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SUPPLEMENTARY INFORMATION

Diradical character from the local spin analysis

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Contents

1 The local spin analysis

In the local spin analysis, the $\langle\hat{S}^2\rangle_A$ values indicate and quantify the presence of local spin *within* the molecule, namely on atom/fragment A. The magnitude and sign of the diatomic contributions $\langle\hat{S}^2\rangle_{AB}$ with $B \neq A$ inform about the nature of the couplings between these local spins. The physical interpretation of the $\langle\hat{S}^2\rangle_A$ and particularly $\langle\hat{S}^2\rangle_{AB}$ values is somewhat intricate, and has been recently discussed in detail in several papers.[1,2] We provide here a brief account of its general characteristics for ideal systems.

When two perfectly localized spins are coupled as a singlet, a proper multireference wave function is needed to account for the spin properties of the system. In that case, the local spin analysis yields $\langle\hat{S}^2\rangle_A = 3/4$ and $\langle\hat{S}^2\rangle_{AB} = -3/4$, which account for the expected overall $\langle\hat{S}^2\rangle = 0$. The $\langle\hat{S}^2\rangle_A$ value is consistent with the corresponding $\langle\hat{S}^2\rangle = s(s+1)$ value for the isolated one-electron system and the negative sign of $\langle\hat{S}^2\rangle_{AB}$ indicates that the two local spins are coupled as a singlet (entangled). With a single-determinant broken symmetry description of the same system one would obtain similarly $\langle\hat{S}^2\rangle_A = 3/4$, but now $\langle\hat{S}^2\rangle_{AB} = -1/4$, for an overall value of $\langle\hat{S}^2\rangle = 1$. Both $\langle\hat{S}^2\rangle_A$ and $\langle\hat{S}^2\rangle_{AB}$ monotonically decrease as the two spins become more amd more delocalized. In the limiting case of a closed-shell single-determinant description, all local spin contributions exactly vanish.

If the two perfectly localized spins on centers A and B are parallel, the local spin analysis would yield $\langle\hat{S}^2\rangle_A = 3/4$ and $\langle\hat{S}^2\rangle_{AB} = 1/4$, for an overall value of $\langle\hat{S}^2\rangle = 2$, as expected for a triplet. The one-center term is again consistent with a one-electron system, and the positive sign of the diatomic contribution now indicates that the local spins are parallel. In a parallel-spins situation, if the two spins are not perfectly localized the value of $\langle \hat{S}^2 \rangle_{AB}$ decreases, but that of $\langle \hat{S}^2 \rangle_A$ increases. The latter is an indication of partial triplet character on the given center.

2 Local spin analysis of diradicals and diradicaloids

Tetramethyleneethane (TME) is a well-studied diradical.[3,4] This molecule has been optimized under three different symmetry constrains, namely D_2, D_{2h} and D_{2d} at the CASSCF level of theory. The active space included 6 electrons and 6 orbitals (in the D_{2h} symmetry they correspond to the set of 6 π orbitals.) The lowest energy structure has D_2 symmetry, with a C_1-C_2-C_4-C_5 dihedral angle (α) of 70.6 deg (see Figure 1).

The results of the local spin analysis are gathered on Table 1. The atomic and diatomic spin components are almost independent of the rotation with respect to the central C-C bond. The vertical singlet-triplet gaps, sometimes used to assess the radical character,[4] are not too different for the D_2, D_{2h}, and D_{2d} structures (-1.33, -3.91, and -2.05 kcal/mol, respectively). We will focus on the results obtained for the global minimum (D_2 symmetry). The main spin centers are C_1 and the symmetry equivalent C_3, C_5, and C_6, with $\langle \hat{S}^2 \rangle_{\mathrm{C}}$ values of 0.35 and 0.36 for the singlet and triplet states (the local spin involving the H atoms is negligible). The diatomic spin terms $\langle \hat{S}^2 \rangle_{\mathrm{C}_1,\mathrm{C}_2}$ and $\langle \hat{S}^2 \rangle_{\mathrm{C}_1,\mathrm{C}_3}$ (and their symmetry equivalents) also equal in both electronic states. The sign of these spin contributions indicates the alternation of the spins within each allyl fragment, as indicated in Figure 1.

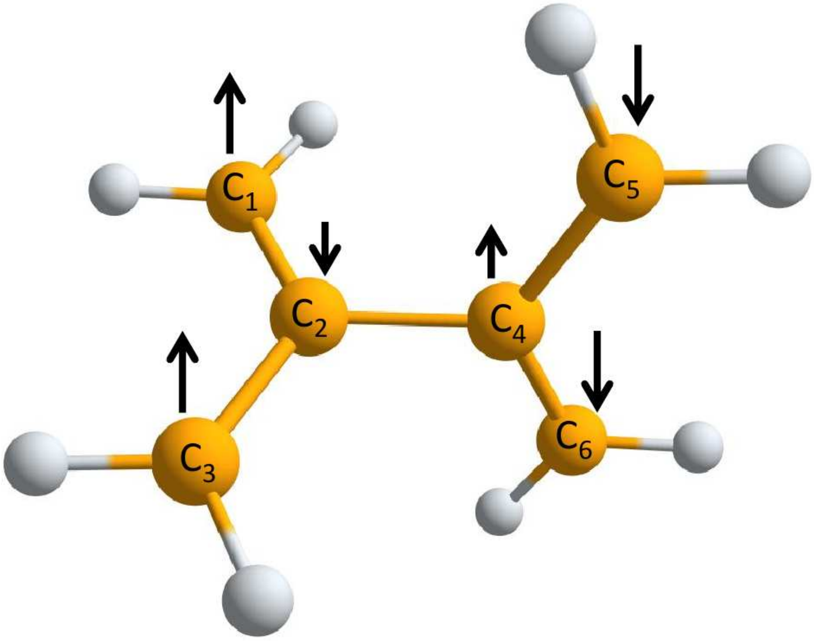

Figure 1: Numbering scheme of tetrathyleneethane (TME) and local spin distribution of the singlet state.

The main differences between the local spin distribution of the singlet and triplet states are found in the diatomic terms involving the C atoms on the different allyl fragments. In the singlet state, the atoms 1, 3, and 4 have parallel spins, as indicated by the sign of $\langle\hat{S}^2\rangle_{\mathrm{C}_1,\mathrm{C}_3}$ and $\langle\hat{S}^2\rangle_{\mathrm{C}_1,C_4}$ terms, whereas centers 2, 5, and 6 exhibit antiparallel arrangement with respect to them. The diatomic terms $\langle\hat{S}^2\rangle_{\mathrm{C}_1,\mathrm{C}_5}$ present a rather small value of -0.17. However, this value accounts for most of the expected diatomic spin contribution of -3/4 between the two allyl centers, as there are four such diatomic contributions equivalent by symmetry. In the triplet state, the local spins on the C atoms of one of the allyl moieties are flipped with respect to the singlet state. The four symmetry-equivalent diatomic terms $\langle \hat{S}^2 \rangle_{\mathrm{C}_1,\mathrm{C}_5} = 0.05$ account for the spin-spin interactions between the allyl moieties.

Table 1: Local spin analysis of the TME molecule for the singlet (S) and triplet (T) states of different geometries.

Atom/Atom pair	D_2 ($\alpha = 70.6$)		D_{2h} ($\alpha = 0$)		D_{2d} ($\alpha = 90$)	
Fragment/ Fragment pair	S	T	S	T	S	T
C_1	0.36	0.37	0.36	0.37	0.35	0.37
C_2	0.14	0.14	0.14	0.14	0.14	0.14
C_1,C_2	-0.09	-0.09	-0.08	-0.09	-0.09	-0.09
C_1,C_3	0.08	0.08	0.08	0.08	0.08	0.08
C_1,C_4	0.03	-0.01	0.03	0.00	0.03	-0.01
C_1,C_5	-0.17	0.05	-0.17	0.04	-0.17	0.05
C_1,C_6	-0.18	0.05	-0.19	0.04	-0.17	0.05
C_2,C_4	-0.01	-0.01	-0.02	-0.02	-0.01	0.00
allyl	0.77	0.80	0.79	0.81	0.76	0.79
allyl$_1$,allyl$_2$	-0.77	0.20	-0.79	0.19	-0.76	0.21

The diatomic spin contribution between atoms C_2 and C_4 is almost zero. Moreover, the one- and two-center contributions involving atoms C_1, C_2 and C_3 are very similar to those observed for a single allyl radical.[5] In fact, summing up all one- and two-center contributions for all atoms of each allyl moiety gives a local spin on each fragment very close to 3/4 in all cases (see bottom of Table 1). Thus, the TME molecule can be regarded as a diradical made up from two independent allyl radicals bonded by the central carbon atoms. The local spin analysis unravels the spin distribution among all centers or fragments on the same footing both different electronic states, *i.e., even if no spin density exists.*

Diphosphadiboretanes and their analogues are some of the most controversial diradicaloid systems discussed in the literature. For these systems we have carried out the local spin analysis with both an unrestricted single-determinant (UB3LYP) and a CASSCF(2,2) wave function for comparision, and for both their singlet and triplet states. The results are gathered on Table 2.

Table 2: Local spin analysis of four-member ring diradicaloids for different spin states and levels of theory

		$\langle \hat{S}^2 \rangle_A / \langle \hat{S}^2 \rangle_{AB}$			
Molecule	Atom/Atom pair	CASSCF		UB3LYP	
		Singlet	Triplet	Singlet	Triplet
$(CH)_2(C'H_2)_2$	C	0.58	0.59	0.59	0.59
	C'	0.05	0.05	0.05	0.06
	C-C	-0.46	0.15	-0.16	0.16
$(BH)_2(PH_2)_2$	B	0.10	0.27	0.00	0.32
	P	0.09	0.26	0.00	0.22
	B-B	-0.04	0.03	0.00	0.05
$(BH)_2(NH_2)_2$	B	0.19	0.28	0.20	0.31
	N	0.14	0.25	0.15	0.24
	B-B	-0.07	0.03	-0.03	0.05

The local spin values (atomic terms) for singlet states are very similar for CASSCF(2,2) and UB3LYP methods, provided a broken-symmetry solution is found for the latter. For singlet states, the species with a larger local spin contributions is $(CH)_2(CH_2)_2$. The value for the CASSCF(2,2) wave function (0.58) is not too far from that expected for a perfectly localized electron (3/4). In $(BH)_2(NH_2)_2$ the local spin is significantly smaller (0.19), which should indicate a much weaker diradical character. In the case of the diphosphadiboretane species the local spin is almost negligible (0.10), consistent with a residual diradical character.

For triplet states the local spin analysis yields very similar one- and two-center contributions for both methods. This is not surprising since with a CASSCF(2,2) approach the $m_S = |S|$ state is described by a ROHF wave function. The atomic contributions of $(CH)_2(CH_2)_2$ are essentially the same as in the singlet state. The diatomic term involving the two main local spin centers is now positive, indicating parallel arrangement of the spins. In the case of $(BH)_2(PH_2)_2$ and $(BH)_2(NH_2)_2$ the four atoms of the ring exhibit similar but small contributions. In fact, the sum of the terms reported on Table 2 is still far from the overall $\langle \hat{S}^2 \rangle \approx 2$ value. This is because the hydrogen atoms (omitted thus far) exhibit small but significant contributions of ca. 0.05-0.10. Thus, these species do not exhibit significant spin centers and the molecular spin is delocalized over all atoms.

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