



The combination of density functional theory with multi-configuration methods – CAS-DFT

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Abstract

CAS-DFT is presented as a method that allows an economical simultaneous treatment of static and dynamic correlation effects in molecules with multi-reference character. Central problems of CAS-DFT concern the double counting of dynamic correlation effects and the choice of the proper input quantities for the DFT functional. Also, the question of treating both active and inactive orbitals in a consistent way is discussed. Test calculations with CAS-DFT for the ring opening of dioxirane and the excitation energies of methylene prove that the method works reasonably. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

There are many chemically interesting molecules and reaction systems that are characterized by strong static electron correlation effects and thus require a multi-configuration (MC) or multi-reference (MR) approach for an adequate treatment of the wavefunction. Examples comprise molecules with low-lying excited or degenerate ground states (Jahn–Teller molecules, low-spin biradicals, etc.) or reaction systems, which include homolytic dissociation. In these cases, a correct quantum-chemical description can only be obtained if both static and dynamic electron correlation is appropriately covered. As long as the systems under consideration consist of just a few atoms, they can be treated with high accuracy employing high-level methods such as MR-CI [1,2] or MR-AQCC [3]. However, these methods are beyond

feasibility for many interesting problems such as the formation of biochemically active singlet biradicals in the Bergman and Myers cyclization reaction, which have been studied intensely by quantum-chemical methods in the last years [4,5] because some of these biradicals are interesting candidates for anti-tumor agents. Hence, there is a need for a method that on the one hand allows to cover both static and dynamic electron correlation effects reasonably accurately, while it on the other hand allows to describe larger systems of chemical interest. This implies that the method must not be too expensive, should produce reliable results even with a moderate basis, and, finally, must not scale too strongly with the system size.

A method that performs surprisingly well at low computational costs is Kohn–Sham (KS) density-functional theory (DFT) [6,7]. The modern gradient-corrected functionals for the exchange and correlation (XC) energy [8–10] have made DFT a reliable tool for quantum-chemical calculations, which is used

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more and more widely (see, e.g., Ref. [11]). These functionals employ model XC holes to cover an unspecified part of the XC energy. However, the model XC holes give an incorrect description in situations with strong static electron correlation effects, thus leading to poor DFT results in these cases. Simple modifications of the existing functionals would not suffice to improve DFT results and, therefore, a class of completely new (and computationally much more expensive) functionals would be necessary to properly account for static correlation effects. Still, given the success and low expenses of DFT, it is attractive to extend this approach to systems with multi-reference character. An appealing way to do so is to combine the capabilities of MC theory and DFT in the way that static electron correlation effects are covered by MC theory while dynamic correlation effects are described within DFT. In this spirit, a number of methods has been proposed over the years [12–19], of which the recent method of Miehlich, Stoll and Savin (MSS) is particularly remarkable since it considers explicitly the problems of a combination of MC and DFT methods [20]. One of the main problems of MC-DFT is the related to the question how to separate energy contributions covered by each of the two approaches, i.e. how to avoid a partial double counting of electron correlation effects.

In this Letter, we present a new CAS-DFT method, in which the static correlation effects are described by the complete-active-space self-consistent-field (CASSCF) approach [21]. The new CAS-DFT method is based on the recent work of MSS [20], but develops it further with respect to the needed separation of the correlation energy contributions. In particular, the difference between active and inactive orbitals is taken into account to correctly describe dynamic correlation effects. This allows to decrease the active space in the CASSCF description without loss of consistency and facilitates economical but still reliable calculations for larger systems.

2. Theory

In the formulation of Levy [22], DFT is based on the functional

$$F[\varrho] = \min_{\Psi \rightarrow \varrho} \langle \Psi | \hat{T} + \hat{V}_{ee} | \Psi \rangle, \quad (1)$$

where the minimization is carried out over all properly antisymmetric trial wavefunctions Ψ that integrate to the density ϱ . The ground-state energy for an external potential v is then found by a search over all ϱ that integrate to the total particle numbers N as

$$E[v] = \min_{\varrho \rightarrow N} F[\varrho] + \int d^3r \varrho v. \quad (2)$$

The form of the functional $F[\varrho]$ is unknown. To transform Eq. (1) into a practical calculation scheme, one decomposes $F[\varrho]$ into one term that covers the major part of the total energy and can be evaluated exactly and another term that represents the many-body problem of interacting particles. The most common scheme of this kind is the Kohn–Sham (KS) formalism [7], which divides $F[\varrho]$ into the KS energy $F_{\text{KS}}[\varrho]$ and the exchange (X) and correlation (C) energy $E_{\text{XC}}[\varrho]$ as follows:

$$F[\varrho] = F_{\text{KS}}[\varrho] + E_{\text{XC}}[\varrho], \quad (3)$$

$$F_{\text{KS}}[\varrho] = \min_{\Phi \rightarrow \varrho} \langle \Phi | \hat{T} | \Phi \rangle + \frac{1}{2} \int d^3r \int d^3r' \frac{\varrho(\mathbf{r})\varrho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}, \quad (4)$$

with the Φ being antisymmetric trial functions that can be built up from a set of orthonormal one-particle orbitals ψ_1, ψ_2, \dots (normally, Φ is a single-determinant trial wavefunction, but not so for low-spin open-shell states, see e.g. Ref. [23]). In the KS formalism, both static and dynamic correlation contributions should be contained in the energy term E_{XC} ; however, the available XC functionals only describe dynamic correlations reliably. Accordingly, KS-DFT fails for systems with strong static correlation effects. On the other hand, static correlations can be well described by a CAS (more generally, a multi-reference) wavefunction with a moderately-sized active space. It is thus promising to develop an approach that combines a CAS treatment of the static correlation effects with a DFT treatment of the dynamic correlation effects. To develop such an algorithm, we modify the KS approach (see Eqs. (3) and (4)) in two ways: (i) the search is done over all CAS trial wavefunctions for a given size of the active space; and (ii) in Eq. (4), the Hartree energy is replaced by the full electron interaction energy of the trial wavefunction. This implies that the exchange

energy and the static correlation energy are covered by the analogue to $F_{\text{KS}}[\rho]$ in Eq. (3) and that $E_{\text{XC}}[\rho]$ is replaced by a term that covers the dynamic correlation energy only.

Modifications (i) and (ii) lead to the CAS-DFT scheme:

$$F[\rho] = F_{\text{KS}}^{\text{CAS-DFT}}[\rho] + E_{\text{C}}^{\text{CAS-DFT}}[\rho], \quad (5)$$

$$F_{\text{KS}}^{\text{CAS-DFT}}[\rho] = \min_{\Psi^{\text{CAS}} \rightarrow \rho} \langle \Psi^{\text{CAS}} | \hat{T} + \hat{V}_{ee} | \Psi^{\text{CAS}} \rangle. \quad (6)$$

One has to construct an approximation for $E_{\text{C}}^{\text{CAS-DFT}}[\rho]$ to apply this scheme. For this purpose, one can start from the approximate functionals for the C energy used in KS-DFT. These functionals are usually derived with the homogeneous electron gas as starting point and have the form

$$E_{\text{C}}[\rho] = \int d^3r \varepsilon_{\text{C}}(\rho, \nabla\rho, \dots) \Big|_r. \quad (7)$$

The application of these functionals in CAS-DFT raises a number of questions.

Problem 1: Multiplet states are treated differently in KS and CASSCF formalisms. In KS-DFT, multiplets are handled by replacing ρ and N by their spin-resolved counterparts $\rho_{\alpha}, \rho_{\beta}$ and N_{α}, N_{β} , the expression for ε_{C} thus depending on $\rho_{\alpha}, \rho_{\beta}$. However, the spin-resolved densities do not reflect the spin symmetry correctly for CAS methods, which restrict the trial wavefunction (and by this also the spin densities) to the correct spin symmetry. Perdew et al. [24] showed that one can solve this problem by replacing $\rho_{\alpha}, \rho_{\beta}$ by a new pair of key quantities, viz. the total density ρ and the on-top pair density $P(\mathbf{r}, \mathbf{r})$, which is the probability to find two particles at the same position. Total density and on-top pair density give a correct account of the spin symmetry. To use them as input quantities for the usual functionals of spin-resolved DFT, one has to subject them to a variable transformation in the following way [25]:

$$\begin{aligned} \varepsilon_{\text{C}}^{\text{on-top}}(\rho, P) \\ = \varepsilon_{\text{C}} \left(\frac{\rho}{2} + \sqrt{\left(\frac{\rho}{2}\right)^2 - P}, \frac{\rho}{2} - \sqrt{\left(\frac{\rho}{2}\right)^2 - P} \right). \end{aligned} \quad (8)$$

Problem 2: The correlation functional in Eq. (6) must depend on the size of the active space for Ψ^{CAS} . As this size increases, $F_{\text{KS}}^{\text{CAS-DFT}}[\rho]$ covers, beside the static correlation effects, an increasing part of the dynamic correlation effects, which will be covered once more by $E_{\text{C}}^{\text{CAS-DFT}}[\rho]$ if Eq. (7) is used directly. A number of methods were suggested in the literature to avoid this double counting of dynamic electron correlation effects. Lie and Clementi [12,13] proposed to eliminate the double-counting problem largely by choosing the active space as small as possible. The same idea was used by Kraka [18] to develop a GVB-DFT method. Colle and Salvetti [14,15] utilized the information contained in the two-particle density matrix to locally estimate the amount of dynamic correlation energy covered by Ψ^{CAS} . Savin and Flad [19] decomposed the Coulomb interaction energy into a smooth long-range part, which drives the static correlations and a singular, short-ranged part, which gives rise to dynamic correlations.

In our work, we start from the approach suggested by Savin [16] and further developed by MSS [20]. In this approach, first the size of the active space for Ψ_{CAS} is determined locally by calculating the reference density

$$\rho_{\text{ref}}(\mathbf{r}) = \sum_i^{\text{occ}} 2\phi_i(\mathbf{r})\phi_i(\mathbf{r}), \quad (9)$$

where the sum is over all occupied orbitals and both inactive and active orbitals are considered to be doubly occupied. In this way, $\rho_{\text{ref}}(\mathbf{r})$ is a true measure of the size of the active space. The ratio $\rho_{\text{ref}}(\mathbf{r})/\rho(\mathbf{r})$ is ≥ 1 and becomes larger the larger the active space is, i.e. the smaller the amount of the dynamic correlation energy to be covered by $E_{\text{C}}^{\text{CAS-DFT}}$ remains. The DFT correlation energy is then scaled locally by a scaling factor f ($0 \leq f \leq 1$) to avoid this double counting. To determine f , one recalculates the correlation energy of the homogeneous electron gas with the density ρ in a way that is comparable to CASSCF, i.e. one allows excitations from the occupied orbitals only into virtual orbitals up to a certain energy limit, which is adjusted in the way that the active space has just the reference density ρ_{ref} . The resulting correlation energy $\varepsilon_{\text{C}}^{\text{hom}}(\rho, \rho_{\text{ref}})$ is then related to the value $\varepsilon_{\text{C}}^{\text{hom}}(\rho, \rho)$

for all virtual orbitals being included, which yields for f

$$f(\varrho, \varrho_{\text{ref}}) = 1 - \frac{\varepsilon_C^{\text{hom}}(\varrho, \varrho_{\text{ref}})}{\varepsilon_C^{\text{hom}}(\varrho, \infty)}. \quad (10)$$

MSS [20] found an analytic expression for f by parametrizing numerical results published by Savin [16]. The total DFT correlation energy then becomes

$$E_{C, \text{no-core}}^{\text{CAS-DFT}} = \int d^3r f(\varrho, \varrho_{\text{ref}}) \varepsilon_C^{\text{on-top}}(\varrho, \nabla \dots, P, \nabla P, \dots) \Big|_r. \quad (11)$$

In Eqs. (9) and (11), it has been tacitly assumed that all occupied orbitals are treated as active in the CAS calculation, i.e. that there are no inactive (core) orbitals. This is indicated by the subscript no-core in Eq. (11). In practical calculations, however, only those orbitals that are relevant for the static correlations will be treated as active, and the inactive space will be made as large as possible. This leads to an inconsistent treatment of excitations from the inactive orbitals.

Fig. 1 shows which kinds of excitations in terms of inactive (core) orbitals, active orbitals, and virtual orbitals, are covered by a pure CASSCF or a CAS-DFT calculation with and without the scaling of the DFT correlation energy included. One has to distin-

guish between strongly and weakly populated orbitals of the active space to get a correct picture. In CASSCF (Fig. 1a), excitations from inactive orbitals are suppressed completely. When one adds the DFT correlation energy term E_C (CASSCF + C), excitations within and out of the active space (the former leading to a possible double counting of dynamic correlation effects) are included, but also all excitations out of the inactive space (Fig. 1b). Introduction of the scaling factor f (CASSCF + fC, Fig. 1c) corrects the double counting of excitations from strongly into weakly populated active orbitals but discards at the same time excitations from inactive orbitals into weakly populated active orbitals. In the case of a chemical reaction, during which the form and energy of the active orbitals will change according to the changes of the chemical environment, the extent to which the latter excitations are covered in the correlation energy will also vary and lead to errors in the description of the reaction in question.

We correct this inconsistency by adding an extra term $E_{C, \text{core}}^{\text{CAS-DFT}}$ to the DFT correlation energy according to Eq. (12):

$$E_C^{\text{CAS-DFT}} = E_{C, \text{no-core}}^{\text{CAS-DFT}} + E_{C, \text{core}}^{\text{CAS-DFT}}. \quad (12)$$

$E_{C, \text{core}}^{\text{CAS-DFT}}$ is constructed from the correlation energy $\varepsilon_C^{\text{on-top}}$ for the density ϱ_{core} and the on-top pair density P_{core} related to the inactive orbitals. By appropriate scaling, the part of the correlation energy

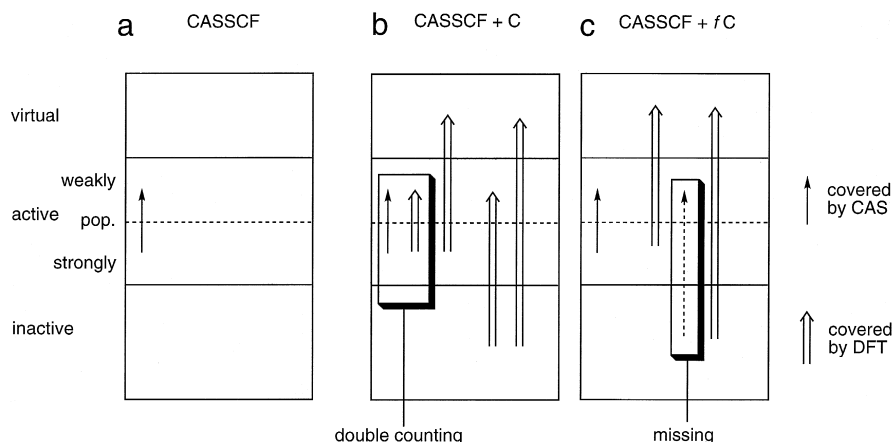


Fig. 1. Excitations that contribute to the correlation energy in: (a) a CASSCF calculation; (b) in a CASSCF + C calculation; and (c) a CASSCF + fC calculation. Single arrows show excitations covered by the CASSCF wavefunctions, double arrows, excitations covered by the DFT correlation energy. The dashed arrow in (c) is used to point out that this excitation is missing.

related to excitations into weakly populated virtual orbitals is extracted. This eventually leads to

$$E_{C,\text{core}}^{\text{CAS-DFT}} = \int d^3r [f(\varrho_{\text{core}}, \varrho) - f(\varrho_{\text{core}}, \varrho_{\text{ref}})] \times \varepsilon_C^{\text{on-top}}(\varrho_{\text{core}}, \nabla\varrho_{\text{core}}, P_{\text{core}}, \nabla P_{\text{core}}, \dots) \Big|_r. \quad (13)$$

Problem 3: The correct way to determine the CAS-DFT energy is to solve the CAS-DFT equations self-consistently. However, the orbitals do not depend strongly on the DFT correlation-energy contribution as previous investigations with GVB-DFT showed [18]. Hence, for energy calculations it is a reasonable approximation to insert Ψ^{CASSCF} into the CAS-DFT energy functional and to determine the CAS-DFT energy in a one-step procedure rather than obtaining $\Psi^{\text{CAS-DFT}}$ in an iterative procedure leading to self-consistency.

Problem 4: As for the choice of an appropriate functional for E_C , MSS [20] showed that a gradient-corrected functional is required since LDA functionals overestimate dynamic correlation effects. A reasonable choice were the Lee–Yang–Parr (LYP) functional [10], which has been used widely with success in the last years. In the present context, however, it is advantageous to employ the Colle–Salvetti (CS) functional [14,15], on which the LYP functional is actually based. The CS functional was derived in the context of the Hartree–Fock (HF) formalism utilizing the total density and the pair density as input quantities, i.e. actually those quantities required for CAS-DFT. Hence, one does not need the variable transformation of Eq. (8), in particular one can avoid complex arguments that would occur for $P > \varrho^2/2$ (which is typical of low-spin open-shell systems). Therefore, the CS functional is used for the CAS-DFT calculations presented in this work.

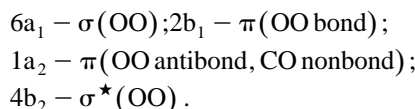
3. Results and discussion

The CAS-DFT method was implemented within the COLOGNE 99 [26] program package. For the CASSCF calculations, we used the GAUSSIAN 98 [27] and GAMESS program packages [28]. In view of the computer time needed for a CASSCF calculation, the

computational cost for the one-step DFT correction are moderate. For a self-consistent CAS-DFT calculation, the computational costs for the DFT step are of the same order of magnitude as those for the CASSCF calculation and, accordingly, CAS-DFT requires about twice as much time as a CASSCF calculation. In no case should the computational cost be dominated by the DFT corrections as is often the case with other correlation methods.

In this work, we discuss two application examples of CAS-DFT that reflect advantages and disadvantages of the method. The first example concerns the ring opening of dioxirane **1** via **TS(1-2)** to methylenebis(oxy) **2** (see Fig. 2) that is an important reaction in atmospheric chemistry and that was recently investigated by accurate multi-reference averaged quadratic coupled-cluster (MR-AQCC) calculations [29].

A correct theoretical description of the energetics for this reaction requires a coverage of both static and dynamic correlation effects: The breaking of the O–O bond on the way from **1** to **2** leads to strong static correlation while dynamic correlation effects, on the other hand, decrease due to the breaking of the O–O bond. The ground state (GS) of **1** is defined by the electron configuration $\dots 6a_1^2 2b_1^2 1a_2^2 4b_2^0 (^1A_1, 4\pi)$ where the orbitals have the following character:



Ring opening to **1** formally involves a rotation of the two $2p\pi$ electron pairs at the O atoms into the

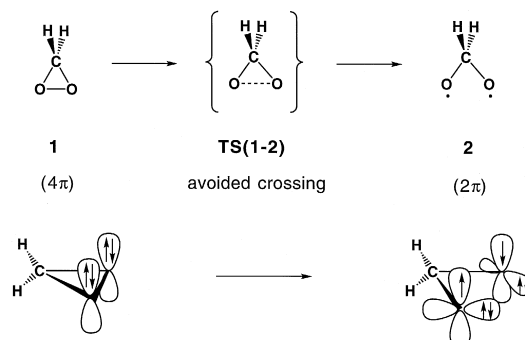


Fig. 2. Ring opening of dioxirane (**1**) to methylenebis(oxy) (**2**). The electron configuration of reactant and product is schematically shown.

ring plane so that both the $6a_1 - \sigma(\text{OO})$ and the $4b_2 - \sigma^*(\text{OO})$ become doubly occupied and, consequently, σ -bonding between the O atoms is no longer possible. At the equilibrium O–O distance of **2** (close to **2**) the two π MOs $1a_2$ and $2b_1$ are of comparable energy and, therefore, both the $\dots 6a_1^2 1a_2^2 4b_2^2$ and the $\dots 6a_1^2 2b_1^2 4b_2^2$ electron configuration contribute to the $^1A_1, 2\pi$ GS of **2**, which corresponds to a low-lying excited state of dioxirane obtained by $2b_1 \rightarrow 4b_2$ or $1a_2 \rightarrow 4b_2$ double excitation. The $^1A_1, 4\pi$ and $^1A_1, 2\pi$ states undergo an avoided crossing close to **TS(1-2)**. Hence, a consistent description of the ring opening reaction of **1** requires the inclusion of orbitals $6a_1$, $2b_1$, $1a_2$, and $4b_2$ into the active space thus leading to a (6,4) space. CASSCF and CASSCF-DFT calculations for the ring opening of **1** were carried out with a 6-311 + G(2df, 2pd) basis set [30] at the CASSCF geometry (Table 1) and compared with the corresponding MR-AQCC results of Cremer et al.[29].

The energies listed in Table 1 reveal that CASSCF underestimates both the reaction barrier and the reaction energy. CASSCF does not cover dynamic electron correlation, which is more important for **1** than for **2** (one electron pair more in the former case) and, thus, underestimates the stability of **1** which leads to the errors observed. CASSCF + C increases both the energy barrier and the reaction energy, however, this increase is still not sufficient in the case of the barrier (16.9 kcal/mol) while it leads already to an exaggeration of the reaction energy (8.8 kcal/mol)

in comparison to the MR-AQCC results. Both observations are relevant for the understanding of the CASSCF description. First, the active space chosen is still not large enough to get a reasonable CASSCF description for the barrier. Calculations with a (12, 11) active space suggest that barrier and reaction energy are underestimated at the CAS(6,4) level. Second, dynamic correlation effects are exaggerated at the CASSCF + C level where the double counting of dynamic correlation should be weaker for **2** than for **TS(1-2)** or **1** since in the former case the O–O bond is completely broken. CASSCF + fC reduces the correlation energy by 6% (from 827 to 776 mhartree, see Table 1) in the case of **1** and suggests that similar corrections apply for **TS(1-2)** and **2**. This cannot be correct since one bond is broken and the corresponding electron pair separated in the ring opening process. MR-AQCC suggests that this process together with the corresponding electron reorganization and geometry relaxation requires 4.6 kcal/mol. As will be discussed in more detail below for the CH_2 molecule, the scaling factor f in CASSCF + fC does not distinguish appropriately between doubly and singly occupied orbitals (as required for **2**). Hence the correction for double counting will be underestimated by 3–4 kcal/mol in the case of **2**.

About half of the double-counting corrections corresponds to core correlation effects (25 mhartree in the case of **1**, Table 1), which should not be included in the scaling process. The relative changes in these

Table 1
CASSCF and CAS-DFT energies for the ring opening of dioxirane calculated with the 6-311 + G(2df, 2pd) basis ^a

Method	E(1)	Corr. contr.	%	ΔE (TS(1-2))	ΔE (2)
CASSCF	-188.72704			10.5	1.9
CASSCF + C	-189.55435	827.31	100	16.9	8.8
CASSCF + fC	-189.50275	51.60	6	13.1	4.4
CAS-DFT	-189.52796	25.21	3	17.4	7.4
Correction		5.90	< 1		3.4
MR-AQCC	-189.33736			20.3	4.6
error				-2.9	-1.2

^a Absolute energies in hartree, correlation contributions (Corr. contr.) in mhartree, relative energies in kcal/mol. Scaling, core and open-shell corrections are given in% of the total DFT correction. The CASSCF calculations have been done in a (6,4) active space at B3LYP/6-311 + G(2df, 2pd) geometries (**1**: $r(\text{OO}) = 1.541$; $r(\text{CO}) = 1.400$; $r(\text{CH}) = 1.080$ Å; $\alpha(\text{HCH}) = 115.7^\circ$; **TS(1-2)**: $r(\text{OO}) = 2.103$; $r(\text{CO}) = 1.377$; $r(\text{CH}) = 1.087$ Å; $\alpha(\text{HCH}) = 110.7^\circ$; **2**: $r(\text{OO}) = 2.370$; $r(\text{CO}) = 1.379$; $r(\text{CH}) = 1.089$ Å; $\alpha(\text{HCH}) = 109.2^\circ$). The MR-AQCC result was taken from Ref. [29].

Table 2
 CASSCF(6, 6) and CAS(6, 6)-DFT energies for the three lowest states of methylene ^a

Method	Basis set	³ B ₁	Corr. contr.	%	¹ A ₁	¹ B ₁
CASSCF	cc-pVDZ	-38.96057			11.9	43.7
	cc-pVTZ	-38.97092			10.5	41.1
	cc-pVQZ	-38.97355			10.2	40.6
CASSCF + C	cc-pVDZ	-39.16702	206.45		6.4	34.1
	cc-pVTZ	-39.17730	206.38		5.4	32.4
	cc-pVQZ	-39.17980	206.25		5.2	32.1
CASSCF + fC	cc-pVDZ	-39.10805	59.97	28.6	8.1	37.3
	cc-pVTZ	-39.11816	59.14	28.6	6.9	35.1
	cc-pVQZ	-39.12078	59.02	28.6	6.6	34.7
CAS-DFT	cc-pVDZ	-39.11043	2.38	1.1	8.0	37.4
	cc-pVTZ	-39.12067	2.51	1.2	6.9	35.2
	cc-pVQZ	-39.12321	2.43	1.1	6.6	34.8
Expt.					8.7 ± 0.5 ^b	33.4 ^c

^a Absolute energies in hartree, correlation contributions (Corr. contr. in mhartree, relative energies in kcal/mol). Scaling and core corrections are given in% of the total DFT correction. CASSCF(6, 6)/cc-pVDZ geometries were used (³B₁: *r*(CH) = 1.102 Å, α(HCH) = 131.0°; ¹A₁: *r*(CH) = 1.138 Å, α(HCH) = 100.0°; ¹B₁: *r*(CH) = 1.103 Å, α(HCH) = 134.1°).

^b Ref. [35].

^c Ref. [36].

core correlations are significant since they are larger for the closed-shell system **1**, which has more electron pairs. Accordingly, they increase both barrier (by 4.3 kcal/mol) and reaction energy (by 3.0 kcal/mol, Table 1) without being able to compensate the error made for biradical **2**. Including an empirical correction of 4 kcal/mol (Table 1), both barrier and reaction energy are slightly underestimated (by 2.9 and 1.2 kcal/mol), which is reasonable in view of the fact that a larger active space would lead to an increase of the energy parameters.

Table 2 lists full-valence CASSCF and CAS-DFT energies for the three lowest states of the methylene

molecule **3** (³B₁, ¹A₁, ¹B₁). The two lowest S–T splittings of methylene represent challenging calculational problems, which can only be described correctly using advanced ab initio methods [31–33]. For the CAS-DFT calculations, we applied Dunning's cc-pVDZ, cc-pVTZ, and cc-pVQZ basis sets [34] to study the influence of the basis set.

The CASSCF calculations overestimate both the ¹A₁–³B₁ and the ¹B₁–³B₁ splittings. The ¹A₁ state has a doubly occupied a₁ orbital (see Fig. 3) and ¹B₁ has a singlet coupling between the electrons in the a₁ and b₁ orbitals. Hence, these states have stronger dynamic correlations than the ³B₁ state, for which

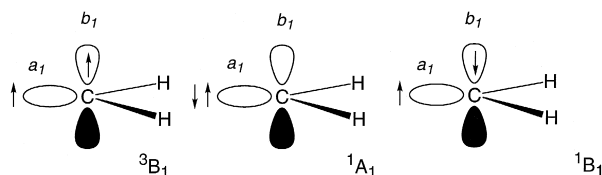


Fig. 3. Schematic drawing of the three lowest states (³B₁, ¹A₁, and ¹B₁) of methylene. The occupation of the a₁ and b₁ molecular orbitals is indicated.

the electrons in the a_1 and b_1 orbitals couple to a triplet. This gives rise to the error in the CASSCF description. The error is considerably larger for the $^1B_1-^3B_1$ splitting than for the $^1B_1-^1A_1$ splitting, which may indicate that CASSCF covers for the 1A_1 state a larger part of the dynamic correlation energy than in the other two cases.

The DFT correlation correction is almost independent of the basis set (206 mhartree, Table 2), which is also true for the scaling and the core correction and reflects the fact that DFT in general has a small basis set truncation error. When the DFT correction in CASSCF + C is added, the $^1A_1-^3B_1$ splitting is underestimated by 3.5 kcal/mol for the cc-pVQZ basis. This is in line with the conjecture that a part of the dynamic correlation energy in the 1A_1 is already covered by the CASSCF description and is thus counted doubly at the CASSCF + C level. The $^1B_1-^3B_1$ splitting at the CASSCF + C level is underestimated by 1.3 kcal/mol for the cc-pVQZ basis. The 1B_1 and 3B_1 states have the same electron configuration and differ only in multiplicity, so it is plausible that double counting of energies affects them in a similar way thus leading to error compensation.

The scaling of the DFT correlation energy at the CASSCF + fC level reduces the correlation energy by $\sim 30\%$ (60 mhartree, Table 2) and, by this, the exaggeration of dynamic correlation thus increasing the splittings. The $^1B_1-^3B_1$ splitting is by 1.3 kcal/mol too large. The $^1A_1-^3B_1$ splitting agrees now better with the experimental value, however, it still deviates by 2.1 kcal/mol. Again, this deviation indicates an inconsistency in the determination of the scaling factor f that systematically underestimates the correlation energy in open-shell systems compared to that of closed-shell ones. This becomes clear when considering a set of CAS-DFT(2,2) calculations for the three states of CH_2 with the active space being spanned by the a_1 and b_1 orbitals. For the 1A_1 state, the scaling factor gives a correct account of the correlation energy covered by CASSCF(2,2). For the 3B_1 and 1B_1 states, in distinction, the CASSCF(2,2) calculations are equivalent to restricted open-shell HF calculations, which means that CASSCF does not contain any correlation energy and the scaling factor should be equal to one. However, the two singly occupied orbitals lead to $q < q_{ref}$ and hence $f < 1$ (see Eqs. (9) and (10)). The

correlation energy in the two open-shell states is thus underestimated, which of course will also, although less pronounced, occur in CASSCF calculations with larger active spaces. The deviation for the $^1A_1-^3B_1$ splitting due to this error is ~ 2 kcal/mol and also explains the overestimation of the $^1B_1-^3B_1$ splitting: dynamic correlation effects are stronger in the 1B_1 than the 3B_1 state, hence the 1B_1 should be affected more strongly by the underestimation of the DFT correlation energy. For a further improvement of the CAS-DFT method, a way to determine f should be found that takes the differences between closed-shell and open-shell systems into account.

The $E_{C,core}^{CAS-DFT}$ terms contribute with at most 0.1 kcal/mol to the energy splittings in line with the fact that the inactive space contains only the C 1s electron and that the chemical environment of the C atom is similar in all three cases.

4. Conclusions and outlook

CAS-DFT provides a description for both static and dynamic correlation effects at moderate computational costs. The proper separation of dynamic correlations covered by the CASSCF method and the DFT term is one of the crucial questions within CAS-DFT. The approach proposed by Savin [16] and MSS [20] gives a good starting point for such a separation. It is, however, necessary to distinguish not only between active and virtual orbitals but also between active and inactive orbitals, in particular when systems with many inactive orbitals are considered that may change in the course of a chemical reaction. CAS-DFT provides reasonable accuracy for multi-reference problems at low additional cost as discussed in this work. A possible simplification is given by the fact that the DFT correlation energy corrections are almost independent of the basis set used and can be satisfactorily determined at the VDZP or VTZP level of theory. For the CASSCF step calculations with a large basis set are necessary as typical of all wavefunction-based correlation methods. However, one can add correlation corrections to the CASSCF result obtained in a cheap way with a smaller basis set.

An important task for future work is to modify the definition of the scaling factor f so that it describes

closed- and open-shell states in a more balanced way.

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