A spin-restricted ensemble-referenced Kohn–Sham method and its application to diradicaloid situations

Michael Filatov [1], Sason Shaik [*]

The Institute of Chemistry and the Lise Meitner-Minerva Centre for Computational Quantum Chemistry, The Hebrew University, 91904 Jerusalem, Israel

Abstract

The energy and density of situations with strong non-dynamic correlation are formulated as weighted sums (ensembles) of energies and densities of symmetry-adapted reference KS determinants. A computational scheme termed the spin-restricted ensemble-referenced Kohn–Sham (REKS) method is devised for these cases. An optimal set of orthonormal one-electron orbitals and their optimal occupation numbers are obtained from minimization of the ground state energy with respect to the density. The REKS method is applied to several model problems, rotation in C_2H_4, dissociation of H_2, and the singlet-triplet energy gaps in substituted trimethylene diradicals. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

Density functional theory (DFT) [1–3] has become one of the most popular tools in computational quantum chemistry. While density functionals simulate quite well [4], albeit in a somewhat unspecified way, dynamic many-particle correlations, they encounter problems [5,6] in accounting for non-dynamic correlation due to degeneracy or near-degeneracy of several electronic configurations. Strong non-dynamic correlation is ubiquitous and appears in bond-breaking processes, in bond rearrangements at transition points (avoided crossing), in fractionally occupied degenerate electronic configurations, in many excited states, etc. Generally such correlations are spin and spatial symmetry-dependent and as such are specific for different symmetry situations. This specificity makes it difficult (if ever possible) to describe the static electron correlation problem with a single universal density functional.

The idea to simulate strong non-dynamic correlation by fractional occupation numbers (FONs) of degenerate or nearly degenerate orbitals was first introduced by Slater et al. [7]. Subsequently, the idea has been explored in a DFT–FON approach and applied to small molecules [8,9] and metal clusters [10]. The FON notion rests on a firm basis in cases when the ground state density has to be represented by a weighted sum (ensemble) of single determinant densities [3,11,12]. Thus, by constructing a nearly exact Kohn–Sham (KS) potential for C_2 from accurate ab initio MR–CI densities it was demonstrated that this density cannot be fitted to a KS formulation

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[*] Corresponding author. Fax: +972 26 585345; e-mail: sason@yfaat.ch.huji.ac.il
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unless the $1\pi_u$ and $3\sigma_g$ orbitals are taken with fractional occupations [13]. These computational simulations show unambiguously that the true density in systems with strong correlation can be represented with fractional occupation numbers [13]. [2]

The most conventional density functionals do not explicitly incorporate spin and spatial symmetry constraints. Hence, when fractionally occupied one-electron orbitals are used, these functionals yield energy of some configurationally averaged state and not of the state of desired spin and spatial symmetry [10]. The present Letter tackles the problem and introduces a computational scheme based on the ensemble representation of the ground state density and capable of handling states of pure spin and spatial symmetry, using the conventional and widely available density functionals. The scheme relies on our symmetry-adapted spin-restricted open-shell Kohn–Sham method [15,16] that is extended in a fully variational form to handle situations with strong non-dynamic correlation. Our considerations will be limited to systems possessing only two degenerate or nearly degenerate electronic configurations, such as diradicals, diradicaloid transition states, stretched σ-bonded molecules, etc. In Section 2, we briefly outline the principles of the approach while the associated equations are collected in Appendix A. In Section 3 the method is applied to bond-breaking in model systems (dissociation of H_2 and rotation in ethylene, and to substituted trimethylene diradicals).

2. Methodology

Consider a system, atom or molecule, with two degenerate or nearly degenerate electronic configurations, $(\ldots\phi_r^2\phi_s^0)$ and $(\ldots\phi_r^0\phi_s^2)$. For the sake of convenience, it is assumed that the orbitals ϕ_r and ϕ_s belong to different irreducible representations in the respective molecular symmetry group. In such a system with strong non-dynamic correlation, the ground state density can be represented as a weighted sum of densities of individual configurations [13]:

$$\rho_{g.s.}(\boldsymbol{r}) = \frac{n_r}{2}\rho(\phi_r^2\phi_s^0) + \frac{n_s}{2}\rho(\phi_r^0\phi_s^2);$$

$$n_r + n_s = 2; \qquad n_r, n_s \geq 0. \qquad (1)$$

The weighting factors n_r and n_s in Eq. (1) can be viewed as fractional occupation numbers (FONs) of the orbitals ϕ_r and ϕ_s in the ground state density.

In a situation where the configurations, $(\ldots\phi_r^2\phi_s^0)$ and $(\ldots\phi_r^0\phi_s^2)$, are strictly degenerate due to symmetry, the occupation numbers should be equal to one another to ensure totally symmetric ground state density as required by symmetrized Kohn–Sham theory [17,18]. In DFT calculations with FONs (DFT–FON) [7–10] the occupation numbers are obtained from minimization of the energy with respect to these numbers. The minimization can result in 'canonical' values of n_r and n_s, zero or two, or can lead to fractional occupations which deviate substantially from the 'canonical' values [8–10]. It is important to note, however, that the variational principle cannot be obeyed for an arbitrary variation in occupation numbers, but only for ensemble representable densities like Eq. (1) [14].

In the DFT–FON approach, inserting the density from Eq. (1) into the DFT energy expression one can derive [9] for the ground state energy Eq. (2):

$$E_{g.s.} = \frac{n_r}{2}E(\phi_r\overline{\phi}_r) + \frac{n_s}{2}E(\phi_s\overline{\phi}_s)$$

$$+ n_r n_s R(\rho_{g.s.}, \phi_r, \phi_s). \qquad (2)$$

Here $E(\phi_r\overline{\phi}_r)$ denotes the density functional energy of the configuration $(\ldots\phi_r^2\phi_s^0)$ and $R(\rho_{g.s.}, \phi_r, \phi_s)$ is the residual term which collects all those DFT energy parts that cannot be reduced to energies of individual configurations. In principle, this energy representation, Eq. (2), is exact. However, to calculate the energy of a state of pure spin and spatial symmetry, it is necessary to introduce the symmetry dependence into the residual term $R(\rho_{g.s.}, \phi_r, \phi_s)$. There exist neither easy nor straightforward practical solutions to the problem. Hence, in practical applications of the DFT–FON method only configurationally averaged states can be calculated using the conventional density functionals [10].

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[2] In Ref. [14] it has been poined out that the fractional occupation numbers in DFT should follow from ensemble averaging only, while arbitrary FONs which do not obey this requirement are not allowed in DFT.

In previous works [15,16], we applied the ensemble approach to states that degenerate by symmetry, and introduced a symmetry-adapted spin-restricted open-shell Kohn–Sham (ROKS) method. Imposing a number of restrictions on the Kohn–Sham single determinants and one-electron orbitals, it was possible to represent the energy of a multiplet state or a state with strong symmetry-dependent non-dynamic correlation in a symmetry-adapted weighted sum form of single determinant Kohn–Sham energies,

$$E^{\Gamma,S} = \sum_L c_L E(\Phi_L); \quad \sum_L c_L = 1 \qquad (3)$$

where Γ is the irreducible representation and S the total spin. In Eq. (3), the energies $E(\Phi_L)$ of single Kohn–Sham determinants Φ_L are calculated using conventional symmetry-independent density functionals [1,2]. The density, in turn, is represented as a weighted sum of densities of single determinants having the same weighting factors as in Eq. (3). By construction, the density is totally symmetric in the respective symmetry point group.

$$\rho^{\Gamma,S}(\boldsymbol{r}) = \sum_L c_L \, \rho(\Phi_L). \qquad (4)$$

The energy of the pure symmetry state, Eq. (3), is then minimized with respect to the density, Eq. (4), and a self-consistent set of orthonormal one-electron orbitals is obtained from a single eigenvalue equation [15,16]. In the present Letter, we generalize this spin-restricted computational scheme for systems in which strong non-dynamic correlations are not only symmetry-related but are also due to accidental-degeneracy, or nearly so, of two electronic configurations, e.g. as in diradicaloid species.

Let us start from a situation where the configurations in the molecular orbital space $(\ldots \phi_r^2 \phi_s^0)$ and $(\ldots \phi_r^0 \phi_s^2)$ are strictly degenerate and the orbitals ϕ_r and ϕ_s are subspecies of the same two-dimensional irreducible representation (e.g. 90°-twisted ethylene in D_{2d} symmetry). In what follows, we adopt the delocalized representation for the degenerate orbitals, such that they span the same set of atoms in a molecule [16]. In this case, two distinct singlet states, formally 'covalent'- and 'ionic'-types, can be constructed from the configurations $(\ldots \phi_r^2 \phi_s^0)$ and $(\ldots \phi_r^0 \phi_s^2)$. In the case of twisted ethylene, these

states are characterized by irreducible representations B_1 and A_1 in D_{2d} symmetry group. Their ROKS energies were derived from symmetry considerations [16] and are given by Eqs. (5) and (6), respectively.

$$E^{^1B_1} = \tfrac{1}{2}E(\phi_r\overline{\phi}_r) + \tfrac{1}{2}E(\phi_s\overline{\phi}_s) - \tfrac{1}{2}E(\phi_r\overline{\phi}_s)$$
$$- \tfrac{1}{2}E(\phi_s\overline{\phi}_r) + E(\phi_r\phi_s), \qquad (5)$$

$$E^{^1A_1} = \tfrac{1}{2}E(\phi_r\overline{\phi}_r) + \tfrac{1}{2}E(\phi_s\overline{\phi}_s) + \tfrac{1}{2}E(\phi_r\overline{\phi}_s)$$
$$+ \tfrac{1}{2}E(\phi_s\overline{\phi}_r) - E(\phi_r\phi_s). \qquad (6)$$

Strictly speaking, the negative weighting factors are not allowed in the ensemble KS approach [3,11–13]. However, restrictions imposed on the KS determinants in the ROKS scheme [15,16] guarantee that the energy remains finite even with the negative weighting factors. Moreover, the use of such factors provides an opportunity to compute states of correct spin and spatial symmetry with symmetry-independent density functionals. Had strictly positive weighting factors been allowed in the ROKS energy expressions, then only a mixture of the singlet states $^1B_1$ and $^1A_1$ would have resulted by use of conventional symmetry-independent density functionals. Thus, the ROKS energy representation with non-positive weighting factors corrects for the lack of symmetry in approximate density functionals by introducing the symmetry dependence through a special choice of the weighting factors [15,16].

Next, let us rotate the CH_2 groups in the D_{2d} twisted ethylene by a small angle such that the point group symmetry becomes D_2, thereby lifting the degeneracy of ϕ_r and ϕ_s orbitals. In the D_2 group, both the $^1B_1$ and $^1A_1$ states belong to the same irreducible representation A, and should therefore interact with each other. If the non-interacting reference wavefunctions of these states,

$$\Psi^{^1B_1} = \frac{1}{\sqrt{2}}\left(|\phi_r\overline{\phi}_r| - |\phi_s\overline{\phi}_s|\right) \qquad (7)$$

and

$$\Psi^{^1A_1} = \frac{1}{\sqrt{2}}\left(|\phi_r\overline{\phi}_r| + |\phi_s\overline{\phi}_s|\right), \qquad (8)$$

are considered as diabatic states within the conventional ab initio framework, then the coupling matrix

element of the full interacting Hamiltonian will be given by

$$D = \left\langle \Psi^{1B_1} | \hat{H} | \Psi^{1A_1} \right\rangle = \tfrac{1}{2} \left(E(\phi_r \overline{\phi}_r) - E(\phi_s \overline{\phi}_s) \right) \tag{9}$$

and the lowest adiabatic state ^1A will be given by

$$E^{1A} = \tfrac{1}{2} \left(E^{1B_1} + E^{1A_1} \right) - \sqrt{ \tfrac{1}{4} \left(E^{1B_1} - E^{1A_1} \right)^2 + D^2 } . \tag{10}$$

Let us now transform this energy expression, Eq. (10), such that it can be applied in the ensemble KS approach. Introducing the parameter γ,

$$\gamma = \frac{D \left(E^{1A} - E^{1B_1} \right)}{D^2 + \left(E^{1A} - E^{1B_1} \right)^2} \tag{11}$$

the energy E^{1A} can be rewritten as

$$\begin{aligned}
E^{1A} &= \left(\tfrac{1}{2} + \gamma \right) E(\phi_r \overline{\phi}_r) + \left(\tfrac{1}{2} - \gamma \right) E(\phi_s \overline{\phi}_s) \\
&\quad + \left(1 - 4\gamma^2 \right)^{1/2} \left(E(\phi_r \phi_s) - \tfrac{1}{2} E(\phi_r \overline{\phi}_s) \right. \\
&\quad \left. - \tfrac{1}{2} E(\phi_s \overline{\phi}_r) \right) \\
&= \frac{n_r}{2} E(\phi_r \overline{\phi}_r) + \frac{n_s}{2} E(\phi_s \overline{\phi}_s) \\
&\quad + \left(n_r n_s \right)^{1/2} \left(E(\phi_r \phi_s) - \tfrac{1}{2} E(\phi_r \overline{\phi}_s) \right. \\
&\quad \left. - \tfrac{1}{2} E(\phi_s \overline{\phi}_r) \right) \tag{12}
\end{aligned}$$

where n_r and n_s are the occupation numbers of orbitals ϕ_r and ϕ_s, given as

$$n_r = 1 + 2\gamma , \tag{13}$$

$$n_s = 1 - 2\gamma . \tag{14}$$

The density for the singlet state ^1A can be defined by use of the zeroth-order wavefunction as the non-interacting reference wavefunction:

$$\begin{aligned}
\rho^{1A}(r) &= \left(\tfrac{1}{2} + \gamma \right) \rho(\phi_r \overline{\phi}_r) + \left(\tfrac{1}{2} - \gamma \right) \rho(\phi_s \overline{\phi}_s) \\
&\quad + \left(1 - 4\gamma^2 \right)^{1/2} \left(\rho(\phi_r \phi_s) - \tfrac{1}{2} \rho(\phi_r \overline{\phi}_s) \right. \\
&\quad \left. - \tfrac{1}{2} \rho(\phi_s \overline{\phi}_r) \right) . \tag{15}
\end{aligned}$$

In Eq. (15), the three terms in parentheses precisely compensate each other, but are retained deliberately to show that both the energy, Eq. (12), and the density, Eq. (15), are presented as weighted sums with the same weighting factors. Constructing the densities of individual configurations from the same set of one-electron orbitals (ϕ_k for the closed-shell core and the 'active' orbitals ϕ_r and ϕ_s), the density, Eq. (15), can be rewritten as

$$\begin{aligned}
\rho^{1A}(r) &= \sum_{k \in \text{core}} 2|\phi_k(r)|^2 + n_r |\phi_r(r)|^2 + n_s |\phi_s(r)|^2 .
\end{aligned} \tag{16}$$

thus demonstrating that n_r and n_s are indeed fractional occupation numbers of orbitals ϕ_r and ϕ_s.

As such, the energy and the density of the ground state of a system with strong non-dynamic correlation due to near-degeneracy of two electronic configurations (e.g. diradicals) are represented in a form of symmetry-adapted weighted sums of single determinant energies and densities. The weighting factors are merely fractional occupation numbers of the (nearly) degenerate orbitals. Based on this representation, a self-consistent computational scheme can be constructed, by analogy with the DFT–FON method, to optimize simultaneously the occupation numbers and the one-electron orbitals. The weighted sum (ensemble) scheme has an advantage over the standard symmetry-independent DFT–FON approach, since the former enables one to calculate total energies of states of pure symmetry [15,16] with standard functionals.

There is an analogy between the derived energy formula, Eq. (12), and the DFT–FON energy expression, Eq. (2). Eq. (12) is derived from a consideration of the configuration interference near the high-symmetry point where $n_r \approx n_s$. Close to the 'normal' state, where $n_r \approx 2$ and $n_s \approx 0$ (e.g., ground state of planar D_{2h}-symmetric ethylene), the DFT–FON energy expression, Eq. (2), shows that the coefficient in front of the residual term $R(\rho_{g.s.}, \phi_r, \phi_s)$ vanishes with a rate that is linear in occupation numbers. Such an extra term is obviously redundant for the 'normal' state ($n_r \approx 2$ and $n_s \approx 0$) and should also vanish in Eq. (12). The rate of this vanishing, however, cannot be estimated based on the consideration of orbitally degenerate, or nearly so, situations. To create a smooth interpolation between the ensemble ROKS description for states at the high-symmetry or orbitally-degenerate point, on the one hand, and the conventional KS description for the 'normal' states, on the other, the last term in Eq. (12) is scaled by a

factor $(n_r \cdot n_s)^a$ with an exponent which can vary from zero to $1/2$. Based on numerical evaluation, the exponent $a = 1/4$ yields good results. The so-obtained self-consistent energies of 'normal' states are practically indistinguishable from the conventional KS energies (within a fraction of a kcal/mol). At the same time, the onset of the ensemble description is fast en-route to the vicinity of a high-symmetry point (or a point where the 'active' orbitals become degenerate accidentally). Thus, the transition from the 'normal' state to the ensemble occurs smoothly and no artificial humps develop on the potential energy surface of a diradicaloid species. When the exponent is too large ($a \approx 1/2$) the ensemble description begins to develop only in the vicinity of the orbital degeneracy point, a situation which can lead to some distortions of the potential energy surface. Small variations of the exponent near the value of $1/4$ do not lead to well pronounced changes of the results.

Thus, the value $a = 1/4$ is adopted in the self-consistent computational scheme which we propose to denote a spin-restricted ensemble-referenced Kohn–Sham method (REKS). The name of the method is chosen to emphasize two key features: (i) *that the method relates to the variational energy of a symmetry-adapted density, and* (ii) *that the method is not a configuration interaction approach in the traditional sense, and it does not involve the calculation of additional electron repulsion and exchange terms.*

The final formulae for the REKS energy and density are then:

$$
\begin{aligned}
E^{\text{REKS}} &= \left(\tfrac{1}{2} + \gamma\right) E\left(\phi_r \overline{\phi}_r\right) + \left(\tfrac{1}{2} - \gamma\right) E\left(\phi_s \overline{\phi}_s\right) \\
&\quad + \left(1 - 4\gamma^2\right)^{3/4} \left(E\left(\phi_r \phi_s\right) - \tfrac{1}{2} E\left(\phi_r \overline{\phi}_s\right) \right. \\
&\quad \left. - \tfrac{1}{2} E\left(\phi_s \overline{\phi}_r\right) \right) \\
&= \frac{n_r}{2} E\left(\phi_r \overline{\phi}_r\right) + \frac{n_s}{2} E\left(\phi_s \overline{\phi}_s\right) \\
&\quad + \left(n_r n_s\right)^{3/4} \left(E\left(\phi_r \phi_s\right) - \tfrac{1}{2} E\left(\phi_r \overline{\phi}_s\right) \right. \\
&\quad \left. - \tfrac{1}{2} E\left(\phi_s \overline{\phi}_r\right) \right),
\end{aligned}
\tag{17}
$$

$$
\rho^{\text{REKS}}(\boldsymbol{r})
= \sum_{k \in \text{core}} 2|\phi_k(\boldsymbol{r})|^2 + n_r|\phi_r(\boldsymbol{r})|^2 + n_s|\phi_s(\boldsymbol{r})|^2 .
\tag{18}
$$

Applying the same technique as in our previous works [15,16], the energy, Eq. (17), is minimized with respect to the density, Eq. (18). The same restrictions as in the ROKS [15,16] method are imposed on the one-electron orbitals and single determinants. The orbitals, in turn, are subdivided into the closed-shell 'core' orbitals with occupations fixed to two and 'active' orbitals, ϕ_r and ϕ_s, that are fractionally occupied with occupation numbers calculated self-consistently according to Eqs. (13) and (14). Under these restrictions, energy minimization is performed with respect to the orbitals (under the constraint of orthonormality) and to the parameter γ in Eqs. (13), (14), (17) and (18). The corresponding one-electron equations are given in the Appendix.

3. Results and discussion

The computational scheme described above has been implemented in the CADPAC5 quantum-chemical package [19]. The self-consistent calculations as well as the analytical gradients are available. Three different gradient-corrected density functionals, BP86 [19,20], BLYP [21,22], and FT97 [23], have been used. The three functionals are used to demonstrate that the proposed scheme yields qualitatively the same results with any density functional.

Let us consider two model problems; the rotation in ethylene around the C=C bond, and the dissociation of the H_2 molecule. These simple examples represent a wide class of chemically important problems such as diradicaloid transition states and the dissociation of single bonds. The calculations for these systems employed the TZ2P basis set [24].

For rotation in C_2H_4, molecular geometries for the planar (D_{2h}) and 90°-twisted (D_{2d}) ethylene have been optimized with the REKS method. Molecular structures at the intermediate rotation angles are interpolated linearly between these limiting structures. In Fig. 1, the potential energy profile along the torsional mode calculated with the REKS/BLYP method is shown in comparison with the curve calculated using the conventional single-reference [1] RKS/BLYP method. Calculations with other density functionals yield qualitatively the same results and are not shown for economy.
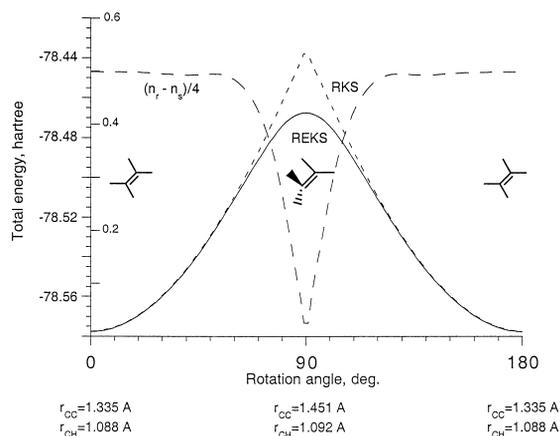
Fig. 1. REKS (solid line) and RKS (short dashed line) potential curves along twisting mode in ethylene (see text for details).

As can be seen from Fig. 1, the conventional RKS approach [1] is not capable of predicting a smooth torsional curve yielding a sharp cusp at 90° degrees of rotation. The torsional barrier from RKS calculations is overestimated by almost 20 kcal/mol, whereas the REKS method yields reliable torsional barriers (see Table 1). The dependence of the parameter γ ($\gamma = (n_r - n_s)/4$) of Eqs. (13) and (14) on the torsional angle, presented in the same plot, shows that γ varies smoothly from its 'normal' value of ca. 0.5 (0.498543 from REKS/BLYP) for planar ethy-

lene to zero for the 90°-twisted conformation. γ begins to deviate markedly from its 'normal' value for torsions of more than ca. 60°, where single reference density becomes insufficient.

Table 1 collects optimized C=C bond lengths and total energies calculated with the REKS and RKS methods for planar and 90°-twisted ethylene. A comparison of these data shows that for the 'normal' state, i.e. planar ethylene, both computational approaches yield almost indistinguishable results. The REKS total energies deviate by 0.1–0.2 kcal/mol and the optimized C=C bond lengths by 0.0006–0.0007 Å from the respective RKS values.

The same picture holds for the hydrogen molecule, for which optimized bond lengths and total energies are also presented in Table 1. The H_2 potential curves calculated with BLYP are shown in Fig. 2, where the straight horizontal line corresponds to the dissociation limit calculated as a sum of energies of separate atoms. The Figure demonstrates that the REKS approach is strictly size-consistent and dissociates H_2 into two separate hydrogen atoms, whereas the conventional RKS method correlates to a higher energy situation.

Turning to diradicals, we calculated singlet-triplet energy separation in propane-1,3-diyl (**1**) and 2,2-dufluoropropane-1,3-diyl (**2**). These 1,3-diradicals have been objects of intense interest [26], both theoretically and experimentally. It has been established

Table 1

Comparison of total energies and geometries from REKS and RKS calculations of C_2H_4 and H_2 (TZ2P basis set)

	BP86		BLYP		FT97	
	REKS	RKS	REKS	RKS	REKS	RKS
C_2H_4						
C=C[a], Å	1.3338	1.3331	1.3351	1.3345	1.3398	1.3393
$E(D_{2h})$[b], a.u,	−78.61997	−78.61961	−78.57765	−78.57742	−78.57980	−78.579570
$E(D_{2d})$[b], a.u.	−78.51287	−78.47704	−78.46754	−78.43601	−78.46941	−78.43758
Rot. barrier[c], kcal/mol	67.2	89.5	69.1	88.7	69.3	89.1
H_2						
H–H[d], Å	0.7479	0.7474	0.7438	0.7433	0.7454	0.7452
$E(r_e^{REKS})$, a.u.	−1.17736	−1.17723	−1.16897	−1.16884	−1.18134	−1.18126

[a] Optimized for planar ethylene at the respective computational level.
[b] All geometries are determined with REKS.
[c] Experimental value 65 kcal/mol [25].
[d] Optimized at the respective computational method.
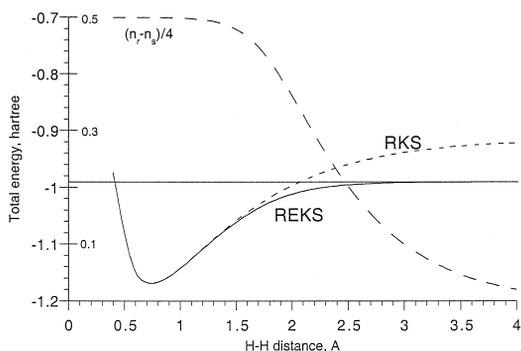
Fig. 2. REKS (solid line) and RKS (short dashed line) potential curves for bond breaking in H_2 (see text for details).

from (2/2)CASPT2N/6-31G* calculations [26] that the triplet is the ground state of the unsubstituted trimethylene **1** with the lowest singlet lying 0.7 kcal/mol above, whereas the ground state of **2** is a singlet with the triplet state being 4.8 kcal/mol higher. Thus, these species represent good examples for assessing the quality of the REKS computational scheme.
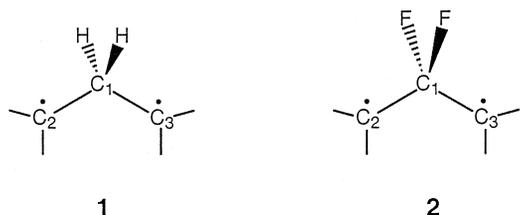
Using the same three density functionals as above and employing the 6-31G* basis set [27] we calculated total energies and molecular geometries for the $^3B_2$ and $^1A_1$ states of **1** and **2**. Triplets were calculated with the ROKS method [15,16]. Singlets were calculated with both REKS and RKS [1] methods. The results are collected in Table 2.

Inspection of these results shows that the RKS method strongly underestimates the singlet-triplet energy separation and, with some density functionals (BP86), the method predicts the wrong ground state for the diradicals. The singlet-triplet gaps calculated with the REKS method are in excellent agreement with CASPT2N calculations [26] and a correct ground

state is predicted with any density functional. The inclusion of non-dynamic correlation has a pronounced effect on molecular geometries of singlet species. In general, geometries optimized for $^1A_1$ states with REKS method are close to respective triplet geometries.

Table 2
Energies and molecular geometries for singlet and triplet states of 1,3-diradicals. Calculations employ the 6-31G* basis set

	BP86[a]	BLYP[a]	FT97[a]
propane-1,3-diyl[b]			
$^3B_2$			
C_1C_2, Å	1.494	1.499	1.500
C_2C_3, Å	2.509	2.520	2.521
E, a.u.	−117.79091	−117.71433	−117.72400
$^1A_1$			
C_1C_2, Å	1.491	1.497	1.495
	1.454	*1.461*	*1.462*
C_2C_3, Å	2.586	2.597	2.611
	2.659	*2.665*	*2.674*
E, a.u.	−117.78974	−117.71312	−117.72342
	−117.77195	*−117.69737*	*−117.71005*
ΔE_{st}, kcal/mol	−0.7	−0.8	−0.4
	−11.9	*−10.6*	*−8.8*
CASPT2N[c]	[**−0.7**]		
2,2-difluoropropane-1,3-diyl[b]			
$^3B_2$			
C_1C_2, Å	1.487	1.490	1.490
C_2C_3, Å	2.542	2.552	2.554
C_1F, Å	1.407	1.417	1.426
E, a.u.	−316.27755	−316.18684	−316.09220
$^1A_1$			
C_1C_2, Å	1.468	1.468	1.468
	1.445	*1.447*	*1.450*
C_2C_3, Å	2.443	2.442	2.434
	2.350	*2.364*	*2.364*
C_1F, Å	1.411	1.423	1.433
	1.427	*1.439*	*1.447*
E, a.u.	−316.28529	−316.19564	−316.10177
	−316.27435	*−316.18742*	*−316.09469*
ΔE_{st}, kcal/mol	4.9	5.5	6.0
	−2.0	*0.4*	*1.6*
CASPT2N[c]	[**4.8**]		

[a] Triplet states calculated with ROKS method, singlets with REKS (normal font) and RKS (in italics).
[b] C_1 is the central carbon in the propane-1,3-diyl skeleton.
[c] In brackets are ab initio (2/2)CASPT2N/6-31G* singlet-triplet splittings from Ref. [26].

4. Conclusions

A computational scheme capable of treating non-dynamic correlation in singlet diradicaloid species was devised. An optimal set of orthonormal one-electron orbitals and their optimal occupation numbers was obtained by minimization of the ground state energy with respect to the density. Only those fractional occupation numbers (and their variations) which are consistent with the ensemble representability [11–13] of the ground state density were considered in constructing and minimizing the ground state energy [14]. The ground state energy is represented as a weighted sum of energies of symmetry-adapted single Kohn–Sham determinants with weighting factors associated with the fractional occupation numbers of 'active' orbitals. REKS has an affinity to the DFT–FON method [7–10]. However, in contrast to DFT–FON, REKS enables one to calculate energies of states of pure symmetry using conventional symmetry-independent density functionals [15,16].

The application of the REKS scheme to a number of model systems (rotation in ethylene, dissociation of H_2, and singlet-triplet splittings in 1,3-diradicals) shows the effectiveness of the new approach. Thus, smooth potential curves for rotation around the double C=C bond, potential curves for single bond breaking which correlate to the correct dissociation limit, and reliable singlet-triplet energy gaps in diradicals; were obtained with REKS using any conventional density functional.

Acknowledgements

Appendix A

The REKS energy

$$E^{REKS} = \sum_{L=1}^{5} c_L(\gamma) E(\Phi_L) \qquad (A.1)$$

(see Eqs. (12) and (17) for definitions of coefficients $c_L(\gamma)$ and determinants Φ_L) is minimized with respect to the parameter γ, Eq. (11), on the interval $[-0.5, 0.5]$ and to the one-electron orbitals ϕ_i under the constraint of orthonormality. For a given value of γ, the self-consistent orbitals are the solutions of the equation

$$\hat{F}|i\rangle = \varepsilon_i|i\rangle \qquad (A.2)$$

with the effective Hamiltonian (see Refs. [15,16,28] for details)

$$
\begin{aligned}
\hat{F} = \sum_{L=1}^{5} c_L(\gamma) &\left[\frac{\hat{F}_L^\alpha + \hat{F}_L^\beta}{2} \right. \\
&+ \sum_{m=r,s} \left[\hat{g}_m \left\{ \frac{(n_m - 2n_{m,L}^\alpha)}{2n_m} \hat{F}_L^\alpha \right.\right. \\
&+ \left.\frac{(n_m - 2n_{m,L}^\beta)}{2n_m} \hat{F}_L^\beta \right\} \hat{\rho}_m \\
&+ \hat{\rho}_m \left\{ \frac{(n_m - 2n_{m,L}^\alpha)}{2n_m} \hat{F}_L^\alpha \right. \\
&+ \left.\left.\left. \frac{(n_m - 2n_{m,L}^\beta)}{2n_m} \hat{F}_L^\beta \right\} \hat{g}_m \right]\right]
\end{aligned} \qquad (A.3)
$$

where $\hat{\rho}_m = |m\rangle\langle m|$ with $\hat{g}_m = \beta_m \sum_{k \in core} |k\rangle\langle k| + \frac{1}{2}\sum_{m=r,s}|m\rangle\langle m| - 1$ with $\beta_m = 2/(2 - n_m)$ and n_r and n_s are defined in Eqs. (13) and (14). $n_{m,L}^\sigma$ is the integer occupation number of the m-th σ-spin-orbital in the determinant Φ_L (see Refs. [15,16] for details). The one-electron operators associated with the determinant Φ_L are

$$
\begin{aligned}
\hat{F}_L^\sigma = \hat{H} &+ \sum_{k \in core} 2\int \phi_k^*(r_2) r_{12}^{-1} \phi_k(r_2)\,dr_2 \\
&+ \sum_{m=r,s} \left(n_{m,L}^\alpha + n_{m,L}^\beta\right)\int \phi_m^*(r_2) r_{12}^{-1} \\
&\times \phi_m(r_2)\,dr_2 + V_{xc,L}^\sigma; \quad \sigma = \alpha, \beta,
\end{aligned} \qquad (A.4)
$$

where $V_{xc,L}^\sigma$ is the Kohn–Sham potential constructed for the determinant Φ_L (see Refs. [15,16] for details).

Having obtained the orbitals from Eq. (A.2), the new value of the parameter γ is calculated from the

condition $\partial E^{\mathrm{REKS}}/\partial\gamma = 0$. The procedure is repeated iteratively until convergence.

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