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Density functional theory for open-shell singlet biradicals

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Abstract

The description of open-shell singlet (OSS) σ–π biradicals by density functional theory (DFT) requires at least a two-configurational (TC) or, in general, a MC-DFT approach, which bears many unsolved problems. These can be avoided by reformulating the TC description in the spirit of restricted open shell theory for singlets (ROSS) and developing an exchange-correlation functional for ROSS-DFT. ROSS-DFT turns out to lead to reliable descriptions of geometry and vibrational frequencies for OSS biradicals. The relative energies of the OSS states obtained at the ROSS-B3LYP/6-311G(d,p) level are often better than the corresponding ROSS-MP2 results. However, in those cases where spin polarization in a conjugated π systems plays a role, DFT predicts the triplet state related to the OSS state 2–4 kcal/mol too stable.

1. Introduction

One of the major research goals in current chemistry is the investigation and description of enediyne antibiotics, which have the extraordinary capability of cleaving DNA and, by this, qualify as potential anticancer drugs [1]. The biological activity of the enediynes results from the fact that they, if properly triggered, can undergo cyclization to aromatic singlet biradicals, which are the actual DNA cleaving tools of the enediynes. Hence, the isolation, identification and characterization of singlet biradicals has become a key element of the research on enediyne antibiotics, both from the experimental [2,3] and the theoretical side [4,5]. While experimentally there are methods available to generate and to trap singlet biradicals at low temperature in a matrix, their identification and characterization, e.g. with the help of infrared spectroscopy, requires close collaboration between experimentalists and theoreticians where the latter provide calculated reference spectra to be compared with measured spectra [2–5].

A reliable quantum chemical description of singlet biradicals requires the use of multi configuration (MC) or multi reference (MR) methods, preferably in connection with CI or perturbation theory to provide an accurate account of dynamic electron correlation. While this is possible for small molecules, calculations are no longer feasible for substituted enediynes and their biradical counterparts, in particular if the calculation of analytical first and second energy derivatives for the determination of geometry and vibrational spectra becomes necessary. In this work, we make a first step in attacking the problem of describing typical MR systems such as open-shell singlet (OSS) biradicals with the help of density functional theory (DFT). DFT has the advantage of being not very costly and covering (although in an unspecified way) a relatively large amount of dynamic

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correlation effects so that DFT results are sometimes comparable in accuracy with those of CCSD(T) or at least MP2 results [6].

Of course, DFT as it is mostly used, is based on single-determinant Kohn–Sham theory [7] and, therefore, fails in a similar way as Hartree–Fock (HF) theory to treat a MR problem properly. There exist several relatively simple possibilities of replacing HF by a two-configurational (TC) description, as for example TCSCF or GVB [8], to obtain the correct wavefunction of systems such as an OSS biradical and to add dynamic correlation to this description by Møller–Plesset (MP) perturbation theory [9]. While these methods make a technical, although not very accurate, solution of the problem in orbital space possible, TC-DFT leads to serious complications, although first solutions for atoms and H_2 have been suggested recently by Miehlich et al. [10]. Any TC description implies some spatial separation of the two single electrons of an OSS biradical and, by this, a lowering of the Coulomb repulsion. If one adds a density functional for describing exchange-correlation (XC) effects, the TC functional will be based on the one-electron density, which is not adjusted for the lowering of the Coulomb repulsion by the TC description. Accordingly, dynamic electron correlation will be overestimated by TC-DFT. The conversion of a closed shell system into an OSS biradical can no longer be described consistently.

The problem of combining an MC approach with DFT can be avoided by reformulating a TC description within single-determinant restricted Kohn-Sham theory [7]. This can be done by using techniques worked out for restricted open shell HF (ROHF) theory for low-spin cases, in particular the OSS case [11]. A combination of ROHF with a dynamic electron correlation method such as MP2 was shown to be useful in describing OSS states [12]. In this work, we describe the extension of ROHF theory for OSS states to DFT with the goal of calculating OSS biradicals with a restricted open-shell singlet (ROSS) DFT method that will be based on the correct form of the wavefunction but which includes in addition the dynamic electron correlation effects of a DFT method. We will develop, implement and apply ROSS-DFT in particular to $\sigma-\pi$ OSS biradicals, which can only be described by MC methods since their ground state wavefunctions are linear combinations of two strictly equivalent determinants.

2. Theory

In the following, we consider an electron system with doubly occupied orbitals φ_i, φ_j, etc. (core orbitals), two singly occupied orbitals φ_r and φ_s and virtual orbitals φ_a, φ_b, etc. The indices p,q are used for unspecified orbitals out of the total set of orbitals. For quantities related to the core space as a whole, the index c is used and, correspondingly, index v for the virtual space. The total densities for each spin direction will be denoted by $n_{\uparrow,\downarrow}$ where we will distinguish between the core density per spin direction, $n_c(\boldsymbol{r}) = \sum_i \varphi_i^*(\boldsymbol{r})\varphi_i(\boldsymbol{r})$ and the singly-occupied space densities $n_p(\boldsymbol{r}) = \varphi_p^*(\boldsymbol{r})\varphi_p(\boldsymbol{r})$ ($p = r,s$). For the $\sigma-\pi$ biradicals considered in this work, one single electron occupies a σ and the other a π orbital, both electrons being coupled to a singlet so that the wavefunction in its simplest form is given by (1)

$$\Psi = \hat{A}\left\{ \Phi(\text{core}) \frac{1}{\sqrt{2}} \left[\varphi_r(1)\varphi_s(2) + \varphi_s(1)\varphi_r(2) \right] \left[\alpha(1)\beta(2) - \beta(1)\alpha(2) \right] \right\} \tag{1}$$

and, accordingly, would require a TC or better description.

An electronic-structure calculation based on DFT requires a search for the state with the lowest energy under the constraint that the total spin-up and spin-down particle numbers, $N_{\uparrow,\downarrow}$ should have certain fixed values (see, e.g. Ref. [13]):

$$E_0 = \min_{n_{\uparrow,\downarrow} \to N_{\uparrow,\downarrow}} \left\{ F[n_\uparrow, n_\downarrow] + \int \mathrm{d}^3 r v(\boldsymbol{r}) \left[n_\uparrow(\boldsymbol{r}) + n_\downarrow(\boldsymbol{r}) \right] \right\} \tag{2a}$$

$$F[n_\uparrow, n_\downarrow] = \min_{\Psi \to n_{\uparrow,\downarrow}} \langle \Psi | \hat{T} + \hat{V}_{ee} | \Psi \rangle \tag{2b}$$

where v is the external potential and $\hat{T}$ and $\hat{V}_{ee}$ are the kinetic and electron-electron energy operators, respectively.

This approach is not suitable for searching for the OSS state since the OSS and any lower or higher lying closed-shell state have the same $N_{\uparrow,\downarrow}$ values. If one had the exact exchange-correlation (XC) energy available, DFT would describe that singlet state with the lowest energy. However, the usual approximations used for the XC energy are based on the adiabatic-connection scheme [14], i.e. a fictitious procedure in which the strength of the electron-electron interaction is turned down from its real value to zero so that the wavefunction is converted into that of a reference system with non-interacting electrons. Due to the approximate character of the XC functional, a restricted Kohn-Sham method will always lead to a description of a closed-shell singlet rather than the OSS state. With an unrestricted open-shell approach, a closed-shell state (of little physical relevance) will be described provided this is lowest in energy or, if the OSS state is lowest in energy, an artificial state is obtained that is adiabatically coupled to the unrestricted open-shell state and that does not represent a reasonable approximation to the real OSS state. Hence, in no case does single-determinant Kohn-Sham DFT give a satisfactory description of the OSS state.

One can improve the situation by further constraining the minimum-energy search of Eq. (2) in the sense that just trial wavefunctions of particular (space and/or spin) symmetry are used. In this way, Eq. (2) is replaced by Eq. (3).

$$E_0^S = \min_{n_{\uparrow,\downarrow} \to N_{\uparrow,\downarrow}} \left\{ F^S[n_\uparrow, n_\downarrow] + \int \mathrm{d}^3 r v(\boldsymbol{r}) \left[n_\uparrow(\boldsymbol{r}) + n_\downarrow(\boldsymbol{r}) \right] \right\} \tag{3a}$$

$$F^S[n_\uparrow, n_\downarrow] = \min_{\Psi \to n_{\uparrow,\downarrow}, \Psi \in S} \langle \Psi | \hat{T} + \hat{V}_{ee} | \Psi \rangle \tag{3b}$$

where S denotes the symmetry in question and the minimization must be restricted to such $n_{\uparrow,\downarrow}$ that are compatible with S. Eq. (3) leads to different functionals F for each symmetry S.

Since in all interesting cases, the closed-shell and OSS state have different spatial symmetries because of differences in the electron configurations, a symmetry-constrained search can be used to determine the OSS state, provided one can construct a reasonable approximation to the functional F^{OSS}. In this work such an approximation is constructed by considering that (i) a triplet (T) state can well be described within DFT and (ii) that the T and OSS states are related in some respect. Accordingly, we derive F^{OSS} by modifying the energy functional for the T state. At the HF level, the energy of the T state is $2K$ below that of the corresponding OSS state built with the same orbitals, where $K = \langle \varphi_r \varphi_s | \varphi_s \varphi_r \rangle$ is the the exchange energy of the two electrons occupying φ_r and φ_s.

If dynamic electron correlation is considered, the energy of the OSS state will be lowered relative to that of the T state. In the latter case, correlations between electrons r and s should be relatively small because these electrons avoid each other by virtue of exchange correlation already covered at the HF level. In the OSS state, however, exchange effects make these two electrons cluster, which should result in stronger correlation effects.

The change in the exchange energy can be described by adding $2K$ to the total energy of the T state. Since most approximations for the XC energy are closely related to the case of the homogeneous electron gas, which is not a reasonable starting point for describing an OSS situation, it is better to calculate the exact exchange integral K. The extra computational cost for K is negligible in hybrid-functional calculations and still moderate within a pure DFT approach.

The weak Coulomb correlations in the T state are covered in the DFT description in the way of equal-spin corrections, which are relatively weak. In the OSS case, the r–s correlations enter as different-spin correlations into the energy expression, which can be done simply by replacing the T correlation energy $E_c^{\mathrm{DFT}}[n_c + n_r + n_s, n_c]$ by $E_c^{\mathrm{DFT}}[n_c + n_r, n_c + n_s]$. This expression is, strictly speaking, appropriate for a state where there is no exchange between electrons r and s. Thus, it may still underestimate electron correlation as will be discussed in the next section.

The ROSS-DFT energy functional for an OSS biradical is given by

$$E = 2\sum_i \langle \varphi_i|\hat{h}|\varphi_i\rangle + \langle \varphi_r|\hat{h}|\varphi_r\rangle + \langle \varphi_s|\hat{h}|\varphi_s\rangle + \sum_i \langle \varphi_i|\hat{J}|\varphi_i\rangle + \tfrac{1}{2}\langle \varphi_r|\hat{J}|\varphi_r\rangle + \tfrac{1}{2}\langle \varphi_s|\hat{J}|\varphi_s\rangle$$
$$- a_{\mathrm{HF}}\left(\sum_i \langle \varphi_i|\hat{K}_c + \tfrac{1}{2}\left(\hat{K}_r + \hat{K}_s\right)|\varphi_i\rangle + \tfrac{1}{2}\langle \varphi_r|\hat{K}_c + \hat{K}_r + \hat{K}_s|\varphi_r\rangle + \tfrac{1}{2}\langle \varphi_s|\hat{K}_c + \hat{K}_r + \hat{K}_s|\varphi_s\rangle\right)$$
$$+ 2\langle \varphi_r\varphi_s|\varphi_s\varphi_r\rangle + E_x^{\mathrm{DFT}}[n_c + n_r + n_s; n_c] + E_c^{\mathrm{DFT}}[n_c + n_r; n_c + n_s]. \quad (4)$$

In Eq. (4), a_{HF} is the weight factor for HF exchange in hybrid DFT schemes ($a_{\mathrm{HF}} = 0$ for pure DFT). The functional F^{OSS} is readily obtained from (4) by omitting the external potential terms, i.e. replacing the core Hamiltonian $\hat{h}$ by the kinetic energy operator $\hat{t}$. For $a_{\mathrm{HF}} = 1$ and $E_x^{\mathrm{DFT}} = E_c^{\mathrm{DFT}} = 0$ and the energy expression for ROHF in the case of an OSS state is reproduced.

From the total energy (4), we can derive the Fock operators for orbital spaces c, r and s by considering the change of E for small changes $|\varphi_p\rangle \to |\varphi_p\rangle + \lambda|\varphi'_p\rangle$, where orthonormality of the orbitals is not necessarily required at this stage of the derivation. Taking the derivative with respect to λ for $\lambda = 0$ leads to Eq. (5), in which the Fock and Coulomb operators of Eqs. (6)–(9) are used.

$$E' = \left(2\sum_i \langle \varphi_i|\hat{F}^c|\varphi'_i\rangle + \langle \varphi_r|\hat{F}^r|\varphi'_r\rangle + \langle \varphi_s|\hat{F}^s|\varphi'_s\rangle\right) + \text{c.c.}, \quad (5)$$

$$\hat{F}^c = \hat{h} + \hat{J} - a_{\mathrm{HF}}\left(\sum_i \hat{K}_i + \tfrac{1}{2}\left(\hat{K}_r + \hat{K}_s\right)\right) + \tfrac{1}{2}\left(v_{x\uparrow}^{\mathrm{DFT}} + v_{x\downarrow}^{\mathrm{DFT}}\right) + \tfrac{1}{2}\left(v_{c\uparrow}^{\mathrm{DFT}} + v_{c\downarrow}^{\mathrm{DFT}}\right), \quad (6)$$

$$\hat{F}^r = \hat{h} + \hat{J} - a_{\mathrm{HF}}\left(\sum_i \hat{K}_i + \hat{K}_r + \hat{K}_s\right) + 2\hat{K}_s + v_{x\uparrow}^{\mathrm{DFT}} + v_{c\uparrow}^{\mathrm{DFT}}, \quad (7)$$

$$\hat{F}^s = \hat{h} + \hat{J} - a_{\mathrm{HF}}\left(\sum_i \hat{K}_i + \hat{K}_r + \hat{K}_s\right) + 2\hat{K}_r + v_{x\uparrow}^{\mathrm{DFT}} + v_{c\downarrow}^{\mathrm{DFT}} \quad (8)$$

$$\hat{J} = 2\sum_i \hat{J}_i + \hat{J}_r + \hat{J}_s. \quad (9)$$

According to ROHF theory [11,15] and its generalization to DFT, the Kohn–Sham orbitals can be found by diagonalizing Fock matrix (10)

$$\mathbf{F} = \begin{bmatrix} \mathbf{F}_{cc} & \mathbf{F}_{cr} & \mathbf{F}_{cs} & \mathbf{F}_{cv} \\ \mathbf{F}_{rc} & F_{rr} & F_{rs} & \mathbf{F}_{rv} \\ \mathbf{F}_{sc} & F_{sr} & F_{ss} & \mathbf{F}_{sv} \\ \mathbf{F}_{vc} & \mathbf{F}_{vr} & \mathbf{F}_{vs} & \mathbf{F}_{vv} \end{bmatrix}, \quad (10)$$

where off-diagonal elements are given by (11)

$$F_{ir} = 2F_{ir}^c - F_{ir}^r, \quad (11a)$$
$$F_{is} = 2F_{is}^c - F_{is}^s, \quad (11b)$$
$$F_{ia} = F_{ia}^c, \quad (11c)$$
$$F_{rs} = F_{rs}^r - F_{rs}^s, \quad (11d)$$
$$F_{ra} = F_{ra}^r, \quad (11e)$$
$$F_{sa} = F_{sa}^s. \quad (11f)$$

In an SCF procedure, the singly occupied orbitals φ_r and φ_s are rotated in such a way that the energy is minimized for otherwise fixed orbitals (such a rotation does not affect the total electronic structure in the high-spin case but it does in the low spin case). For a molecule of high symmetry, φ_r and φ_s can represent different one-dimensional irreducible representations (as e.g. in the case of a σ and a π orbital) or span the basis for a two-dimensional irreducible representation so that they are transformed into each other by some of the symmetry operations. In this work we have considered just the first case, i.e. the non-interacting KS reference state is a TC state built of two exactly degenerate single-determinant states. However, an extension of ROSS-DFT to the second situation is straightforward and just requires a suitable rotation between φ_r and φ_s.

In this work ROSS-DFT was programmed and used to calculate OSS energies. In addition, analytical energy gradients, needed for geometry optimizations, were derived for ROSS-DFT. The derivative of the energy E of Eq. (4) with respect to a geometry parameter x for $x = 0$ is given by Eq. (12)

$$\begin{aligned} E' = & \sum_{\mu\nu} P_{\mu\nu} h'_{\mu\nu} + \frac{1}{2} \sum_{\mu\nu\lambda\sigma} P_{\mu\nu} P_{\lambda\sigma} \langle\, \mu\lambda|\nu\sigma \,\rangle' \\ & - a_{\mathrm{HF}} \sum_{\mu\nu\lambda\sigma} \left[\left(P^c_{\mu\nu} + P^r_{\mu\nu} + P^s_{\mu\nu} \right) \left(P^c_{\lambda\sigma} + P^r_{\lambda\sigma} + P^s_{\lambda\sigma} \right) + P^c_{\mu\nu} P^c_{\lambda\sigma} \right] \langle\, \mu\lambda|\sigma\nu \,\rangle' \\ & + E_x^{\mathrm{DFT}\prime}\left[n_c + n_r + n_s, n_c \right] + E_c^{\mathrm{DFT}\prime}\left[n_c + n_r, n_c + n_s \right] + 2 \sum_{\mu\nu\lambda\sigma} P^r_{\mu\nu} P^s_{\lambda\sigma} \langle\, \mu\lambda|\sigma\nu \,\rangle' + \left(E' \right)_P, \end{aligned} \tag{12}$$

where the last term of (12) is defined by

$$\left(E' \right)_P = 2 \sum_{\mu\nu} P^{c\prime}_{\mu\nu} F^c_{\mu\nu} + \sum_{\mu\nu} P^{r\prime}_{\mu\nu} F^r_{\mu\nu} + \sum_{\mu\nu} P^{s\prime}_{\mu\nu} F^s_{\mu\nu}. \tag{13}$$

In Eqs. (12) and (13), Greek indices refer to basis functions, the MO coefficient matrix is given by **C** and the elements of the density matrices $\mathbf{P}^c$, $\mathbf{P}^r$ and $\mathbf{P}^s$ are defined by $P^c_{\mu\nu} = \sum_i C^*_{\mu i} C_{\nu i}$, $P^{\{r,s\}}_{\mu\nu} = C^*_{\mu\{r,s\}} C_{\nu\{r,s\}}$. The total density matrix can be calculated from the expression $\mathbf{P} = 2\mathbf{P}^c + \mathbf{P}^r + \mathbf{P}^s$. All the derivatives are explicit derivatives with respect to the external parameter x, e.g. the derivative of E_x^{DFT} in Eq. (12) does not account for changes in the density matrices. Determination of the derivatives of the density matrix, which would require a perturbation calculation, can be avoided by using the fact that the expansion coefficients correspond to the minimum-energy state of the energy functional. One can replace the derivatives of **P** with the help of a term depending on the derivatives of the overlap matrix **S** and the energy-weighted density matrix **W**, both expressed in terms of basis functions

$$\mathbf{W} = \mathbf{C}\mathbf{W}^{\mathrm{MO}}\mathbf{C}^{\dagger}, \tag{14}$$

where $\mathbf{W}^{\mathrm{MO}}$ is the MO representation of **W**, which can be assembled from the three matrices $\mathbf{F}^{c,r,s}$ according to

$$\mathbf{W}^{\mathrm{MO}} = \begin{bmatrix} 2\mathbf{F}^c_{cc} & \mathbf{F}^r_{cr} & \mathbf{F}^s_{cs} & 0 \\ \mathbf{F}^r_{rc} & F^r_{rr} & F^s_{rs} & 0 \\ \mathbf{F}^s_{sc} & F^s_{sr} & F^s_{ss} & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix}. \tag{15}$$

With (14) and (15), one obtains for Eq. (13) expression (16).

$$\left(E' \right)_P = - \sum_{\mu\nu} S'_{\mu\nu} W_{\nu\mu}. \tag{16}$$

The result shows that the calculation of analytical energy gradients within ROSS-DFT can largely be based on the methods worked out for ROHF [11].

Extension to analytical second derivatives is straightforward, however in this work we used a numerical procedure to calculate the vibrational spectra of OSS biradicals. In this connection, it was necessary to calculate

distorted systems with lower symmetry, for which the matrix element F_{rs} could not be put to zero. This leads sometimes to convergence problems, which however, can be managed by a balanced level shifting between the energies of orbitals φ_r and φ_s. The ROSS-DFT method (including analytical energy gradients) was implemented both for normal and hybrid functionals into the program package COLOGNE96. [16] All reference calculations were carried out with the program package GAUSSIAN94. [17]

3. Results and discussions

In Table 1, ROSS-DFT energies for the $^1\Delta$ state and S–T splittings with regard to the $^1\Delta/^3\Sigma$ states of NH, NF, OH^+ and O_2 are listed. In addition, bond lengths and harmonic bond stretching frequencies are given for the OSS and T state. Calculations were carried out with a variety of functionals including Becke 88 exchange [18] + Lee–Yang–Parr correlation (BLYP) [19], Becke's three-parameter hybrid exchange + Lee–Yang–Parr

Table 1
Geometries, energies and vibration frequencies (cm^{-1}) for the open-shell singlet $^1\Delta$ and triplet $^3\Sigma$ states of NH, NF, OH^+ and O_2 [a].

Method	Basis	r		E	ΔE	ω	
		$^1\Delta$	$^3\Sigma$	$^3\Sigma$	($^1\Delta - ^3\Sigma$)	$^1\Delta$	$^3\Sigma$
NH, a $^1\Delta$ and X $^3\Sigma^-$							
BLYP	6-31G(d,p)	1.056	1.058	−55.201803	37.9	3148.	3115.
	6-311G(d,p)	1.053	1.055	−55.217463	36.8	3146.	3113.
B3LYP	6-31G(d,p)	1.044	1.046	−55.219743	37.7	3284.	3250.
	6-311G(d,p)	1.042	1.044	−55.234528	36.8	3279.	3248.
MP2	TZ2P	1.030	1.030		38.5		
Expt.		1.034	1.036		35.9…39	3188.	3282.
NF, a $^1\Delta$ and X $^3\Sigma^-$							
BLYP	6-31G(d,p)	1.338	1.346	−154.421522	32.7	1139.	1116.
	6-311G(d,p)	1.336	1.344	−154.470951	32.3	1104.	1081.
B3LYP	6-31G(d,p)	1.314	1.324	−154.433000	33.3	1220.	1187.
	6-311G(d,p)	1.309	1.319	−154.479589	33.1	1192.	1158.
MP2	TZ2P	1.301	1.318		34.2		
Expt.		1.308	1.317		34.3		
OH^+, a $^1\Delta$ and X $^3\Sigma^-$							
BLYP	6-31G(d,p)	1.055	1.054	−75.238545	49.5	2944.	2941.
	6-311G(d,p)	1.050	1.050	−75.262026	49.0	2947.	2945.
B3LYP	6-31G(d,p)	1.041	1.041	−75.242261	49.3	3079.	3078.
	6-311G(d,p)	1.037	1.036	−75.264666	49.0	3080.	3081.
MP2	TZ2P	1.023	1.021		52.1		
Expt.			1.029		50.5		
O_2, a $^1\Delta_g$ and X $^3\Sigma_g^-$							
BLYP	6-31G(d,p)	1.241	1.239	−150.313337	27.9	1503.	1516.
	6-311G(d,p)	1.233	1.231	−150.360257	27.5	1478.	1491.
B3LYP	6-31G(d,p)	1.215	1.213	−150.316113	27.8	1648.	1660.
	6-311G(d,p)	1.206	1.204	−150.360821	27.5	1630.	1643.
MP2	TZ2P	1.262	1.249		24.3		
Expt.		1.215	1.207		22.6	1483.	1580.

[a] Bond lengths in Å, absolute energies in Hartree, energy differences in kcal mol^{-1}. MP2 values from Ref. [12], exp. data from Ref. [25].

correlation (B3LYP) [20], Perdew–Wang91 (PW91) [21] and the Vosko–Wilk–Nusair VWN5 functional [22]. For each functional the VDZP basis 6-31G(d,p) [23] and the VTZP basis 6-311G(d,p) [24] were employed. Results for the PW91 and VWN5 functionals did not differ much from BLYP results and, therefore, only the latter are shown in Table 1.

ROSS-DFT leads to a reasonable description of the S–T splittings and bond properties of the OSS states, where on average B3LYP results are better than BLYP results and VTZP results are better than VDZ results when compared to experimental data [25]. The B3LYP/6-311G(d,p) splitting for NH (36.8 kcal/mol, Table 1) is within the range of experimental values; for NF and OH^+ (33.1 and 49.0 kcal/mol), it differs by 1 to 1.5 kcal/mol from the corresponding experimental values. In the case of O_2, the B3LYP/6-311G(d,p) splitting (27.5 kcal/mol) is 5 kcal/mol larger than the experimental energy difference of 22.6 kcal/mol, which is parallel to the fact that the OO bond length is underestimated (1.206 vs. 1.216 Å, Table 1). ROSS-MP2 [12] severely overestimates the OO bond length (1.262 Å), however predicts the S–T splitting somewhat better (24.3 kcal/mol, Table 1) than ROSS-DFT.

In Tables 2 and 3, DFT energies and equilibrium geometries for the $^1B_1/^3B_1$ states of methylene and the $^1A''/^3A''$ states of formaldehyde are compared with the available experimental [25] and ROSS-MP2 data [12]. Again, B3LYP/6-311G(d,p) results are more accurate than those obtain with BLYP or the smaller basis set. They reflect geometric and energetic differences between the high-spin and low-spin states correctly. For CH_2, the S–T splitting (32.2 kcal/mol, Table 2) is just 1 kcal/mol below the experimental value, which has to be seen on the background that the relative energies of both the $^1A_1$ ground state and the two excited states $^1B_1/^3B_1$ are reasonably described at the DFT level while MP2 fails in this respect (Table 2). ROSS-MP2 predicts the $^1A_1$ state just 18.3 kcal/mol below the $^1B_1$ state while the accurate value should be 24.4 kcal/mol (Table 2), which is better reproduced by ROSS-DFT. ROSS-DFT also performs well for formaldehyde although the S–T splitting (10.9 kcal/mol, Table 3) is 2.5 kcal/mol larger than the experimental value of 8.4 kcal/mol [25] (MP2: 8.8 kcal/mol [12]). However, the relative energies of the $^1A''/^3A''$ states with regard to the $^1A_1$ ground state of formaldehyde (81.4 and 70.5 kcal/mol, Table 3) differ by just 0.8 and 1.5 kcal/mol, respectively, from the corresponding experimental values while MP2 fails by about 9 kcal/mol [12] to correctly predict these energy differences. DFT overestimates the stability of the T state (1–2 kcal/mol), which is also observed for O_2 (5 kcal/mol, Table 1) and which could mean that certain correlation effects are underestimated at the ROSS-DFT level.

As for the calculated OSS geometries, major deviations from experimental values are observed for the HCH angle in CH_2, $^1B_1$ (148.3 vs 142.8° exp., Table 2) and the out-of-plane angle in $CH_2=O$, $^1A''$ (36.7 vs. 31° exp.,

Table 2
Equilibrium geometries and energies for the $^1B_1$ and $^3B_1$ excited states of methylene [a].

Parameter	BLYP		B3LYP		MP2	Expt.
	6-31G(d,p)	6-311G(d,p)	6-31G(d,p)	6-311G(d,p)		
$E(^3B_1)$	−39.069872	−39.086415	−39.096189	−39.111141		
$\Delta E(^1B_1-{}^3B_1)$	34.4	31.7	34.7	32.2	34.6	33.4 [b]
$\Delta E(^1B_1-{}^1A_1)$	23.3	21.4	22.3	20.8	18.3	24.4
$\Delta E(^1A_1-{}^3B_1)$	11.1	10.3	12.4	11.4	16.3	9. [c]
r(CH), $^1B_1$	1.081	1.079	1.075	1.074	1.070	1.073
r(CH), $^3B_1$	1.089	1.086	1.082	1.080	1.072	1.077
∠(HCH), $^1B_1$	147.8	149.6	146.7	148.3	142.4	142.8
∠(HCH), $^3B_1$	132.9	134.1	132.1	133.6	133.1	134.0

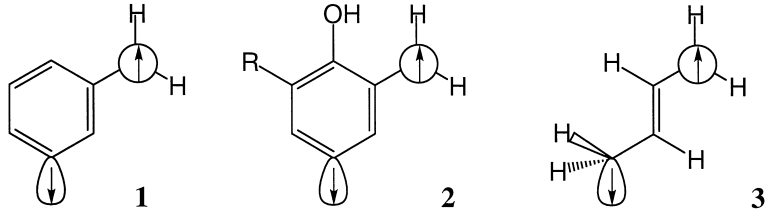
[a] Absolute energies in Hartree, energy differences in kcal mol^{-1}, bond lengths in Å, bond angles in deg. Exp. data from G. Herzberg, Electronic Spectra of Polyatomic Molecules, Van Nostrand Reinhold, New York, 1966, MP2 value for $^1B_1$ from Ref. [12]. [b] Extrapolated value from C.W. Bauschlicher Jr., Chem. Phys. Lett. 74 (1980) 273. [c] D.G. Leopold, K.K. Muarry, A.E. Stevens Miller, W.C. Lineberger, J. Chem. Phys. 83 (1985) 4849.

Table 3
Energies and geometries of the $^3A''$ and $^1A''$ states of formaldehyde, $H_2C=O$. [a]

Parameter	BLYP		B3LYP		MP2	Expt.
	6-31G(d,p)	6-311G(d,p)	6-31G(d,p)	6-311G(d,p)		
$E(^1A_1)$	−114.474828	−114.510161	−114.990876	−115.025662		
$\Delta E(^1A''-{}^3A'')$	12.4	12.6	10.7	10.9	8.8	8.4
$\Delta E(^1A''-{}^1A_1)$	81.8	81.9	81.2	81.4	89.4	80.6
$\Delta E(^3A''-{}^1A_1)$	69.4	69.3	70.5	70.5	80.6	72.0
r(CH), $^1A''$	1.108	1.106	1.096	1.094		1.09
r(CH), $^3A''$	1.117	1.116	1.102	1.101		
r(CO), $^1A''$	1.338	1.330	1.336	1.330		1.32
r(CO), $^3A''$	1.314	1.307	1.313	1.306		1.31
∠(HCH), $^1A''$	114.9	115.2	116.8	117.3		119.
∠(HCH), $^3A''$	110.5	110.5	113.8	114.0		
τ, $^1A''$	39.1	37.8	37.9	36.7		31.
τ, $^3A''$	46.1	45.3	43.4	42.8		35.

[a] Bond lengths in Å, bond angles in deg, absolute energies in Hartree, energy differences in kcal mol^{-1}. τ is the out-of-plane angle, i.e. 180° minus the angle between the C–O bond and the bisector of the H–C–H angle. Exp. data from G. Herzberg, Electronic Spectra of Polyatomic Molecules, Van Nostrand Reinhold, New York, 1966, MP2 values from Ref. [12].

Table 3). In these cases, however, the potential energy surface is rather flat (E increases by 0.15 kcal/mol and 0.22 kcal/mol, respectively when experimental angles are used) so that improvements in the density functional and/or the basis set may lead to a better prediction of these angles.



Encouraged by the ROSS-DFT results for small molecules we calculated also a number of derivatives of the α-3-dihydrotoluene biradical **1**, which as mentioned in the introduction is presently at the focus of research on enediyne antibiotics [1,26]. Geometries and vibrational frequencies of these biradicals are in line with what one can predict on the basis of moderate CASSCF calculations (relatively small active space, small VDZ basis) and infrared measurements carried out by Sander et al. [26]. In so far ROSS-DFT presents an economical and reliable alternative to CASSCF or MCSCF calculations, which for biradicals **1** and **2** could become rather expensive, if not impossible, if carried out for an active space with 10 electrons and more employing a TZ2P or even larger basis set. However, ROSS-DFT calculations for biradicals such as **1** and **2** lead to a problem, which is also inherent in the calculation of the OSS state of O_2.

In the biradicals **1** and **2**, the singly occupied orbitals φ_r and φ_s are of σ and π nature and are largely localized at C atoms, which are 3.7–4.2 Å apart depending on whether the through-space distance or the through-bond distance is considered. Hence, the direct exchange interaction of the two electrons r and s in the T state is rather weak ($K \leq 1$ kcal/mol) and, accordingly, for an ROHF calculation the T would be predicted to be just slightly below the OSS state.

However, there is an indirect interaction between electrons r and s, which is mediated by the electrons in the doubly occupied space. If the r electron possesses up spin, then the exchange potential connected with it will

attract spin-up electrons of the doubly occupied space, which leads to spin polarization of the electron system. A spin-up surplus density will be found in those regions where the *r* electron is concentrated, while spin-down density will dominate in other regions. Accordingly, the *s* electron sees not only the *direct* exchange potential of the *r* electron but also the additional exchange potential build up in the doubly-occupied space. This can lead to further destabilization or stabilization of the OSS state depending on where the *s* electron is localized: if it is concentrated in regions where the *r* electron also possesses a high density, then the indirect interaction leads to an additional stabilization of the T state. Otherwise, in particular if the two electrons prefer disjunct regions (corresponding to a localization of the orbitals φ_r and φ_s at different C atoms), the *s* electron will see a down-spin surplus density and, consequently, the local exchange potential will favour a situation in which the *s* electron possesses a down spin. Hence, the *indirect* mechanism stabilizes the OSS state.

In the biradicals **1** and **2**, the direct exchange interaction is small while the *indirect* interaction between electrons *r* and *s* leads to a stabilization of the OSS state, which according to CASSCF(9,8)/3-21G calculations carried out in this work becomes the ground state of biradical **2** ($R = CH_3$) lying 3.5 kcal/mol below the T state. While ROSS-DFT correctly accounts for the direct exchange interaction between electrons *r* and *s*, it does not cover spin polarization in the doubly occupied space caused by the *indirect* interaction. This is due to the fact that the orbitals of the doubly occupied space are restricted to be the same for up and down electron spin. Consequently, the OSS state of **1** and **2** is always predicted by ROSS-DFT to be slightly above the T state.

A proper account of spin polarization could be obtained by using spin-dependent orbitals, which leads to an unrestricted DFT (UDFT) description. UDFT, however, describes an artificial state, which can be a mixture of the OSS and T state and, possibly, higher lying zwitterionic closed-shell singlet states of **1** and **2** so that a UDFT description becomes useless. Alternatively, the spin polarization problem could be solved by the mixed MCSCF-DFT approach proposed by Miehlich et al. [10]. However, as pointed out above, a relatively large active space would be needed and the computational cost would become high, which is contrary to the goal of developing a method with a high efficiency/cost ratio.

At the present stage we have solved the problem of spin polarization and an accurate calculation of S–T splittings in a case such as **1**, by combining ROSS-DFT with CASSCF calculations in form of a hybrid method. For a small reference system such as **3**, S–T splittings are correctly determined by the CASSCF calculations and, then, the S–T splitting of the target system is determined according to

$$\Delta E(S\text{–}T) = \Delta E(S\text{–}T,\mathrm{DFT},\mathbf{1}) + \Delta E(S\text{–}T,\mathrm{CASSCF},\mathbf{3}) - \Delta E(S\text{–}T,\mathrm{DFT},\mathbf{3}) \quad (17)$$

However, our current work aims at solving the spin polarization problem in a more direct way. Also, ROSS-DFT is presently extended to biradical systems, for which orbitals φ_r and φ_s form one two-dimensional irreducible representation and two singlet states of comparable energy exist. In these cases, appropriate *r*-*s* orbital rotations are needed to obtain the lowest OSS state.

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