$$

In Eqs. (9) and (10) n_i can be a fractional number depending on the particular point in the reaction path considered and the kind of wavefunction used to describe it. It is straightforward to see that when there is one single natural orbital with occupation number 2 we have $\rho_< = \rho_> = \rho/2$, while two natural orbitals each with occupation number 1 implies $\rho_> = 0$, $\rho_< = \rho$. With these new densities, it is possible to provide a unified description of the correlation energy both at equilibrium and dissociation distances with the expression

$$E_c[\rho_<, \rho_>]. \tag{11}$$

The total energy can now be estimated as

$$E \approx E_{\mathrm{MCSCF}} + E_c[\rho_<, \rho_>]. \tag{12}$$

The last column in Table I shows the correct behavior of our method. As an additional illustration, we show in Fig. 1 the potential energy curves for the H_2 ground state evaluated using Eq. (2) with a MCSCF wave function (labeled MCSCF+B88) and Eq. (12) (labeled MCSCF+$\mathrm{B88}_{><}$), where B88 indicates the Becke 1988 correlation functional.[63] We see that both approaches give similar results near the equilibrium distance, which is consistent with the MCSCF description having a natural orbital with occupation number close to 2, and therefore

$$\frac{\rho}{2} = \rho_\alpha = \rho_\beta \approx \rho_> \approx \rho_<. \tag{13}$$

Near the dissociation limit, however, only Eq. (12) shows the correct behavior.

We will wrap up the description of our method by stressing some key ideas.

(1) The method can be applied to UHF determinants,

$$E \approx E_{\mathrm{UHF}} + E_c[\rho_<, \rho_>], \tag{14}$$

and, for certain systems, this could be preferable [61] to the conventional approach of Eq. (1).

(2) The method can be applied to MC wave functions, though it is advisable to use the smaller wave function that is able to give a qualitatively correct description of the system. The use of sophisticated MCSCF or configuration-interaction CI wave functions together with our method will result in an overestimation of the correlation energy due to the double-count problem.

(3) Any spin-dependent functional can be used to implement this method, by just replacing the spin-densities in its expression by the new $\rho_>$ and $\rho_<$ densities.

III. RESULTS AND DISCUSSION

The procedure described above is now checked by using it in several contexts where combination of MC wave functions and DFT functionals may be a sound alternative: the evaluation of spectroscopic constants of diatomic molecules, the calculation of the automerization barrier of cyclobutadiene, and the estimation of energy differences between triplet and open-shell singlets in the helium atom and the methylene molecule.

A. Spectroscopic constants of diatomic molecules

Here we will estimate the value of the equilibrium bond length (R_e) the harmonic vibrational energy (ω_e) and the homolytic dissociation energy (D_e) of several diatomic molecules. We have focused our study on a group of 11 diatomics, namely, H_2, LiH, HF, HCl, Li_2, C_2, N_2, O_2, F_2, Cl_2, and ClF. This set comprises well-known examples of single-, double-, and triple-bond homonuclear and heteronuclear, closed- and open-shell molecules with first- and second-row atoms. Despite their simple atomic composition, these molecules represent a challenge regarding the changes involved in their electronic structures upon their dissociation into the ground states of the constituent atoms.

For single-bond diatomics, a correct description of both spatial and spin symmetries along the whole dissociation process can be achieved by means of a GVB PP wave function using just one pair of correlated orbitals. This is equivalent to a two-configuration MCSCF calculation [2], which is actually the reference wave function we have chosen for H_2, LiH, HF, HCl, Li_2, F_2, Cl_2, and ClF. Unfortunately, the lack of interpair correlation in a GVB PP description of a multiply bonded molecule makes it an unsuitable wave function to correctly describe the dissociation into the corresponding ground states of the two atoms involved (see, e.g., Ref. [64]). Thus, for C_2, N_2, and O_2 we have been forced to go beyond the GVB PP and use a proper reference MCSCF wave function which correctly describes the bond rupture [33,65]. In the limit of infinite internuclear distance the energy obtained with these MCSCF wave functions reduces to the sum of

TABLE II. Exact equilibrium distances (in Å) for the ground state of several diatomics and deviations (calculated minus exact) using several methods with the 6-311G++(3df,3p) basis set. The mean absolute error (MAE) over the set of 11 molecules considered is also printed at the end of the table.

Molecule	Exact[a]	B3LYP	BLYP	MCSCF	$B88_{><}$[b]	$LYP_{><}$[b]	$PW_{><}$[b]	B88[c]	LYP[c]	PW[c]
H_2	0.741	0.002	0.005	0.014	0.007	0.007	0.009	0.007	0.007	0.009
LiH	1.596	−0.004	0.003	0.040	0.004	0.002	0.011	0.005	0.002	0.012
HF	0.917	0.005	0.016	−0.002	−0.010	−0.009	−0.013	−0.010	−0.009	−0.009
HCl	1.275	0.007	0.016	0.012	−0.002	−0.001	−0.002	−0.002	−0.001	−0.002
Li_2	2.673	0.033	0.041	0.258	0.147	0.134	0.170	0.154	0.144	0.177
C_2	1.243	0.005	0.014	−0.018	−0.030	−0.030	−0.028	−0.033	−0.033	−0.031
N_2	1.098	−0.006	0.006	−0.002	−0.012	−0.011	−0.012	−0.011	−0.011	−0.012
O_2	1.208	−0.003	0.022	0.006	−0.013	−0.010	−0.018	−0.012	−0.009	−0.018
F_2	1.412	−0.017	0.019	0.057	−0.001	0.008	−0.014	0.002	0.010	−0.012
Cl_2	1.988	0.024	0.054	0.047	−0.008	0.004	−0.018	−0.008	0.004	−0.018
ClF	1.628	0.014	0.046	0.028	−0.016	−0.009	−0.022	−0.016	−0.009	−0.022
MAE		0.011	0.022	0.044	0.023	0.020	0.029	0.024	0.022	0.029

[a] Exact values taken from the "NIST Chemistry WebBook" [77].

[b] Results obtained by adding the energy of the correlation functional evaluated with the transformed spin densities $\rho_>$ and $\rho_<$ to the MCSCF energy.

[c] Results obtained by adding the energy of the correlation functional evaluated with the MCSCF spin densities to the MCSCF energy.

restricted open-shell Hartree-Fock (ROHF) calculations on each atom [66].

Once the energy of the MCSCF wave function is obtained we correct it by adding the correlation energy calculated from the MCSCF spin densities by three different correlation energy functionals, namely, the Lee, Yang, and Parr (LYP) functional [67], the Perdew-Wang generalized gradient approximation (GGA) functional (PW GGA II) [68], and Becke's meta-GGA functional [63]. We refer to these calculations as MC+LYP, MC+PW, and MC+B88, respectively. We also correct the MCSCF energy with the correlation energy provided by these three functionals but evaluated via the transformed $\rho_>$ and $\rho_<$ spin densities described in the previous section. In the following, the latter calculations will be termed MC+$LYP_{><}$, MC+$PW_{><}$, and MC+$B88_{><}$, respectively.

All the MC and KS DFT calculations have been performed using the GAMESS program [69] with the augmented Pople's "triple-split" 6-311G++(3df,3p) basis set [70–72], while the numerical integration method used for the correlation energy functionals is that proposed in Refs. [73,74]. The values of ω_e and R_e corresponding to the MCSCF and MC +correlation calculations have been obtained by fitting a set of 16 points on the dissociation curves around the equilibrium bond length at intervals of 0.005 Å to a cubic polynomial in R^{-1}. The R_e values corresponding to DFT calculations have been analytically determined using GAMESS. However, limitations in the GAMESS program force the numerical approximation of the DFT Hessian needed to evaluate ω_e by twice differentiating the DFT energy. The values for D_e are obtained by subtracting the energy at a large interatomic distance (10 Å for H_2 and HF, 30 Å for Li_2, and 20 Å for the rest) from that at R_e.

Tables II–IV show the values obtained for the spectroscopic constants using the above methods, as well as those obtained by means of UKS DFT calculations using the popular Becke three-parameter Lee-Yang-Parr (B3LYP) hybrid functional and Becke–Lee-Yang-Parr (BLYP) functional exchange-correlation functionals [67,75,76]. The results indicate that correcting MCSCF energies by correlation energy functionals leads to shorter equilibrium bond lengths and larger harmonic vibrational energies, irrespective of the correlation energy functional considered, as previously discussed in the literature [80]. Overall, this is a step in the right direction, which explains the improvement found, on average, for R_e and ω_e estimates with respect to MCSCF uncorrected ones. Both MC+C and MC+$C_{><}$ bond lengths and frequencies (C denoting one of LYP, PW, or B88) are of a quality similar to those from UKS DFT calculations using the BLYP functional, although the best estimates for these properties correspond to the B3LYP method. Note that the values of R_e and ω_e corresponding to MC+C calculations are quite similar to those from MC+$C_{><}$ ones, as might be expected from the discussion in Sec. II.

The major improvement, however, corresponds to the dissociation energies yielded by the MC+$C_{><}$ method which are of the same quality as the B3LYP results for the three functionals tested. This improvement is easy to understand: while the MC+C calculations always overestimate the energy when $R \to \infty$ as commented above, thus *underestimating* D_e, the MC+$C_{><}$ gives the correct energy, leading to mean average errors (MAEs) of $\sim$4 kcal mol^{-1} for the 11 molecules tested and the three functionals considered.

B. Automerization barrier of cyclobutadiene

We now apply our method to a situation where KS DFT calculations fail to provide good results: the automerization

TABLE III. Exact harmonic vibrational frequencies (in cm^{-1}) for the 11 diatomics considered and deviations using several methods with the 6-311G++(3df,3p) basis set. See caption and notes of Table II.

Molecule	Exact	B3LYP	BLYP	MCSCF	$\mathrm{B88}_{><}$	$\mathrm{LYP}_{><}$	$\mathrm{PW}_{><}$	B88	LYP	PW
H_2	4401	47	−21	−179	−92	−89	−93	−94	−90	−95
LiH	1406	9	−20	−104	−39	−27	−45	−40	−28	−46
HF	4138	−50	−204	0	122	109	162	120	109	161
HCl	2991	−43	−135	−81	21	17	49	20	16	48
Li_2	351	−11	−13	−86	−54	−47	−44	−55	−54	−48
C_2	1855	15	−30	86	165	163	169	174	168	175
N_2	2359	83	−32	18	90	91	107	85	87	103
O_2	1580	59	−82	−22	75	59	120	72	56	115
F_2	917	128	38	−240	−77	−95	−44	−95	−108	−55
Cl_2	560	−20	−58	−57	5	−6	24	5	−7	24
ClF	786	−5	−64	−94	−7	−17	13	−9	−19	11
MAE		43	63	88	68	66	79	70	67	80

barrier of cyclobutadiene. It has been established that the ground state of this molecule is a singlet with rectangular shape (see, e.g., Refs. [81–90] and references therein). Its automerization reaction represents the interconversion between two rectangular geometries of D_{2h} symmetry through a square transition state of D_{4h} symmetry. The latter is a diradical because each of the two degenerate nonbonding π-e_g molecular orbitals is singly occupied, thus requiring more than just a single determinant to be adequately described, which explains why the barrier height predicted by Hartree-Fock or KS-DFT calculations is extremely wrong [55,88,91].

The MCSCF wave function that we have chosen to accommodate the four π electrons involved in the automerization process is, basically, a two-pair GVB PP wave function (b_{1u}, a_u and b_{3g}, b_{2g} being the symmetries of the corresponding pairs of orthogonal orbitals) where interpair correlation has been allowed by including also those determinants where each of the above four orbitals is singly occupied [64]. We report in Table V accurate activation barriers from multireference coupled-cluster (MRCC) calculations performed in Refs. [88,90]. Table V also lists the B3LYP, BLYP, MCSCF, MC+C, and $\mathrm{MC+C}_{><}$ estimates of the barrier calculated at the corresponding D_{4h} and D_{2h} MCSCF optimized geometries (also given in Table V). The $\mathrm{MC+C}_{><}$ results are strikingly good, with deviations of ∼0.3 (C=B88), ∼0.5(C=LYP), and ∼1.7 (C=PW) kcal mol^{-1} with respect to the average of the MRCC values reported. On the other hand, B3LYP and BLYP functionals overestimate the activation barrier by as much as ∼14–15 kcal mol^{-1} while the MCSCF wave function used here underestimates it by ∼5 kcal mol^{-1}. It should also be emphasized that MC+C calculations lead to even lower barriers than MCSCF ones. The main reason for

TABLE IV. Exact dissociation energies (in kcal mol^{-1}) for the ground state of the 11 diatomics considered and deviations using several methods with the 6-311G++(3df,3p) basis set. See caption and notes of Table II.

Molecule	Exact[a]	B3LYP	BLYP	MCSCF	$\mathrm{B88}_{><}$	$\mathrm{LYP}_{><}$	$\mathrm{PW}_{><}$	B88	LYP	PW
H_2	109.5	0.6	−0.2	−14.2	8.4	9.8	6.2	−8.6	−7.3	−5.5
LiH	57.7	0.6	0.2	−13.2	5.1	8.7	3.8	−8.3	−6.4	−6.1
HF	141.3	−1.6	−0.2	−26.7	0.6	−1.2	−1.2	−13.4	−13.4	−10.2
HCl	106.4	−1.7	−2.1	−15.9	7.8	6.3	7.4	−5.0	−5.4	−1.1
Li_2	24.4	−3.7	−3.9	−14.2	−1.2	1.8	−1.1	−10.9	−11.3	−9.0
C_2	146.0	−27.5	−11.2	−48.6	−7.1	−9.7	−4.0	−24.2	−28.3	−19.6
N_2	228.5	−0.7	11.3	−58.8	−2.1	2.9	3.6	−37.3	−37.3	−28.7
O_2	120.3	2.8	15.6	−29.7	2.5	−0.2	6.0	−10.1	−11.8	−4.4
F_2	38.2	−2.4	10.1	−22.8	0.3	−3.8	−3.2	−10.3	−11.0	−9.5
Cl_2	58.0	−3.7	−0.5	−19.5	4.9	−0.6	4.8	−3.7	−7.0	−0.4
ClF	60.2	−0.6	6.5	−24.0	1.4	−3.0	−0.8	−8.2	−9.9	−6.6
MAE		4.2	5.6	26.1	3.8	4.4	3.8	12.7	13.5	9.2

[a] Exact values evaluated from the experimental atomization energies at 0 K reported in the “Computational Chemistry Comparison and Benchmark DataBase” [78], corrected by the zero-point energy (see, e.g., Ref. [79], p. 100) calculated from the spectroscopic constants reported in Ref. [77].

TABLE V. Automerization barrier of cyclobutadiene using the 6-311G++(3df,3p) basis set and several methods. See notes of Table II.

MRCC	B3LYP^{a,b}	BLYP^{a,b}	MCSCF^{b}	B88$_{><}$^{b}	LYP$_{><}$^{b}	PW$_{><}$^{b}	B88^{b}	LYP^{b}	PW^{b}
[6.6^{c}, 7.0^{d}]	22.2	20.9	1.7	7.1	6.3	5.1	1.1	1.6	1.5

[a] Closed-shell spin-restricted Kohn-Sham calculations.

[b] Barrier heights evaluated at the MCSCF/[6-311G++(3df,3p)] optimized geometries; rectangular: $R_{C=C}=1.370$ Å, $R_{C-C}=1.524$ Å, $R_{C-H}=1.070$ Å, $\angle(H,C,C)=134.86^{\circ}$; square: $R_{C-C}=1.444$ Å, $R_{C-H}=1.069$ Å.

[c] Multireference coupled-cluster singles and doubles with approximate triples (MRCCSD)(T)/[3s2p1d/1s] barrier height from Ref. [88] calculated at the corresponding optimized geometries; rectangular: $R_{C=C}=1.367$ Å, $R_{C-C}=1.570$ Å, $R_{C-H}=1.103$ Å, $\angle(H,C,C)=134.73^{\circ}$; square: $R_{C-C}=1.467$ Å, $R_{C-H}=1.104$ Å.

[d] Multireference Brillouin-Wigner coupled-cluster singles and doubles with approximate triples (MR BWCCSD)(T)/[cc-pVTZ] barrier height from Ref. [90] calculated at the corresponding optimized geometries; rectangular: $R_{C=C}=1.354$ Å, $R_{C-C}=1.564$ Å, $R_{C-H}=1.079$ Å, $\angle(H,C,C)=134.94^{\circ}$; square: $R_{C-C}=1.451$ Å, $R_{C-H}=1.078$ Å.

the superior behavior of MC+C$_{><}$ over MC+C is that the open-shell singlet character of a system is *better* described by a standard correlation energy density functional if the two singly occupied orbitals are considered to be in the high-spin state, as our method does in this case. Otherwise the functional interprets the absence of spin polarization yielded by the MCSCF spin densities as a closed-shell system, overestimating the correlation energy [31]. This is further tested below for the energy difference between triplet and open-shell singlet states.

C. Energy differences between triplet and open-shell singlet states

We estimate the energy difference between two states differing in the spin coupling of the electrons, namely, the $^{3}B_1$ and $^{1}B_1$ states in CH_2, and the lowest excited 2 ^{3}S and 2 ^{1}S states in He. We approximate these states with (2,2)complete active space self-consistent field (CASSCF) reference wave functions to minimize the double count of the correlation energy, using the (1s,2s) and (a_1,b_1) active spaces for He and CH_2 respectively. The 6-311++G(3df,3p) basis set was used for CH_2, while the smaller size of He allowed us to use the larger augmented correlation-consistent polarized valence quintuple-zeta (aug-cc-pV5Z) basis set [92,93] on this system.

The MCSCF triplet-singlet splittings estimated by the above wave functions, as well as from MC+C and MC+C$_{><}$ calculations are listed in Table VI. Although the (2,2)CASSCF wave functions provide the correct energy ordering, with the triplet being more stable than the open-shell singlet, they overestimate the triplet-singlet splittings by 5.4 and 4.02 kcal/mol in CH_2 and He, respectively. The MC+C results, on the other hand, severely underestimate the triplet-singlet splittings, mainly because the open-shell singlet correlation is overestimated. The amount of overstabilization of the open-shell singlet varies with the specific functional used, with the PW functional providing the best result.

Finally, we see that the MC+C$_{><}$ methods correct the overestimation of the (2,2)CASSCF energy difference without severely underestimating it as in MC+C calculations, leading to rather good values on average for the three functionals considered. This correction is mostly due to the lower correlation energy introduced by our method for the open-shell singlet states by effectively increasing their high-spin character.

IV. CONCLUSIONS

We have proposed a size-consistent method to combine multiconfigurational wave functions with standard correlation energy functionals used in Kohn-Sham DFT calculations. In order to avoid the double count of the correlation energy the method should be applied to small active spaces in MC calculations, which is also advantageous from the point of view of its computational cost. The good results achieved for the spectroscopic constants of several diatomic molecules shows the importance of adequately addressing

TABLE VI. Energy difference (in kcal mol^{-1}) between triplet and open-shell singlet states from (2,2)CASSCF calculations. See notes of Table II.

System	States	Reference^{a}	MCSCF^{b}	B88$_{><}$^{b}	LYP$_{><}$^{b}	PW$_{><}$^{b}	B88^{b}	LYP^{b}	PW^{b}
He	2 ^{3}S-2 ^{1}S	18.39	22.41	13.83	14.52	18.29	5.10	6.97	10.51
CH_2	$^{3}B_1$-$^{1}B_1$	33.4	38.79	37.23	37.18	38.08	25.01	25.09	29.77

[a] He values are from theoretical energies reported in Ref. [94] considering infinite nuclear mass and neglecting relativity effects. CH_2 values are from quadratic configuration interaction singles and doubles (CISD)+Q energies extrapolated to the complete basis set limit reported in Ref. [95].

[b] He values calculated with the aug-cc-pV5Z basis set. CH_2 values calculated with the 6-311G++(3df,3p) basis set at the (2,2)CASSCF/6-311G++(3df,3p) optimized geometries; $^{3}B_1$: $R_{C-H}=1.070$ Å, $\angle(H,C,H)=129.48^{\circ}$; $^{1}B_1$: $R_{C-H}=1.065$ Å, $\angle(H,C,H)=141.39^{\circ}$.

the size-consistency problem in a consistent manner throughout the whole dissociation process. The method looks promising for describing open-shell systems, as evidenced by the rather good estimates it gives for the activation barrier of cyclobutadiene and the energy difference between triplet and open-shell singlet states of He and CH_2.

ACKNOWLEDGMENTS

Financial support from Spanish Ministerio de Educación y Ciencia (MEC) and the European Regional Development Fund through Project No. CTQ2004-06519/BQU, as well as from the Universidad de Alicante (Grant No. VIGROB2005-096) is gratefully acknowledged. A.J.P.J. thanks the Spanish MEC and the Generalitat Valenciana for economic support within the "Ramón y Cajal" program. The Extensible Computational Chemistry Environment Basis Set Database is funded by the U.S. Department of Energy. The Pacific Northwest Laboratory is a multiprogram laboratory operated by Battelle Memorial Institute for the U.S. Department of Energy under Contract No. DE-AC06-76RLO 1830. Contact David Feller or Karen Schuchardt for further information.

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