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Investigation of a hybrid TCSCF-DFT procedure

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Abstract. In this work a family of hybrid TCSCF-DFT procedures for treating inherently two-configurational species is introduced and applied to the low-lying singlet and triplet states of B_2 and C_2H_4. The hybrid procedures permit self-consistent determination of the orbitals in both the TCSCF and Kohn-Sham subspaces.

Key words: Density functional theory –
Two-configurational self-consistent field

1 Introduction

Electronic structure methods capable of providing "chemical accuracy" for ground and electronically excited states must include both dynamical and non-dynamical correlation effects. This has led to the development of multireference-based procedures, the most popular of which are multireference configuration interaction with single and double excitations (MRSDCI) [1, 2], multireference second-order perturbation theory (CASPT2) [3, 4] and multireference coupled cluster (MRCC) methods [5, 6]. All three of these approaches can be used to calculate the properties of small molecules, accurately but due to the steep scaling of the computational cost with the number of electrons correlated, they cannot be used for large systems.

Density functional theory (DFT) has proven to be a reliable and inexpensive approach for describing dynamical correlation [7–10] and is applicable to systems containing up to several hundred atoms. In this approach, the exchange-correlation energy is computed as the integral of a functional of the electron density (and in some cases also the gradient of the density). However, most implementations of DFT are based on the Kohn-Sham approach [8] in which a wavefunction given by a single Slater determinant is introduced for purposes of representing the density in terms of orbital contributions. As a result, with existing functionals, DFT calculations tend to be unreliable for states that are inherently multiconfigurational (in a wavefunction treatment). Two well-known problem cases for DFT are singlet excited states of the form $\frac{1}{\sqrt{2}}(|\ldots t\bar{u}\rangle - |\ldots \bar{t}u\rangle)$ and singlet diradicals with nearly equal weights of the two configurations $|\ldots (t)^2\rangle$ and $|\ldots (u)^2\rangle$ [11–13]. Extensions of DFT to treat such states are of considerable interest. One possible approach is to combine the multiconfigurational self-consistent field (MCSCF) method with DFT in such a way that the near-degeneracy effects are handled through the MCSCF procedure and the majority of the dynamical correlation energy through DFT. One such approach was recently introduced by Malcolm and McDouall [14]. In their MCSCF-DFT procedure the total energy, E^{MM}, was expressed as the sum of the MCSCF energy and a correction term,

$$E^{\mathrm{MM}} = E^{\mathrm{MCSCF}} + E^{\mathrm{corr}} \ , \tag{1}$$

with the correction term, E^{corr}, being defined as

$$E^{\mathrm{corr}} = C^t - C^v \ . \tag{2}$$

In Eq. (2), C^t and C^v are correlation energies computed using standard correlation functionals and employing the total (t) and valence (v) electron densities, respectively. (Here, "valence" is taken to be synonymous with "active" in an MCSCF sense.) This approach is not self-consistent in that the MCSCF orbitals and MCSCF energy are not influenced by the correlation of the core electrons or by the core-valence coupling. In the present study, we describe and test a family of self-consistent MCSCF-DFT procedures, focusing on the special case that the MCSCF space is two-configurational in nature.

2 Theory

In this work we find it convenient to start with a purely MCSCF representation in which there is a set of "core" (inactive) orbitals that are doubly occupied in all configurations and a set of "valence" (active) orbitals with variable occupancy, in keeping with the terminology of Malcolm and McDouall [14]. The so-called

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valence space need not include all valence orbitals in the usual sense. The total MCSCF energy can be written in the form:

$$
\begin{aligned}
E^{\mathrm{MCSCF}} &= E^{c} + E^{v} + E^{cpl} \\
&= h^{c} + J^{c} - K^{c} + h^{v} + J^{v} - K^{v} + J^{cpl} - K^{cpl} ,
\end{aligned}
\tag{3}
$$

where h denotes a one-electron contribution, and J and K denote MCSCF Coulomb and exchange energies, respectively. The superscripts c, v and cpl refer, respectively, to core, valence and coupling contributions to the energy.

For simplicity, we specialize to singlet states described by the two-configurational SCF (TCSCF) wavefunction

$$
|\Psi_{\mathrm{TCSCF}}\rangle = c_t|\ldots(t)^2\rangle + c_u|\ldots(u)^2\rangle \ . \tag{4}
$$

Because of the importance of the singlet-triplet splittings in such systems, we also consider the triplet states described by the restricted open-shell SCF (ROSCF) wavefunction

$$
|\Psi_{\mathrm{ROSCF}}\rangle = |\ldots(t)^1(u)^1\rangle \ . \tag{5}
$$

The energy of the two-configurational singlet state can be expressed as

$$
\begin{aligned}
E^{\mathrm{TCSCF}} = &\sum_i 2h_{ii} + \sum_{ij}(2J_{ij} - K_{ij}) \\
&+ \sum_v^{t,u} c_v^2(2h_{vv} + 2J_{vv} - K_{vv}) + 2c_t c_u K_{tu} \\
&+ 2\sum_v^{t,u} c_v^2 \sum_i (2J_{iv} - K_{iv}) \ ,
\end{aligned}
\tag{6}
$$

with the Euler equations for the optimal orbitals being

$$
\begin{aligned}
&\left\{\hat{h} + \sum_j (2\hat{J}_j - \hat{K}_j) + \sum_v^{t,u} c_v^2 (2\hat{J}_v - \hat{K}_v)\right\}\varphi_i \\
&\quad = \sum_p \varphi_p \epsilon_{pi}, \ \text{for core orbitals}, \\
&\left\{c_v^2\left[\hat{h} + \hat{J}_v + \sum_j (2\hat{J}_j - \hat{K}_j)\right] + c_t c_u \hat{K}_{v-}\right\}\varphi_v \\
&\quad = \sum_p \varphi_p \epsilon_{pv}, \ \text{for } v = t, u \ .
\end{aligned}
\tag{7}
$$

For the triplet state, as described by the ROSCF wavefunction, the energy and orbital equations are given by:

$$
\begin{aligned}
E^{\mathrm{ROSCF}} = &\sum_i 2h_{ii} + \sum_{ij}(2J_{ij} - K_{ij}) \\
&+ \sum_v^{t,u} \frac{1}{2}(2h_{vv} + J_{vv} - K_{vv}) \\
&+ J_{tu} - K_{tu} \ 2\sum_v^{t,u} \frac{1}{2} \sum_i (2J_{iv} - K_{iv}) \ ,
\end{aligned}
\tag{8}
$$

$$
\begin{aligned}
&\left\{\hat{h} + \sum_j (2\hat{J}_j - \hat{K}_j) + \sum_v^{t,u} \frac{1}{2}(2\hat{J}_v - \hat{K}_v)\right\}\varphi_i \\
&\quad = \sum_p \varphi_p \epsilon_{pi}, \ \text{for core orbitals} \ , \\
&\left\{\frac{1}{2}\left[\hat{h} + \sum_j (2\hat{J}_j - \hat{K}_j) + \hat{J}_{v-} - \hat{K}_{v-}\right]\right\}\varphi_v \\
&\quad = \sum_p \varphi_p \epsilon_{pv}, \ \text{for } v = t, u \ .
\end{aligned}
\tag{9}
$$

In Eqs. (6–9) the subscripts $i, j, k \ldots$ refer to core orbitals, the subscripts $t, u, v \ldots$ refer to valence orbitals, and $v^- = t$ for $v = u$, and $v^- = u$ for $v = t$. The summations on the right-hand sides of Eqs. (7) and (9) run over both core and valence orbitals, and the ϵ_{pq} are Lagrange multipliers.

In the first proposed TCSCF-DFT procedure, the electrons in the valence subspace are treated at the TCSCF/ROSCF level, with E^v being computed as $h^v + J^v - K^v$, as in Eqs. (6) and (8), but with the core exchange-correlation energy and the core-valence (i.e., coupling) exchange-correlation energy being calculated within a density functional framework. The core exchange-correlation energy is computed from $(XC)^c = X(\rho^c) + C(\rho^c)$, where X and C denote the exchange and correlation contributions to the energy, calculated using the core density, (ρ^c), and available exchange and correlation functionals. The coupling between the two subspaces can be formally partitioned into Coulomb, exchange and correlation terms. The Coulomb coupling term, J^{cpl}, is well defined in terms of the classical r^{-1} interaction between the Kohn-Sham and TCSCF/ROSCF charge distributions, and the exchange-correlation coupling is denoted as $(XC)^{cpl}$. (Hereafter, we will use TCSCF to denote both TCSCF for singlet states and ROSCF for triplet states when the meaning is clear.) This gives the following expression for the total energy:

$$
E^{\mathrm{TCSCF-DFT}} = h^c + J^c + (XC)^c + E^v + J^{cpl} + (XC)^{cpl} \ . \tag{10}
$$

To proceed further it is necessary to devise a strategy for evaluating $(XC)^{cpl}$. Here this is accomplished by use of the expression

$$
(XC)^{cpl} = (XC)^t - (XC)^c - (XC)^v \ , \tag{11}
$$

where, as before, the superscripts c, v and t refer to the contributions due to the core, valence, and total densities, respectively. The total energy can then be written as:

$$
E^{\mathrm{I}} = h^c + J^c + E^v + J^{cpl} + (X^t - X^v) + (C^t - C^v) \ , \tag{12}
$$

or

$$
E^{\mathrm{I}} = h^c + J^c + X^c + E^v + J^{cpl} + X^{cpl} + (C^t - C^v) \ . \tag{13}
$$

The main shortcoming of this approach is that Eq. (11), which expresses the exchange-correlation coupling in terms of contributions involving the core, valence, and total densities, is not rigorously valid when using standard exchange-correlation functionals. Use of Eq. (11) is expected to be more problematical for the exchange coupling than for the correlation coupling. This suggests alternative energy expressions, E^{II} and E^{III}. In E^{III} both the core exchange energy and the coupling exchange energy are calculated using integrals over orbitals, whereas in E^{II} only the coupling exchange energy is calculated using integrals over orbitals. In both these approaches the core and coupling correlation contributions are calculated as in E^{I}. This gives:

$$E^{\mathrm{II}} = h^c + J^c + X^c + E^v + J^{cpl} - K^{cpl} + (C^t - C^v) \ . \qquad (14)$$

and

$$E^{\mathrm{III}} = h^c + J^c - K^c + E^v + J^{cpl} - K^{cpl} + (C^t - C^v) \ , \qquad (15)$$

E^{III} may be viewed as the self-consistent generalization of the Malcolm and McDouall expression for the energy.

The last expression for the energy, E^{IV}, is defined as

$$E^{\mathrm{IV}} = h^c + J^c + (XC)^c + E^v + J^{cpl} - K^{cpl} \ . \qquad (16)$$

This is obtained from E^{III} by neglecting the correlation contribution to the coupling term. A summary of the treatment of the various contributions to the energy in the different functionals is given in Table 1.

Minimization of the above functionals is straightforward. For example, using the TCSCF description of the singlet state given in Eq. (4), the operator equations appropriate for E^{I} are:

$$\begin{aligned} &\left\{ \hat{h} + \sum_j 2\hat{J}_j + \hat{f}^c_{XC} + 2\sum_v^{t,u} c_v^2 \hat{J}_v + \hat{f}^{cpl,c}_{XC} \right\} \varphi_i \\ &\quad = \sum_p \varphi_p \epsilon_{pi}, \ \text{for core orbitals} \ , \\ &\left\{ c_v^2 \left[\hat{h} + \hat{J}_v + \sum_j 2\hat{J}_j \right] + c_t c_u \hat{K}_{v-} + c_v^2 \hat{f}^{cpl,v}_{XC} \right\} \varphi_v \\ &\quad = \sum_p \varphi_p \epsilon_{pv}, \ \text{for } v = t, u \ , \end{aligned} \qquad (17)$$

where

$$\hat{f}^c_{XC} = \frac{\delta E_{XC}(\rho^c)}{\delta \rho^c} \ , \qquad (18)$$

$$\hat{f}^{cpl,c}_{XC} = \frac{\delta E_{XC}(\rho^t)}{\delta \rho^t} - \frac{\delta E_{XC}(\rho^c)}{\delta \rho^c} \qquad (19)$$

and

$$\hat{f}^{cpl,v}_{XC} = \frac{\delta E_{XC}(\rho^t)}{\delta \rho^t} - \frac{\delta E_{XC}(\rho^v)}{\delta \rho^v} \ . \qquad (20)$$

The corresponding equations for the triplet state are similar, except that the exchange and correlation energies are now functionals of ρ^α and ρ^β, the α and β spin densities, respectively. Similar operator equations can be derived for the other energy functionals. The "CI vector" for the singlet state is found by minimizing the relevant functional with respect to the rotational parameter λ, defined as $c_t = \cos\lambda$, $c_u = \sin\lambda$. A spin-restricted formulation is adopted for the triplet case.

In addition to the limitation of using Eq. (11) with standard functionals to represent the exchange-correlation (in E^{I}) and the correlation coupling (in E^{II} and E^{III}), the TCSCF-DFT formulations outlined above are unbalanced in that they neglect dynamical correlation between the active electrons. This problem can be remedied, to some extent, by increasing the number of the virtual orbitals in the valence space.

Table 1. Treatment of the various contributions to the energy for $E^{\mathrm{I}} - E^{\mathrm{IV}}$ expressions. Exchange interactions designated with "Integral" were evaluated by doing integrals over the appropriate orbitals

	Core exchange	Core correlation	Exchange coupling	Correlation coupling
E^{I}	DFT	DFT	DFT	DFT
E^{II}	DFT	DFT	Integral	DFT
E^{III}	Integral	DFT	Integral	DFT
E^{IV}	DFT	DFT	Integral	–

3 Applications

3.1 Computational details

The TCSCF-DFT approaches described above have been tested on the boron dimer (B_2) and ethylene (C_2H_4). The DFT and TCSCF-DFT calculations were carried out using a modified version of the NWChem electronic structure code [15], and made use of the BeckeLYP exchange-correlation functional, comprised of the Becke88 [16] exchange functional and the LYP [17] correlation functional.

For B_2, the triplet $|\ldots\pi_x\pi_y\rangle$ and singlet $\frac{1}{\sqrt{2}}(|\ldots(\pi_x)^2\rangle - |\ldots(\pi_y)^2\rangle)$ states were considered. (The internuclear axis was taken to be in the z direction). For each theoretical method, the geometries of the two states were optimized by carrying out calculations over a grid of bond lengths, and the singlet-triplet splittings were calculated using these optimized geometries. In addition, force constants were obtained by means of numerical differentiation of the energy. The energy separations, the bond lengths and force constants from the TCSCF-DFT calculations are compared to those of TCSCF (singlet)/ROSCF (triplet), and TCSCF + PT2/ROSCF + PT2 calculations. (Hereafter, we use the term TCSCF-DFT to refer to the methodology for describing both the singlet and triplet states.) The PT2 correction in the case of the singlet state is based on two reference configurations, i.e, it is obtained from a two-reference CASPT2 calculation. Both the 6-31G* [18–20] and aug-cc-pVDZ [21, 22] basis sets were employed.

For C_2H_4, the lowest energy singlet ($|\ldots(\pi)^2\rangle$) and triplet ($|\ldots\pi\pi^*\rangle$) states were considered. For the singlet state explicit mixing with the $|\ldots(\pi^*)^2\rangle$ configuration was included. These calculations were carried using the 6-31G* basis set and the MP2/6-31G* optimized geometry of the singlet state. The energy separations from the TCSCF-DFT calculations are compared with the results of TCSCF/ROSCF, TCSCF + PT2/ROSCF + PT2, and traditional DFT calculations, as well as with experiment.

As mentioned above, TCSCF-DFT calculations with the active spaces used here neglect dynamical correlation between the valence (active) electrons. The importance of active-space correlation on the properties of interest can be estimated by performing CASPT2 calculations using TCSCF/ROSCF reference functions but correlating only the two active electrons, and comparing the results of these calculations with those obtained from TCSCF/ROSCF calculations. The contributions of active space correlation on the bond lengths, force constants, and singlet-triplet gaps are then subtracted from the results of the TCSCF + PT2/ROSCF + PT2 calculations with all orbitals other than the inner 1*s* orbitals correlated in order to obtain estimates of the various properties in the absence of correlation of the two active orbitals. These results are denoted PT2-a. For the systems considered here, the TCSCF + PT2 and PT2-a procedures give similar results.

3.2 Results and discussion

3.2.1 B_2

The bond lengths, force constants, and singlet-triplet separations of B_2 calculated at the different levels of theory are summarized in Table 2. Considering first the results for the bond lengths and force constants, we note that the best agreement with the PT2-a predictions is provided by the E^{IV} energy expression. On the other hand, the E^{I} expression gives bond lengths and force constants in closest agreement with the PT2 predictions. Of the four energy expressions considered only E^{IV} gives a singlet-triplet splitting in good agreement with the PT2 and PT2-a calculations. In fact, the E^{IV} value of the splitting is within a few hundredths of an eV of the PT2-a result. The calculations with the E^{II} and E^{III} energy expressions overestimate the singlet-triplet splitting by 0.34–0.37 eV (as compared to the PT2-a result), while that with the E^{I} expression underestimates it by 0.75 eV.

3.2.2 C_2H_4

Table 3 summarizes for C_2H_4 the vertical singlet-triplet excitation energies obtained with the various theoretical methods. The experimental values of the vertical singlet-triplet splitting in ethylene range between 4.2 and 4.4 eV [23, 24]. This has been verified by high-level ab initio calculations [25]. DFT calculations with the BLYP functional give a singlet-triplet splitting 0.3–0.6 eV larger than experiment. The TCSCF-DFT calculations with the E^{I}–E^{III} expressions give even larger singlet-triplet splittings than obtained from the BLYP calculations, with the error being greatest for E^{I}. The E^{IV} energy expression fares best overall, giving a singlet-triplet splitting within 0.2 eV of both the PT2 and PT2-a values of the splitting and also within 0.2 eV of the experimental splitting.

3.2.3 General remarks

Because E^{I} approximates $(X)^{cpl}$ as $(X)^{t} - (X)^{c} - (X)^{v}$, and because E^{IV} neglects the core-valence correlation, our expectation was that the E^{II} and E^{III} expressions would perform the best. However, our calculations on B_2 and C_2H_4 reveal that E^{II} and E^{III} expressions overestimate the singlet-triplet splittings by a few tenths of an eV (and, in fact, fare somewhat more poorly than does the TCSCF/ROSCF approach) and, moreover, that E^{IV} performs best overall.

There are several sources of error in the present TCSCF-DFT approaches, including (1) neglect of the dynamical correlation in the valence space, (2) the simplified treatment of the exchange coupling between two subspaces, and (3) use of the standard exchange-corre-

Table 2. Equilibrium bond length, r_e (Å), and force constants, f'' (a.u./Å^2), of the triplet $|\ldots\pi_x\pi_y\rangle$ and singlet $\frac{1}{2}(|\ldots(\pi_x)^2\rangle - |\ldots(\pi_y)^2\rangle)$ states of B_2, and the energy gaps ΔE (eV) between these states

	Singlet		Triplet		
	r_e	f''	r_e	f''	ΔE[a]
6-31G* basis set					
TCSCF/ROSCF	1.658	0.64	1.635	0.70	0.85
+ PT2(2-el)[b]	1.671	0.58	1.643	0.66	0.72
+ PT2[c]	1.609	0.87	1.591	0.92	0.75
+ PT2-a[d]	1.596	0.93	1.583	0.96	0.88
E^{I}	1.609	0.85	1.599	0.89	0.13
E^{II}	1.590	0.91	1.570	0.97	1.23
E^{III}	1.631	0.71	1.607	0.77	1.22
E^{IV}	1.595	0.89	1.578	0.93	0.88
aug-cc-pVDZ basis set					
TCSCF/ROSCF	1.677	0.58	1.651	0.65	0.84
+ PT2(2-el)[b]	1.691	0.52	1.659	0.62	0.70
+ PT2[c]	1.637	0.80	1.617	0.86	0.69
+ PT2-a[d]	1.623	0.86	1.609	0.89	0.83
E^{I}	1.625	0.81	1.615	0.85	0.11
E^{II}	1.604	0.87	1.582	0.92	1.20
E^{III}	1.648	0.67	1.621	0.74	1.19
E^{IV}	1.611	0.85	1.592	0.90	0.86

[a] A plus sign implies that the triplet lies below the singlet state.

[b] Only the two π electrons are correlated.

[c] All but the 1*s* electrons are correlated.

[d] Calculated by adding the TCSCF/ROSCF results to the difference of the PT2 and PT2(2-el) results.

Table 3. Vertical excitation energies (eV) from the ground state singlet to the excited $\pi \rightarrow \pi^*$ triplet state of ethylene[a]

	ΔE
SCF/ROSCF	3.74
TCSCF/ROSCF	4.51
+PT2(2-el)[b]	4.63
+PT2[c]	4.75
+PT2-a[d]	4.63
DFT(S)/DFT(T)[e]	4.77
DFT(S)/RODFT(T)[e]	4.84
E^{I}	5.65
E^{II}	4.99
E^{III}	4.99
E^{IV}	4.52
Expt.[f]	4.36

[a] Theoretical results obtained using the 6-31G* basis set
[b] Only the two π electrons are correlated
[c] All but 1s electrons are correlated
[d] See, footnote d of Table 2.
[e] Standard Kohn-Sham DFT calculations
[f] Ref. [23]

lation functionals with partial (i.e., core and valence) densities. As shown in Tables 2 and 3, the first shortcoming is relatively unimportant for the systems considered in this work.

4 Other considerations and extensions

For the energy expressions considered here, the core electrons are described by Kohn-Sham orbitals and the valence electrons by TCSCF orbitals[1]. In general, optimization of the TCSCF-DFT energy expression involves mixing of the orbitals between subspaces. The orbital rotational parameters κ_{pq} defined as

$$\{\varphi^{\mathrm{final}}\} = \{\varphi^{\mathrm{initial}}\}\exp(\kappa), \qquad \kappa = -\kappa^T \tag{21}$$

coupling the Kohn-Sham and TCSCF orbitals are nonredundant. As a result, the gradient of the energy with respect to these parameters is not necessarily zero for non-converged solutions. Inclusion of the core-valence rotations in the orbital optimization procedure results in a mixing between the two subspaces which might lead to "unphysical" results, e.g., switching between valence and core orbitals. For the B_2 and C_2H_4 examples, the valence spaces were chosen to involve π-type orbitals and the core spaces only σ-type orbitals. Thus, for these cases mixing between orbitals in the two subspaces does not occur for symmetry reasons. However, in general, such a "separation" is not possible. Consider, for example, the methylene molecule for which the minimal active space for describing the singlet ground state contains one σ orbital (the carbon lone pair in the singlet state) and a π orbital, perpendicular to the molecular plane. Since the inactive space contains σ orbitals, inactive-active mixing occurs. In exploratory calculations on CH_2, we have found that the core-valence rotational parameters become quite large for the E^{I}, E^{III}, and E^{IV} energy expressions. This problem was less severe with the E^{II} expression, which employs an exact treatment of the core, valence, and coupling exchange. The E^{II} expression gave a singlet-triplet separation of 14.1 kcal/mol, which after correcting for valence correlation becomes 9.5 kcal/mol, in good agreement with the experimental energy separation of 9.0 kcal/mol [26].

In order to obtain a better understanding of the general usefulness of the MCSCF-DFT strategy described in this study, it will be necessary to extend it to include correlation of the valence (active) orbitals. This could be accomplished by increasing the number of the virtual orbitals in the valence space. An alternative, but less straightforward, approach would require developing exchange-correlation functionals for calculating the valence correlation.

The description of the coupling exchange by computing two-electron integrals over the Kohn-Sham and MCSCF orbitals appears to work well, but it would be preferable to formulate it as DFT-like exchange in order to avoid calculation of the four-center two-electron integrals. In addition, it would be desirable to derive a more accurate description of the core and core-valence correlation than is afforded by $C^t - C^v$.

5 Conclusions

A family of self-consistent TCSCF-DFT procedures have been described and applied to determine equilibrium bond lengths and force constants of B_2 and singlet-triplet splittings of B_2 and C_2H_4. The reference spaces were chosen to be two-configurational (TCSCF) for the singlet states and single configurational (ROSCF) for the triplet states. The singlet state considered for B_2 is inherently two-configurational and cannot be described in an ordinary DFT approach. The E^{IV} expression is found to perform the best overall, yielding both singlet-triplet gaps and structural information in excellent agreement with the PT2 and PT2-a predictions. Fair results are also obtained from the E^{II} expression. As anticipated, the poorest results are provided by the E^{I} expression.

For the two applications considered here, the calculations using the E^{III} expression give nearly the same singlet-triplet separations as the Malcolm-McDouall approach, using the same 2-electron active space. Thus, in these two applications, the self-consistency afforded by the present MC-DFT implementation proved not to be important.

To assess the reliability of the proposed MCSCF-DFT algorithms better, it will be necessary to include dynamical electron correlation in the valence space, either by including additional virtual orbitals or through a correlation functional designed for that purpose, and to develop functionals appropriate for describing core-valence exchange interactions.

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[1] For the E^{II} expression, the core exchange energy is calculated as an integral over orbitals, rather than over an exchange functional, so in this case the core orbitals are not actual Kohn-Sham orbitals.

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