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On the diagnostic value of $\langle \hat{S}^2 \rangle$ in Kohn–Sham density functional theory

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Unrestricted density functional theory (UDFT) is, in addition to its application to high spin multiplet systems, an efficient method for describing singlet biradical states. In this connection, spin contamination of the UDFT description as measured by the expectation values of $\hat{S}^2$ is of interest, but is difficult to assess since the calculation of $\langle \hat{S}^2 \rangle$ as the expectation value of a two-particle operator is not possible within the single-determinant approach of DFT. A new way of determining $\langle \hat{S}^2 \rangle$ from the UDFT (UHF or any other) spin magnetization density (SMD) $m_s(\mathbf{r}) = \rho_\alpha(\mathbf{r}) - \rho_\beta(\mathbf{r})$ is described and applied to the stretched H_2 molecule and the singlet state of the *para*-didehydrobenzene biradical for a number of different functionals. Although $\langle \hat{S}^2 \rangle$ as calculated from the Kohn–Sham determinant is found to differ significantly from the corresponding value obtained with the help of the SMD in the case of singlet biradicals, the former result is a diagnostic value and can be used to assess spin contamination of the UDFT description on a qualitative basis.

1. Introduction

Density functional theory (DFT) [1] is nowadays used widely in quantum chemistry, and as a low cost method with relatively high reliability it has largely replaced wavefunction methods such as Møller–Plesset second-order (MP2) perturbation theory or Hartree–Fock (HF) theory [2]. There is a tendency for many applied quantum chemists to use DFT methods in a similar way to wavefunction methods. In this spirit, unrestricted DFT (UDFT) is applied widely for the description of open-shell systems to exploit the higher flexibility of the Kohn–Sham (KS) single-determinant wavefunction and to get a better account of spin polarization effects. UDFT calculations lead to reasonable results at low computational cost in many cases. However, the question of spin contamination in the UDFT singlet state is a matter of controversy. As for UHF and UMP [3], the calculation of $\langle \hat{S}^2 \rangle$ from the UDFT KS determinant leads to a value different from the ideal value $S(S+1) = 0$. One could argue that this is irrelevant and should be ignored or one could consider the UDFT result to be basically wrong because of spin contamination as indicated by the $\langle \hat{S}^2 \rangle$ value. In the latter case, it would be logical to improve the UDFT result by using the sum formula [4] or by employing spin projection methods [5, 6] and to replace UDFT by PUDFT in the same way as UHF is replaced by PUHF or UMP by PUMP (often called PMP) [3].

Given the usefulness of UDFT for singlet biradicals on the one hand and the controversy regarding the spin contamination of UDFT states on the other hand, it is of interest to develop methods to analyse the spin symmetry of a state described by UDFT. In wavefunction theory, one can enforce the correct spin symmetry of the many-particle wavefunction by proper construction, as for spin restricted open-shell methods [7]. Alternatively, if the calculation has been done spin unrestricted, i.e. with arbitrary spin symmetry allowed for the wavefunction [8], one can subsequently use the difference $\langle \hat{S}^2 \rangle - S(S+1)$ as a measure of spin contamination of the wavefunction by contributions with a higher spin multiplicity. For DFT, only the KS reference wavefunction is available, which is related to a fictitious reference system of non-interacting particles. Accordingly, it is not possible to calculate correctly two-particle quantities such as $\langle \hat{S}^2 \rangle$ even if the correct KS reference wavefunction would be known. A value of $\langle \hat{S}^2 \rangle_{\mathrm{UDFT},\Phi}$ differing from $S(S+1)$ does not necessarily indicate that the corresponding many-particle state is spin contaminated, and that one has to cure this problem by constructing the KS wavefunction with correct spin symmetry as done for spin restricted open-shell DFT (RODFT) [9].

The spin symmetry problem within DFT has been discussed by a number of authors. Pople *et al.* [10] argued that the appropriate KS formalism for multiplet

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systems should be unrestricted rather than the open-shell restricted one, and that spin contaminations of the KS reference wavefunction should be ignored. Wang *et al.* [11] used the Löwdin formula [12] to appropriately calculate $\langle \hat{S}^2 \rangle$ for UDFT. They found that the $\langle \hat{S}^2 \rangle$ value calculated from the KS orbitals, while formally not correct, still is reasonably accurate and contains relevant information.

Previous investigations were focused on high spin open-shell states such as doublet radicals or triplet biradicals, [5, 6, 10, 11] but did not consider singlet biradicals. If the exact XC functional were known, then these singlet systems would be described correctly with closed-shell RDFT, and biradical character would be described by the XC energy functional. However, the available approximations for the XC energy functional fail to reflect the strong static correlation effects present in these systems and, therefore lead to a qualitatively incorrect description. The RDFT solution is in addition externally unstable and the minimum energy of an S biradical corresponds to an UDFT solution with broken symmetry, where UDFT gives in general a considerably better description of the system than RDFT does. The UDFT solution has a $\langle \hat{S}^2 \rangle_{\mathrm{UDFT},\Phi}$ value greater than $S(S+1) = 0$ and, depending on the XC functional used and the electronic system considered, adopts values between 0 and 1. In the same way as for high spin open-shell cases, one might argue that in view of the unsolved problem of calculating the correct $\langle \hat{S}^2 \rangle_{\mathrm{UDFT}}$ the $\langle \hat{S}^2 \rangle_{\mathrm{UDFT},\Phi}$ value is not reliable and thus not necessarily an indication of spin contamination of the corresponding many-body state. On the other hand, it is likely that a single-determinant description of a multi-reference problem such as an S biradical suffers from basic problems and, because of this, that reliable characterization of the UDFT solution is desirable.

An alternative and probably more reliable account of spin contamination can be found by investigating one of the key quantities of spin resolved DFT, namely the spin magnetization density (SMD) $m_s(\mathbf{r}) = \rho_\alpha(\mathbf{r}) - \rho_\beta(\mathbf{r})$. (We use the term spin magnetization density in view of the fact that (a) this term is frequently used in solid state physics and (b) the alternative term spin density is often used in connection with the spin resolved densities $\rho_\alpha(\mathbf{r})$ and $\rho_\beta(\mathbf{r})$.) For a pure S state, as for any pure multiplet state with $\hat{S}_z = 0$, the SMD $m_s(\mathbf{r})$ must vanish everywhere. As this is not the case for the UDFT solution, the state described must be a superposition of contributions with different spin multiplicity. The question arises whether $m_s(\mathbf{r})$ can be used not only to indicate spin contamination but also to predict a more reliable value of the expectation values of $\hat{S}^2$, which will be denoted as $\langle \hat{S}^2 \rangle_{\mathrm{UDFT},m_s}$. By comparing $\langle \hat{S}^2 \rangle_{\mathrm{UDFT},\Phi}$ and $\langle \hat{S}^2 \rangle_{\mathrm{UDFT},m_s}$ one can decide on the relevance of the former value as a means of diagnosing spin contamination.

In this work, we derive a method for calculating $\langle \hat{S}^2 \rangle_{\mathrm{UDFT},m_s}$, which is based on comparing the SMDs from the UDFT description of the singlet (S) biradical and the UDFT description for the corresponding triplet (T) biradical. The SMD approach for calculating the expectation value of $\hat{S}^2$ is not restricted to DFT but can be applied also to any quantum chemical method that provides an SMD. Accordingly, we can test the reliability and usefulness of the SMD method at the UHF level of theory utilizing the fact that $\langle \hat{S}^2 \rangle_{\mathrm{UHF},\Phi}$ calculated from the UHF wavefunction represents a reliable reference. The test is performed for the stretched hydrogen molecule, which represents the archetype of an S biradical. Then, the SMD method is applied to the DFT description of stretched H_2 and to the S biradical state of *para*-didehydrobenzene employing a number of different XC functionals. *para*-Didehydrobenzene is the subject of the present research on enediyne antitumour drugs [13, 14] and, therefore it is chosen as a representative of an important class of organic biradicals with similar electronic and structural features. Finally, we will draw conclusions on the diagnostic value of $\langle \hat{S}^2 \rangle_{\mathrm{UDFT},\Phi}$ as calculated from the KS reference wavefunction.

2. The SMD method for calculating $\langle \hat{S}^2 \rangle$

In wavefunction theory, the value of $\langle \hat{S}^2 \rangle$ can be calculated either as an expectation value, which requires the calculation of matrix elements involving T and higher excitations,

$$\langle \hat{S}^2 \rangle = \langle \Psi | \hat{S}^2 | \Psi \rangle / \langle \Psi | \Psi \rangle, \tag{1}$$

or alternatively as a response property from the ground-state energy E_λ of the perturbed Hamiltonian $\hat{H}_\lambda = \hat{H} + \lambda \hat{S}^2$ [3]:

$$\langle \hat{S}^2 \rangle = \left. \frac{\mathrm{d}E(\lambda)}{\mathrm{d}\lambda} \right|_{\lambda=0}. \tag{2}$$

$\langle \hat{S}^2 \rangle$ values calculated with either equation (1) or (2) are identical for HF and MCSCF, but not for MPn or CC methods since the latter do not fulfil the Hellmann–Feynman theorem. At the DFT level, the calculation of $\langle \hat{S}^2 \rangle$ as an expectation value requires knowledge of the two-particle density according to the Löwdin formula, which can be given only in an approximate way [10, 11]. Conversely, calculation of $\langle \hat{S}^2 \rangle$ as a response property would lead to some basic problems in DFT, one of which has to do with the fact that it involves the use of virtual KS orbitals for modelling excited KS determinants.

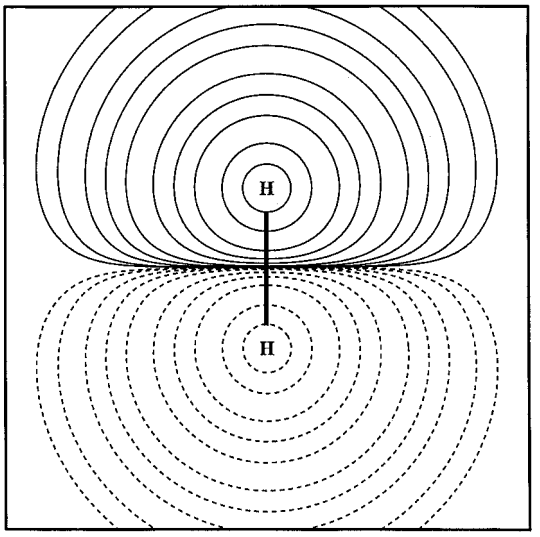
We follow in this work a third approach to the calculation of $\langle \hat{S}^2 \rangle$, which is based on an appropriate $\langle \hat{S}^2 \rangle$ reference value of a suitable reference state and a comparison of the SMDs $m_s(\mathbf{r})$ of these states. Clearly, this limits the application of the new approach, but on the other hand provides a reasonable description of spin contamination of precisely those electron systems in which we are primarily interested.

In figure 1, the SMD $m_s(\mathbf{r})$ of the H_2 molecule stretched to $R = 1.4$ and calculated at the UHF level with a cc-pVTZ basis [15] is shown in the form of a contour line diagram, where solid contour lines denote a surplus of α and dashed contour lines a surplus β spin density. Clearly, the surplus of α spin density is located at the first while a surplus of β spin density is located at the second H atom (see figure 1), thus indicating that at the UHF level the S state is contaminated by a T state with $S_z = 0$.

Since the UHF description of the stretched H_2 molecule is contaminated by just the T state, we now predict the weight of the T component and, accordingly, $\langle \hat{S}^2 \rangle_{\mathrm{UHF}}$ by comparison of the SMD of the broken-symmetry state (figure 1(*a*)) and the SMD of the corresponding T state (figure 1(*b*)) also calculated at UHF. As shown in figure 1, the SMD of the T state is everywhere positive and finite in the centre of the molecule (for the UHF description of the S state it is zero at this location). The SMDs for the S and T states can be used for a determination of spin contamination of the UHF description of the S state provided that the following holds.

(1) The T state appearing as a contamination in the UHF description can be represented by the directly calculated UHF T state. Of course, this assumption can hold only approximately since the T contamination and the UHF T state will differ. The T contamination is a direct result of balancing the mixing of the S ground state and a doubly excited S state within a single-determinant description, and therefore it must differ from the T state for which the wavefunction is optimized at the UHF level. This difference will cause errors in the SMD calculation of $\langle \hat{S}^2 \rangle_{\mathrm{UHF},m_s}$ that can be assessed directly by comparing $\langle \hat{S}^2 \rangle_{\mathrm{UHF},m_s}$ and $\langle \hat{S}^2 \rangle_{\mathrm{UHF},\Phi}$ of the stretched H_2 molecule.

(2) In the general case, the UHF description of a T biradical will also be contaminated. One could think of using the spin restricted open-shell description of the T state (ROHF, RODFT, etc.); however, by this one would lose the advantages of spin unrestricted theory, for example of describing spin polarization correctly. Hence, one



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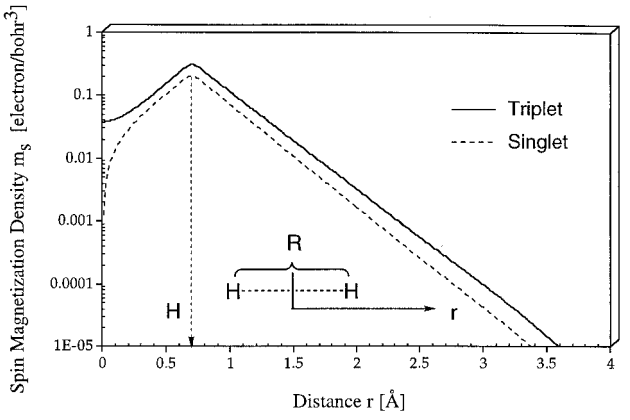

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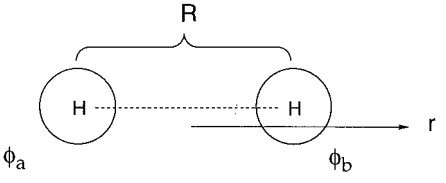

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Figure 1. (*a*) SMD distribution $m_s(\mathbf{r}) = \rho_\alpha(\mathbf{r}) - \rho_\beta(\mathbf{r})$ of the stretched H_2 molecule ($R = 1.4$ Å) in its S ground state calculated at the UHF/cc-pVTZ level of theory and given in the form of a contour line diagram in the plane of the molecule. Solid lines indicate a surplus of α spin, and dashed lines, a surplus of β spin. The following contour lines are used: $0, \pm 0.0001$, ± 0.0002, ± 0.0005, ± 0.001, ± 0.002, ± 0.005, ± 0.01, ± 0.02, ± 0.05, ± 0.1 ea_0^{-3}. (*b*) SMD profile (in ea_0^{-3}) of the S ground state (dotted line) and the first T state (solid line) of the stretched H_2 molecule ($R = 1.4$ Å) calculated at the UHF/cc-pVTZ level of theory and shown as a function of distance r for $0 \leqslant r \leqslant 4$ Å where $r = 0$ is the bond midpoint. (*c*) Schematic drawing of the UHF orbitals ϕ_a and ϕ_b of the S ground state of the stretched H_2 molecule with the definition of bond length R and position parameter r.

has to stick to the UHF description of the T state. Experience shows that its contamination is rather small as reflected by $\langle \hat{S}^2 \rangle_{\mathrm{UHF},\Phi}$ for T states, which normally differs only slightly from $S(S+1) = 2$. Hence, one can neglect the contamination of the T state.

(3) For S biradicals with more than two electrons, one has to consider in addition to the T contamination also contaminations from higher spin multiplets. We assume that these higher contaminations can be neglected.

(4) The T and S states of a biradical possess different geometries. It is assumed that any differences in the two geometries are so small that the SMD of the T state calculated at the S geometry does not differ much from the true SMD of the T state. Actually, this assumption is an extension of assumption (1), and indicates that S and T states are calculated under the same conditions.

Clearly, assumption (1) is the most critical one, and therefore we have chosen stretched H_2 as an appropriate example to test the validity of assumption (1). The SMD method based on assumptions (1) to (4) can be derived in the following way. The UHF wavefunction of the S state is built up from the two UHF orbitals $\psi_a^{\mathrm{S}} = \phi_a\alpha$ and $\psi_b^{\mathrm{S}} = \phi_b\beta$:

$$|\Phi_{\mathrm{UHF}}^{\mathrm{S}}\rangle = \hat{a}_\alpha^\dagger \hat{b}_\beta^\dagger |0\rangle, \tag{3}$$

where the creation operators act on the two orbitals ϕ_a and ϕ_b, which are sketched in figure 1(*c*). Due to breaking of spin symmetry, these orbitals are localized at the first and second H atom, respectively. The SMD of the S state is given by

$$m_2^{\mathrm{UHF,S}} = \phi_a(\mathbf{r})^2 - \phi_b(\mathbf{r})^2. \tag{4}$$

By decomposing $|\Phi_{\mathrm{UHF}}^{\mathrm{S}}\rangle$ into S and T components, one finds that

$$\begin{aligned}\langle \hat{S}^2 \rangle_{\mathrm{UHF}} &= \langle \Phi_{\mathrm{UHF}} | \hat{S}^2 | \Phi_{\mathrm{UHF}} \rangle \\ &= 1 - \langle \phi_a | \phi_b \rangle^2. \end{aligned} \tag{5}$$

In the case of orthogonal orbitals ϕ_a and ϕ_b, $\langle \hat{S}^2 \rangle_{\mathrm{UHF}} = 1$, which corresponds to a 1:1 mixing of S and T contributions in the UHF state (see equation (12) below) whereas $\langle \hat{S}^2 \rangle_{\mathrm{UHF}} < 1$ will occur if ϕ_a and ϕ_b overlap.

The T UHF function is analogously built up of two spin orbitals ψ_a^{T} and ψ_b^{T}, which in general will be independent of the orbitals ψ_a^{S} and ψ_b^{S}. However, employing assumption (1) we assume that the spin orbitals for both the T and the S states are based on the same space orbitals ϕ_a and ϕ_b, i.e. $\psi_a^{\mathrm{T}} = \phi_a\alpha$ and $\psi_b^{\mathrm{T}} = \phi_b\alpha$. In contrast to ψ_a^{S} and ψ_b^{S}, the spin orbitals ψ_a^{T} and ψ_b^{T} generally are not orthogonal to each other, which results from the fact that they are not the canonical orbitals for the two electrons. The overlap $\langle \psi_a | \psi_b \rangle$ is equal to $\langle \phi_a | \phi_b \rangle$ and, according to equation (5), related to $\langle \hat{S}^2 \rangle_{\mathrm{UHF}}$. To account for this overlap, one has to introduce a normalization factor C into the T wavefunction, which then takes the form

$$|\Phi_{\mathrm{UHF}}^{\mathrm{T}}\rangle = C\hat{a}_\alpha^\dagger \hat{b}_\beta^\dagger |0\rangle, \tag{6}$$

$$\begin{aligned} C &= [1 - \langle \phi_a | \phi_b \rangle^2]^{-1/2} \\ &= \langle \hat{S}^2 \rangle_{\mathrm{UHF}}^{-1/2}. \end{aligned} \tag{7}$$

The SMD for the T state is given by

$$\begin{aligned} m_s^{\mathrm{T}}(\mathbf{r}) = \frac{1}{\langle \hat{S}^2 \rangle_{\mathrm{UHF}}} \{ &\phi_a^2(\mathbf{r}) + \phi_b^2(\mathbf{r}) \\ &- [1 - \langle \hat{S}^2 \rangle_{\mathrm{UHF}}]^{1/2} \phi_a(\mathbf{r}) \phi_b(\mathbf{r}) \}. \end{aligned} \tag{8}$$

Comparison of equations (4) and (8) reveals that for an equal mixture of S and T states in the UHF description of the S state (large R and $\langle \phi_a | \phi_b \rangle = 0$), the SMDs of S and T states are identical in the non-bonding region: $m_{\mathrm{s}}^{\mathrm{UHF,S}} = m_{\mathrm{s}}^{\mathrm{UHF,T}} = \phi_a^2$. For smaller R as shown in figure 1(*b*), the two space orbitals ϕ_a and ϕ_b overlap, the S contribution to the UHF S state is larger than the T contribution, $\langle \hat{S}^2 \rangle_{\mathrm{UHF}} < 1$ and $m_{\mathrm{s}}^{\mathrm{UHF,T}}$ is scaled up by a factor $1/\langle \hat{S}^2 \rangle_{\mathrm{UHF}}$ so that $m_{\mathrm{s}}^{\mathrm{UHF,T}} > m_{\mathrm{s}}^{\mathrm{UHF,S}}$ in all regions of the stretched H_2 molecule. In the non-bonding regions where one of the two orbitals dominates, the SMDs of the UHF S and UHF T states are proportional to each other, so that one can determine $\langle \hat{S}^2 \rangle_{\mathrm{UHF},m_{\mathrm{s}}}$ directly from the proportionality factor:

$$\begin{aligned} &|m_{\mathrm{s}}^{\mathrm{UHF}}(\mathbf{r})| = \langle \hat{S}^2 \rangle_{\mathrm{UHF}} m_{\mathrm{s}}^{\mathrm{T}}(\mathbf{r}) \quad \text{for} \quad |\phi_a(\mathbf{r})| \gg |\phi_b(\mathbf{r})| \quad \text{or} \\ &\quad |\phi_b(\mathbf{r})| \gg |\phi_a(\mathbf{r})|. \end{aligned} \tag{9}$$

Hence, one can apply the SMD method if it is possible to identify a suitable region in the molecule where the electron population of one of the open-shell orbitals contributes predominantly to the SMD. In such a region, the relative spin polarization

$$\zeta(\mathbf{r}) = (\rho_\alpha(\mathbf{r}) - \rho_\beta(\mathbf{r}))/\rho(\mathbf{r}) \tag{10}$$

of the S-UDFT state is equal or close to 1. Accordingly, it is reasonable to fit $m_{\mathrm{s}}^{\mathrm{UHF,S}}$ to the ansatz

$$m_{\mathrm{s}}^{\mathrm{UHF,S}} = f m_{\mathrm{s}}^{\mathrm{UHF,T}} \tag{11}$$

employing a least-square criterion. The factor f should lead to a reasonable estimate for $\langle \hat{S}^2 \rangle_{\mathrm{UHF},m_{\mathrm{s}}}$ according to equation (9).

Utilizing $\langle \hat{S}^2 \rangle_{\mathrm{UHF},m_{\mathrm{s}}}$, the percentage of S and T character in the UHF description can be derived from

$$\langle \hat{S}^2 \rangle_{\mathrm{UHF}}^{\mathrm{S}} = x \langle \hat{S}^2 \rangle^{\mathrm{S}} + (1-x) \langle \hat{S}^2 \rangle^{\mathrm{T}}. \tag{12}$$

When this approach is applied to systems with more than two electrons, one must make an additional assumption, viz. that

(5) the core of doubly occupied orbitals is not spin polarized or, alternatively, that its spin polarization in the S and T states is comparable.

This assumption is closely connected to assumptions (2) and (3) above, which play no role in a two-electron system. Experience shows that assumption (5) is not correct; however, differences resulting from spin polarization effects are in general rather small.

The SMD method in its ultimate formulation makes use of the SMDs of the S and T states and considers the orbitals ϕ_a and ϕ_b only as intermediate quantities. This means that the SMD can be applied to any spin unrestricted method such as UMP, UHF-CC or, in particular, UDFT. In the following, we will discuss results obtained with the SMD method at the UHF and UDFT levels of theory, trying to answer questions raised in section 1.

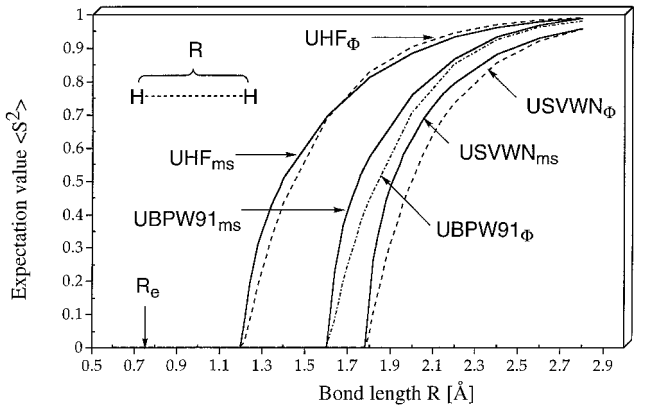
3. Application of the SMD method for calculating $\langle \hat{S}^2 \rangle$

All calculations were carried out using standard theory and Dunning's cc-pVTZ basis set [15]. Seven different functionals representing three basically different approaches in DFT were tested at the UDFT level: 1, the SVWN functional, which is a typical representative of the LSD approach since it combines the Slater exchange functional [16] with the Vosko–Wilk–Nusair correlation function [17]; 2, BP86, 3, BPW91 and 4, BLYP represent functionals using the generalized gradient approximation (GGA); the Becke88 exchange functional [18] based on Slater exchange and corrections involving the gradient of the density is combined with Perdew's gradient corrected correlation functional P86 [19]; the Perdew–Wang-1991 gradient corrected correlation functional [20] or the LYP correlation functional of Lee *et al.* [21]; 5, B3PW91 and 6, B3LYP are Becke's three-parameter hybrid functionals with the fitting parameters $A = 0.80$, $B = 0.72$ and $C = 0.81$; while 7, mPW1PW91, is the one-parameter hybrid functional of Barone and Adamo [23] based on the modified Perdew–Wang exchange functional mPW1 and the Perdew–Wang 91 correlation functional. mPW1PW91 represents a member of the new class of one-parameter hybrid functionals which have been optimized further to extend the applicability of DFT [24]. The single parameter of mPW1PW91, which mixes HF and DFT exchange, is 0.25 as determined by lowest order Görling–Levy perturbaton theory [23]. All calculations were carried out with the quantum chemical programs Cologne 99 [25] and Gaussian 98 [27].

For the calculation of $\langle \hat{S}^2 \rangle_{\mathrm{UHF},m_s}$ and $\langle \hat{S}^2 \rangle_{\mathrm{UDFT},m_s}$, equation (11) was used after selecting an appropriate region to compare the SMDs of the S and T states as calculated with UHF or UDFT. In the case of heavy atoms, we find a shell structure (see below) close to the nucleus, which is probably due to differences in the α and β KS core orbitals (see assumption (5)). Therefore, we restrict the fit procedure to the region 0.5–3 Å away from a reference nucleus in the non-bonding region of the molecule to make sure that equation (9) is fulfilled. In the case of the H_2 molecule, this region is along the bond axis while for the *para*-didehydrobenzene biradical the direction along the outer bisector of the C3C4C5 (see later in figure 4) bond angle was chosen. In figure 2(*a*), calculated $\langle \hat{S}^2 \rangle_{\mathrm{UHF},m_s}$ and $\langle \hat{S}^2 \rangle_{\mathrm{UDFT},m_s}$ values are given as a function of the internuclear distance R of the stretched H_2 molecule (solid lines). They are compared with the corresponding $\langle \hat{S}^2 \rangle_{\mathrm{UHF},\Phi}$ and $\langle \hat{S}^2 \rangle_{\mathrm{UDFT},\Phi}$ values obtained from the UHF or KS wavefunctions.

The RHF description of the H_2 molecule becomes unstable for bond lengths $R \geqslant 1.2$ Å (figure 2(*a*)). With increasing R, the UHF solution becomes increasingly more stable than the RHF solution, while spin contamination of the UHF wavefunction increases from 0 to 1 for $R = 1.2 \rightarrow \infty$. Generally, the possible gain in total energy due to the restricted–unrestricted transition (measurable, e.g. by the energy difference $E(U) - E(R)$) for a given method, is larger the lower the correlation energy the restricted version of this method covers. RHF does not cover any Coulomb correlation at all, and therefore it is less stable and the corresponding UHF state is more spin contaminated for any bond length $R > 1.2$ Å than any of the DFT methods investigated (figure 2(*a*)). RDFT-BPW91 becomes unstable for $R \geqslant 1.52$ Å and RDFT-SVWN for $R \geqslant 1.78$ Å. This reflects the fact that (a) DFT methods cover a considerable amount of dynamic correlation effects; and (b) LSD methods such as SVWN systematically overestimate dynamic electron correlation effects in distinction to gradient corrected methods such as BPW91, which accounts for the smaller instability of RDFT-SVWN as compared to RDFT-BPW91. DFT methods fail to describe static electron correlation effects; however, this is partly compensated by an overestimation of dynamic correlation effects.

Figure 2(*a*) and in particular (*b*), in which the difference $\langle \hat{S}^2 \rangle_{m_s} - \langle \hat{S}^2 \rangle_{\Phi}$ is given as a function of $\langle \hat{S}^2 \rangle_{\Phi}$, reveal the extent to which $\langle \hat{S}^2 \rangle_{\Phi}$ and $\langle \hat{S}^2 \rangle_{m_s}$ agree for the different methods. Obviously, the two values for $\langle \hat{S}^2 \rangle$ differ strongly for small spin contaminations ($\langle \hat{S}^2 \rangle_{\Phi} \leqslant 0.5$) suggesting $\langle \hat{S}^2 \rangle_{m_s} \propto \langle \hat{S}^2 \rangle_{\Phi}^{1/2}$ rather than direct proportionality for $\langle \hat{S}^2 \rangle_{\Phi} \rightarrow 0$. This indicates that assumption (1) becomes less justified the more the two orbitals ϕ_α and ϕ_β overlap. On the other hand, one finds that the



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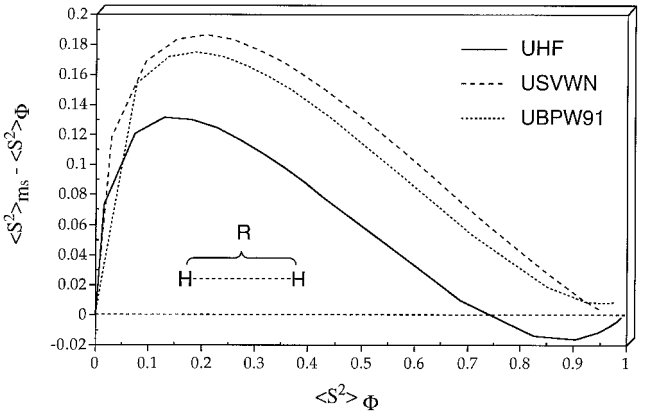

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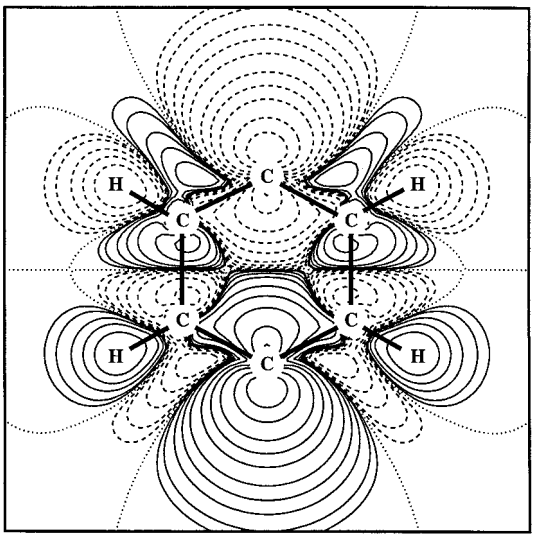
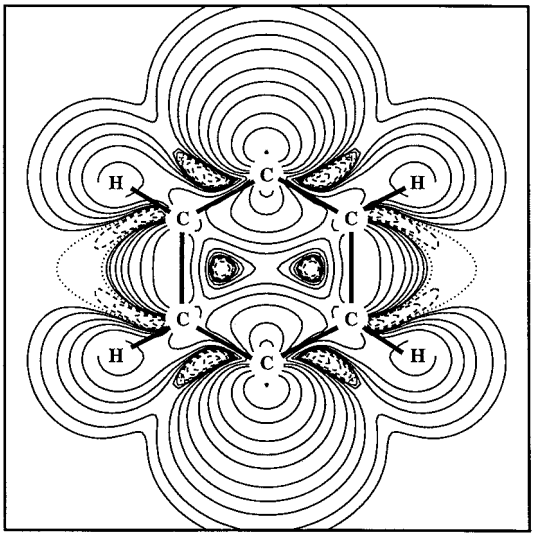
Figure 2. (*a*) $\langle \hat{S}^2 \rangle$ for the stretched H_2 molecule as calculated from the KS determinant and from the SMD given as a function of the bond distance R at the UHF/cc-pVTZ, UBPW91/cc-pVTZ, and USVWN/cc-pVTZ levels of theory. The experimental equilibrium bond length R_e is indicated. Calculated equilibrium bond lengths are: 0.7344 Å (HF/cc-pVTZ); 0.7481 Å (BPW91/cc-pVTZ), 0.7641 Å (SVWN/cc-pVTZ). (*b*) Difference $\Delta\langle \hat{S}^2 \rangle = \langle \hat{S}^2 \rangle_{\mathrm{UDFT},m_s} - \langle \hat{S}^2 \rangle_{\mathrm{UDFT},\Phi}$ calculated at the UHF/cc-pVTZ, UBPW91/cc-pVTZ, and USVWN/cc-pVTZ levels of theory for the stretched H_2 molecule.



(*a*)



(*b*)

Figure 3. SMD distribution $m_s(\mathbf{r}) = \rho_\alpha(\mathbf{r}) - \rho_\beta(\mathbf{r})$ for (*a*) the S ground state and (*b*) first T state of *para*-didehydrobenzene calculated at the UBP86/cc-pVTZ level of theory and given in the form of a contour line diagram in the plane of the molecule. Both calculations were done at the geometry of the S ground state. Solid lines indicate a surplus of α spin, and dashed lines a surplus of β spin. The following contour lines are used: (*a*) 0, ±0.0001, ±0.0002, ±0.0005, ±0.001, ±0.002, 0.005, 0.01, 0.02, 0.05, 0.1, 0.2 e a_0^{-3}, and (*b*) 0, ±0.0001, ±0.0002, ±0.0005, ±0.001, ±0.002, ±0.005, ±0.01, ±0.02, ±0.05, ±0.1 e a_0^{-3}.

two values for $\langle \hat{S}^2 \rangle$ agree well for UHF provided $\langle \hat{S}^2 \rangle_\Phi > 0.5$.

For the UDFT methods, the difference $\langle \hat{S}^2 \rangle_{m_s} - \langle \hat{S}^2 \rangle_\Phi$ is up to 50% larger than the corresponding UHF difference, which indicates that, besides the systematic errors because of orbital overlap, there is a systematic increase in differences, suggesting that $\langle \hat{S}^2 \rangle_{\mathrm{UDFT},\Phi}$ is inaccurate in this region. However, deviations are smaller than 0.1 for $\langle \hat{S}^2 \rangle_\Phi > 0.6$ and decrease to less than 0.02 with increasing $\langle \hat{S}^2 \rangle_\Phi$, which means that $\langle \hat{S}^2 \rangle_{\mathrm{UDFT},\Phi}$ gives a reasonable approximation for the amount of spin contamination under these conditions.

The geometrical parameters of *para*-didehydrobenzene calculated at the UDFT/cc-pVTZ level of theory are listed in table 1. They indicate a regular distortion of the benzene hexagon such that the internal ring angles C6C1C2 and C3C4C5 are widened while the remaining four angles are narrowed. This is the result of rehybridization of the C orbitals from typical sp^2 (as in ben-

Table 1. Geometrical parameters of the S and T states of the *para*-didehydrobenzene biradical calculated at UDFT/cc-pVTZ.[a]

Functional	R(C1C2)	R(C2C3)	R(C1C4)	α(C1C2C3)	α(C3C4C5)
S state					
SVWN	1.345	1.437	2.676	117.5	125.1
BP86	1.368	1.437	2.692	117.3	125.4
BPW91	1.368	1.432	2.686	117.3	125.4
BLYP	1.368	1.443	2.701	117.4	125.3
B3PW91	1.366	1.414	2.658	117.1	125.8
B3LYP	1.366	1.419	2.664	117.1	125.8
MPW1PW91	1.365	1.410	2.654	117.1	125.8
T state					
SVWN	1.365	1.398	2.602	116.2	127.7
BP86	1.381	1.413	2.638	116.4	127.3
BPW91	1.379	1.411	2.636	116.4	127.3
BLYP	1.382	1.416	2.646	116.4	127.2
B3PW91	1.372	1.401	2.622	116.4	127.1
B3LYP	1.373	1.404	2.628	116.4	127.1
MPW1PW91	1.370	1.399	2.619	116.4	127.1

[a] Distances in Å and bond angles α in deg.

zene) toward sp hybrid orbitals at the single electron centres C1 and C4. The orbital containing the single electron can adopt more pπ character and negative charge is shifted from the outside to the inside of the ring, which is of advantage for a through-bond coupling mechanism [27] involving the σ^*(CC) orbitals of bonds C2C3 and C5C6 or the corresponding in-plane π^*_{ip}(CC) orbitals. The geometries for the S and T state of the biradical are similar and, accordingly, justify the assumption that for a comparison of the SMDs of the two states the S geometry can be used. Figure 3(a, b) gives the SMDs for the T and S states of *para*-didehydrobenzene determined at UDFT-BP86/cc-pVTZ. The SMD distributions for the other DFT methods and for UHF look similar. The similarities with the SMDs for the stretched H_2 molecule (figure 1) are obvious. For example, there are again two atoms (C1 and C4) with a surplus of either α spin or β spin density, as found in the case of the UDFT description of the stretched H_2 molecule. Also, there is a typical spin polarization pattern of the SMD for the S (and to some extent also for the T) state, which is best explained with the intra-atomic Hund rule: if at C4 there is a surplus of α density, then C3 and C5 will be the locations of a surplus of β density, the adjoint H atoms the locations of a surplus of α density, etc.

Figure 4 depicts the SMD profiles for the two states calculated at UDFT-BP86/cc-pVTZ along the line connecting the centre of the ring and the position of nucleus C4. Close to the C4 nucleus, at $r - r(\mathrm{C4}) = 0.08$ Å, there is a minimum in the SMD of both S and T

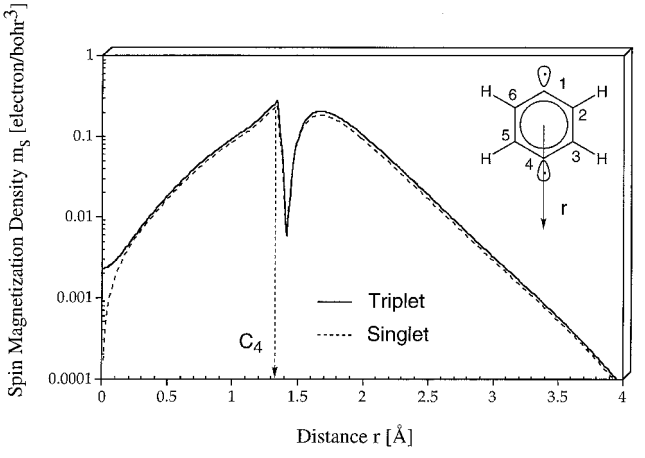


Figure 4. SMD profile (in e a_0^{-3}) of the S ground state (dotted line) and the first T state (solid line) of *para*-didehydrobenzene calculated at the UBP86/cc-pVTZ level of theory and shown as a function of distance r for $0 \leqslant r \leqslant 4$ Å along the bisection of the bond angle C3C4C5, where $r = 0$ corresponds to the centre of the molecule. The inset schematically shows the UDFT orbitals ϕ_a and ϕ_b used for the calculation of $\langle \hat{S}^2 \rangle_\Phi$.

(appearing as a cusp on the logarithmic scale of figure 4), followed by a maximum of the SMD at $r - r(\mathrm{C4}) = 0.34$ Å. The maximum of the SMD can be related to the maximum probability of finding the single electron at C4, which should be closer to the C nucleus than the electron pair of a CH bond (normally 0.7 Å away from the C nucleus). The minimum reflects spin polarization of the core electrons, and can be considered

Table 2. Description of the UDFT broken-symmetry state of *para*-didehydrobenzene with the help of KS orbitals and the SMD.[a]

Functional	% S $m_s(\mathbf{r})$	% S KS orbitals	$\langle\hat{S}^2\rangle_{m_s}$	$\langle\hat{S}^2\rangle_{\Phi}$	$\Delta\langle\hat{S}^2\rangle$
SVWN	69.9	75.5	0.602	0.491	0.111
BP86	55.7	59.5	0.886	0.812	0.074
BPW91	54.5	57.5	0.909	0.854	0.055
BLYP	56.8	61.7	0.864	0.767	0.097
B3PW91	52.2	52.0	0.956	0.963	−0.007
B3LYP	52.3	53.2	0.954	0.939	0.015
MPW1PW91	51.4	51.2	0.971	0.981	−0.010

[a] The percentage of S character is calculated from the fraction x of equation (12) using either the SMD $m_s(\mathbf{r}) = \rho_\alpha(\mathbf{r}) - \rho_\beta(\mathbf{r})$ or Kohn–Sham (KS) orbitals. $\langle\hat{S}^2\rangle_{\Phi}$ and $\langle\hat{S}^2\rangle_{m_s}$ denote the expectation values of $\hat{S}^2$ calculated from KS orbitals and the SMD $m_s(\mathbf{r})$, respectively.

as part of a shell structure at the C nucleus which is strongly perturbed on the other side of the C4 nucleus inside the ring, since rehybridization of the single electron orbital and through-bond interactions (see above) lead to a shift of spin density from the outside to the inside of the ring.

The similarity between the SMD profiles of the S and T states in the particular case of the BP86 functional (figure 4) and for all functionals investigated in this work makes it possible to determine $\langle\hat{S}^2\rangle_{m_s}$ according to equations (9) and (11). Table 1 summarizes $\langle\hat{S}^2\rangle_{\mathrm{UDFT},m_s}$ and $\langle\hat{S}^2\rangle_{\mathrm{UDFT},\Phi}$ values for *para*-didehydrobenzene as obtained for the seven different XC functionals employed in this work. As for the stretched H_2 molecule, the $\langle\hat{S}^2\rangle_{\mathrm{UDFT},m_s}$ values tend to be higher than the corresponding $\langle\hat{S}^2\rangle_{\mathrm{UDFT},\Phi}$ values, with the deviation increasing as $\langle\hat{S}^2\rangle_{\mathrm{UDFT},\Phi}$ decreases. For hybrid functionals, the SMDs indicate an almost equal mixing of S and T states and an $\langle\hat{S}^2\rangle_{\mathrm{UDFT}}$ value close to 1. Differences $\Delta\langle\hat{S}^2\rangle = \langle\hat{S}^2\rangle_{\mathrm{UDFT},m_s} - \langle\hat{S}^2\rangle_{\mathrm{UDFT},\Phi}$ are small, in line with the observation made for stretched H_2 at large distances R.

The more electron correlation effects are covered by a particular unrestricted method, the smaller is spin contamination. This is confirmed by the functionals investigated in this work. SVWN covers the largest amount of correlation effects and, accordingly, it leads to the smallest degree of spin contamination as reflected by the $\langle\hat{S}^2\rangle_{\mathrm{UDFT},m_s}$ values of table 2. At the same time, the difference $\Delta\langle\hat{S}^2\rangle$ is the largest obtained for all functionals. Again, this is in line with the observations made for stretched H_2. With increasing electron correlation, the through-bond coupling mechanism between the single electrons increases (reflected in shorter CC bonds, table 1), rehybridizaion at C1 and C4 becomes stronger, and orbital overlap between ϕ_a and ϕ_b also increases. The KS determinant is less suited to calculating $\langle\hat{S}^2\rangle_{\mathrm{UDFT}}$. Altogether, while $\langle\hat{S}^2\rangle_{\mathrm{UFDT},m_s}$ differs from $\langle\hat{S}^2\rangle_{\mathrm{UDFT},\Phi}$ quantitatively it gives a qualitatively correct account of the spin contamination in the UDFT state. The similarities in the behaviour of $\langle\hat{S}^2\rangle_{\Phi}$ and $\langle\hat{S}^2\rangle_{m_s}$ indicate that assumptions (3) and (5) above are sensible.

4. Conclusion

The SMDs calculated for the S and the T states of a biradical can be used to determine $\langle\hat{S}^2\rangle_{m_s}$ for UDFT. The method works well provided orbitals ϕ_a and ϕ_b do not overlap strongly, which can mostly be guaranteed by selecting a molecular region in which either ϕ_a or ϕ_b dominates. Results show that $\langle\hat{S}^2\rangle_{\mathrm{UDFT},\Phi}$ obtained from the KS determinant differs from $\langle\hat{S}^2\rangle_{\mathrm{UFDT},m_s}$; however, deviations are small enough for us to attribute significant diagnostic value to the former.

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