Determination of Local Spins by Means of a Spin-Free Treatment

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ABSTRACT: This work describes a Mulliken-type partitioning of the expectation value of the spin-squared operator $\langle \hat{S}^2 \rangle$ corresponding to an N-electron system. Our algorithms, which are based on a spin-free formulation, predict appropriate spins for the molecular fragments (at equilibrium geometries and at dissociation limits) and can be applied to any spin symmetry. Numerical determinations performed in selected closed- and open-shell systems at correlated level are reported. A comparison between these results and their counterpart ones arising from other alternative approaches is analyzed in detail.

1. INTRODUCTION

The study of procedures to decompose the expectation value of the spin-squared operator $\langle \hat{S}^2 \rangle$ corresponding to an N-electron system into one- and two-center terms (local spins) has attracted attention of a considerable number of authors in the last years. This interest arises from the ability of the local spins to determine the spin state of an atom or group of atoms in a molecule, radical, cluster, etc., as well as to describe magnetic interactions between the atoms which compose the system. In fact, spin—spin coupling constants can be calculated by means of two-center local spins within the well-known Heisenberg Hamiltonian model. The partitioning of the $\langle \hat{S}^2 \rangle$ quantity has been performed using several approaches. One of them utilizes the technique of local projection operators, in which the total spin-squared operator $\hat{S}^2$ is decomposed into one- and two-center operators associated with the nuclei of the system; then in a subsequent step the expectation values of these operators are evaluated for different approximations of the wave function.[1−7] Alternatively, the partitioning of the expectation value $\langle \hat{S}^2 \rangle$ has also been performed in a direct way.[8−13] Within the framework of this last procedure the quantity $\langle \hat{S}^2 \rangle$, expressed in terms of elements of reduced density matrices and related quantities, is partitioned in the Hilbert space of the atomic basis set according to a Mulliken-type population analysis. More recently, this technique of partitioning has also been extended to the three-dimensional physical space and its results compared with those arising from the Hilbert space.[14]

This work deals with the partitioning of the $\langle \hat{S}^2 \rangle$ quantity in the Hilbert space. Determinations of local spins in that space at the level of single Slater determinant wave functions and higher correlation levels have been described in refs 8, 9, 11, and 13. These reported results are satisfactory from a chemical point of view since they show appropriate spins for the fragments at the dissociation limit and zero local spin values for closed-shell systems described at the restricted Hartree—Fock level. However, at correlated level, the algorithms used to get these results depend on the spin blocks of the second-order reduced density matrix, which, in practice, are not available in most standard codes in quantum chemistry. Besides, these matrix elements depend on the substate S_z corresponding to a determined spin S

for nonsinglet states. Consequently, the values of the terms derived from that $\langle \hat{S}^2 \rangle$ partitioning are S_z dependent. Obviously, the partitioning of a quantity into several components is usually not unique. Hence, it is important to consider other possibilities which can also produce physically reasonable results in those limit cases, provided they present additional theoretical and practical advantages. The aim of this work is to overcome the mentioned drawbacks, reporting an algorithm in terms of spin-free tools, so that the local spins of a system can be calculated for any state of any spin symmetry, fulfilling the physical requirement of uniqueness for the spin multiplet components (in absence of magnetic fields). Our algorithm is based on the use of the one-electron effectively unpaired electron density matrix[15−17] and the two-electron spin-free cumulant matrix of the spin-free second-order reduced density matrix;[18,19] both matrices are directly calculable from the spin-free first- and second-order reduced density matrices, which can be obtained from standard codes.

The organization of this work is as follows. The second section describes a straightforward derivation of the formulas used in refs 11,13 to evaluate one- and two-center local spins at correlated level. In this way, we point out their S_z dependence and the difficulties to access to elements of the cumulant matrix in the spin—orbital representation, in standard codes, mainly for nonsinglet states. In the third section, we propose an alternative algorithm which only utilizes matrix elements of spin-free quantities. In the fourth section, we describe the results obtained from both S_z-dependent and S_z-independent algorithms for some selected closed- and open-shell systems, as well as their corresponding discussion. A study of the dependence of the results on the degree of correlation used is also included in this section. Finally, in the last section we summarize the concluding remarks of this work.

2. PARTITIONING OF $\langle \hat{S}^2 \rangle$ AT CORRELATED LEVEL

A finite basis set of orthonormal orbitals will be denoted by $\{i, j, k, l, ...\}$; in this basis set $^1D_j^i$ and $^2D_{jl}^{ik}$ will stand for the

spin-free matrix elements corresponding to the first- and second-order reduced density matrices of an N-electron system in a state Ψ, respectively. The trace of the first-order reduced density matrix is normalized to $tr(^1D) = N$ and that of the second-order one may be normalized to

$$tr(^2D) = \binom{N}{2}$$

or to $tr(^2D) = N(N-1)$;[11,13] in this work we will use the former procedure. The expectation value of the spin-squared operator $\hat{S}^2$, $\langle\hat{S}^2\rangle = \langle\Psi|\hat{S}^2|\Psi\rangle$, can be expressed as follows:[20,21]

$$\langle\hat{S}^2\rangle = N - \frac{N^2}{4} - \sum_{i,k} {}^2D_{ki}^{ik} \tag{1}$$

Likewise, taking into account the values of those traces, eq 1 can be written as follows:

$$\langle\hat{S}^2\rangle = \frac{3}{4}\sum_i {}^1D_i^i - \frac{1}{2}\sum_{i,k} {}^2D_{ik}^{ik} - \sum_{i,k} {}^2D_{ki}^{ik} \tag{2}$$

The decomposition of these spin-free matrix elements according to their spin orbitals, that is, ${}^1D_j^i = ({}^1D_{j_\alpha}^{i_\alpha} + {}^1D_{j_\beta}^{i_\beta})$ and ${}^2D_{jl}^{ik} = ({}^2D_{j_\alpha l_\alpha}^{i_\alpha k_\alpha} + {}^2D_{j_\alpha l_\beta}^{i_\alpha k_\beta} + {}^2D_{j_\beta l_\alpha}^{i_\beta k_\alpha} + {}^2D_{j_\beta l_\beta}^{i_\beta k_\beta})$, and an appropriate permutation of spin orbitals, based on the anticommutation rules of fermion operators, leads to the following:

$$\langle\hat{S}^2\rangle = \frac{3}{4}\sum_i ({}^1D_{i_\alpha}^{i_\alpha} + {}^1D_{i_\beta}^{i_\beta}) - \sum_{i,k} {}^2D_{i_\beta k_\alpha}^{i_\beta k_\alpha}$$

$$- \frac{1}{2}\sum_{i,k} {}^2D_{k_\alpha i_\alpha}^{i_\alpha k_\alpha} - \frac{1}{2}\sum_{i,k} {}^2D_{k_\beta i_\beta}^{i_\beta k_\beta} - 2\sum_{i,k} {}^2D_{k_\alpha i_\beta}^{i_\alpha k_\beta} \tag{3}$$

A trivial but tedious algebra, which consists in relating the second-order reduced density matrix elements in the spin−orbital representation, with the corresponding elements of its cumulant matrix $\Gamma_{j^\sigma l^{\sigma'}}^{i^\sigma k^{\sigma'}}$ ($\sigma,\sigma' = \alpha,\beta$), that is as follows:[22]

$${}^2D_{j^\sigma l^{\sigma'}}^{i^\sigma k^{\sigma'}} = \frac{1}{2}{}^1D_{j^\sigma}^{i^\sigma}{}^1D_{l^{\sigma'}}^{k^{\sigma'}} - \frac{1}{2}{}^1D_{l^{\sigma'}}^{i^\sigma}{}^1D_{j^\sigma}^{k^{\sigma'}} + \frac{1}{2}\Gamma_{j^\sigma l^{\sigma'}}^{i^\sigma k^{\sigma'}} \tag{4}$$

provides to express eq 3 as follows:

$$\langle\hat{S}^2\rangle = \frac{1}{2}\sum_{i,k}(P^s)_k^i(P^s)_i^k + \frac{1}{4}\sum_{i,k}(P^s)_i^i(P^s)_k^k$$

$$+ \frac{3}{4}\sum_i\left[{}^1D_{i_\alpha}^{i_\alpha} - \sum_k {}^1D_{k_\alpha}^{i_\alpha}{}^1D_{i_\alpha}^{k_\alpha} + {}^1D_{i_\beta}^{i_\beta} - \sum_k {}^1D_{k_\beta}^{i_\beta}{}^1D_{i_\beta}^{k_\beta}\right]$$

$$- \sum_{i,k}\left[{}^2D_{i_\beta k_\alpha}^{i_\beta k_\alpha} - \frac{1}{2}{}^1D_{i_\beta}^{i_\beta}{}^1D_{k_\alpha}^{k_\alpha}\right]$$

$$- \frac{1}{2}\sum_{i,k}\left[{}^2D_{k_\alpha i_\alpha}^{i_\alpha k_\alpha} - \frac{1}{2}{}^1D_{k_\alpha}^{i_\alpha}{}^1D_{i_\alpha}^{k_\alpha} + \frac{1}{2}{}^1D_{i_\alpha}^{i_\alpha}{}^1D_{k_\alpha}^{k_\alpha}\right]$$

$$- \frac{1}{2}\sum_{i,k}\left[{}^2D_{k_\beta i_\beta}^{i_\beta k_\beta} - \frac{1}{2}{}^1D_{k_\beta}^{i_\beta}{}^1D_{i_\beta}^{k_\beta} + \frac{1}{2}{}^1D_{i_\beta}^{i_\beta}{}^1D_{k_\beta}^{k_\beta}\right]$$

$$- 2\sum_{i,k}\left[{}^2D_{k_\alpha i_\beta}^{i_\alpha k_\beta} - \frac{1}{2}{}^1D_{k_\alpha}^{i_\alpha}{}^1D_{i_\beta}^{k_\beta}\right] \tag{5}$$

In eq 5, $(P^s)_j^i = {}^1D_{j_\alpha}^{i_\alpha} - {}^1D_{j_\beta}^{i_\beta}$ are the elements of the spin-density matrix and the second-order reduced density matrix has been

normalized by the value of its trace.

$$tr(^2D) = \binom{N}{2}$$

The derivation of this equation has required to add and to subtract terms in order to express the $\langle\hat{S}^2\rangle$ quantity by means of the spin−orbital components of the cumulant matrix of the second-order reduced density matrix, which are the last four brackets (see eq 4).

Formula 5, which is expressed in an orthogonal basis set, is equivalent to those reported in refs,11 and 13 expressed in nonorthogonal atomic basis sets; a simple basis transformation allows one to pass from this formula to the others. The partitioning of the quantity $\langle\hat{S}^2\rangle$ according to formula 5 transformed to the atomic basis set, requires to know the values of the elements of the second-order reduced density matrix in the spin−orbital representation (${}^2D_{j^\sigma l^{\sigma'}}^{i^\sigma k^{\sigma'}}$, $\sigma,\sigma' = \alpha,\beta$), which usually are not provided by the execution of most standard codes. Apart from this shortcoming, another aspect to take into account is that, as is well-known, those matrix elements depend on the S_z substate of the state Ψ and consequently the local spin results for nonsinglet states turn out to be S_z dependent. Thus, the requirement of uniqueness for the spin multiplet components is not fulfilled by this partitioning. This aspect has been numerically tested in the lowest triplet state of the system HeH$^+$ (see Appendix A). As has been mentioned in the Introduction, the purpose of this work is to set up a spin-free S_z-independent algorithm that avoids these drawbacks. In the next section, we report that algorithm.

3. SPIN-FREE TREATMENT PROPOSAL

We will express the elements of the spin-free second-order reduced density matrix as follows:[18,19]

$${}^2D_{jl}^{ik} = \frac{1}{2}{}^1D_j^i{}^1D_l^k - \frac{1}{4}{}^1D_l^i{}^1D_j^k + \frac{1}{2}\Lambda_{jl}^{ik} \tag{6}$$

in which Λ_{jl}^{ik} stands for the elements of the spin-free cumulant matrix of that second-order reduced density matrix. These matrix elements are related with those of the cumulant matrix ones ($\Gamma_{j^\sigma l^{\sigma'}}^{i^\sigma k^{\sigma'}}$) by the following:[23]

$$\Lambda_{jl}^{ik} = -\frac{1}{2}(P^s)_l^i(P^s)_j^k + \sum_{\sigma,\sigma'}\Gamma_{j^\sigma l^{\sigma'}}^{i^\sigma k^{\sigma'}} \tag{7}$$

However, we will regard the effectively unpaired electron density matrix u, initially defined by Takatsuka et al.[15] as follows:

$$u_j^i = 2{}^1D_j^i - \sum_k {}^1D_k^i{}^1D_j^k \tag{8}$$

The mathematical features of this matrix have been widely studied[16,17,23−25] and utilized in a great variety of population analysis studies.[26−32] Although other formulations of the matrix u have been proposed,[33−35] in this work we will use that formulated by eq 8 whose relation with the Λ matrix turns out to be following:[17]

$$u_j^i = -2\sum_k \Lambda_{jk}^{ik} \tag{9}$$

The substitution of the elements ${}^2D_{ik}^{ik}$ and ${}^2D_{ki}^{ik}$ according to eq 6 and the use of eqs 8 and 9 provide to express the quantity

3561

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$\langle\hat{S}^2\rangle$ in formula 2 as follows:

$$\langle\hat{S}^2\rangle \ = \frac{1}{2}\sum_i u_i^i - \frac{1}{2}\sum_{i,k}\Lambda_{ki}^{ik} \tag{10}$$

However, in order to partition the $\langle\hat{S}^2\rangle$ quantity into one-center and two-center terms it is more useful to express that equation in the basis set of the atomic orbitals $\{\mu,\nu,\lambda,\gamma,...\}$

$$\langle\hat{S}^2\rangle \ = \frac{1}{2}\sum_\mu (uS)_\mu^\mu - \frac{1}{2}\sum_{\mu,\nu,\lambda,\gamma}(S)_\lambda^\mu\Lambda_{\gamma\mu}^{\lambda\nu}(S)_\nu^\gamma \tag{11}$$

where $(S)_\nu^\mu = \langle\mu|\nu\rangle$ are the elements of the overlap matrix of the atomic orbitals.

The decomposition of the expectation value $\langle\hat{S}^2\rangle$ in the Hilbert space of atomic orbitals into one-center terms $\langle\hat{S}^2\rangle_A$ and two-center terms $\langle\hat{S}^2\rangle_{AB}$:

$$\langle\hat{S}^2\rangle \ = \sum_A \langle\hat{S}^2\rangle_A + \sum_{A\neq B}\langle\hat{S}^2\rangle_{AB} \tag{12}$$

is performed assigning every atomic function μ to one nucleus A. Although the matrix $\Lambda_{\gamma\mu}^{\lambda\nu}$ possesses four indices, in this work we have limited to determine only one- and two-center local spins (excluding the three- and four-center contributions) so that two of those indices have been mathematically removed by means of a sum over them. Hence, the expressions for the $\langle\hat{S}^2\rangle_A$ and $\langle\hat{S}^2\rangle_{AB}$ quantities according to eq 11 are as follows

$$\langle\hat{S}^2\rangle_A \ = \frac{1}{2}\sum_{\mu\in A}(uS)_\mu^\mu - \frac{1}{2}\sum_{\mu\in A,\nu\in A}\sum_{\lambda,\gamma}(S)_\lambda^\mu\Lambda_{\gamma\mu}^{\lambda\nu}(S)_\nu^\gamma \tag{13}$$

and,

$$\langle\hat{S}^2\rangle_{AB} \ = -\frac{1}{2}\sum_{\mu\in A,\nu\in B}\sum_{\lambda,\gamma}(S)_\lambda^\mu\Lambda_{\gamma\mu}^{\lambda\nu}(S)_\nu^\gamma \tag{14}$$

Formulas 13 and 14 provide the means to carry out numerical determinations of one-center and two-center local spins, respectively. Because the matrix elements u_ν^μ and $\Lambda_{\gamma\mu}^{\lambda\nu}$ are spin free, S_z-independent quantities, the values of $\langle\hat{S}^2\rangle_A$ and $\langle\hat{S}^2\rangle_{AB}$ arisen from these equations are independent of the quantum number S_z. Consequently, local spin evaluations can be obtained for any state of any spin symmetry, fulfilling the conditions of invariance for all the components of a multiplet state. In practice, the matrices Λ and u are calculated by means of eqs 6 and 8, respectively. Hence, from a computational point of view the unique required matrices to implement local spin determinations are the overlap matrix S and the first- and second-order reduced density matrices ^1D and ^2D, all of them in the spin-free formulation, which are usually drawn from standard codes. In the next section, we report results of local spins arising from this procedure which are compared with those obtained in other treatments.

4. NUMERICAL DETERMINATIONS AND DISCUSSION

The elements of the overlap matrices and those of the spin-free first- and second-order reduced density matrices have been obtained from a modified version of the PSI 3.3 package.[36] In a subsequent step, we have used our own codes to evaluate local spins using eqs 13 and 14 within the spin-free treatment. We have also performed determinations of local spins by means of eq 5, expressed in the atomic basis sets, for singlet states with a unique substate $S_z = 0$, for which the spin blocks of the second-order reduced density matrix can be calculated from its spin-free matrix elements.[37] As has been mentioned in section 2, this procedure was reported in refs 11 and 13. Table 1 gathers the results arising from both algorithms (denoted by *spin-free* and *with spin* in that Table) for singlet states, in order to carry out an appropriate comparison between them. Likewise, in Tables 2 and 3, we report results of systems in doublet and triplet spin symmetries respectively, obtained from eqs 13 and 14. The computational details are shown in these Tables, i.e., the basis sets and the experimental geometries used[38−42] as well as the correlation levels utilized, full configuration interaction (FCI), configuration interaction with single and double excitations (CISD), etc.

A survey of the results for singlet states reported in Table 1 shows that at equilibrium distances, the one- and two-center local spins absolute values are a little lower in the spin-free treatment than in that denominated with spin. However, these series of values become almost coincident at distances near the dissociation limits of these molecules. As can be observed in that Table, in both treatments the systems H_2^a, Li_2^a, Be_2^a, and $C_2H_4^a$ exhibit values for the one-center local spins which are very close to those corresponding to the dissociated fragments. In the case of the ethylene molecule, the values reported for the system denoted by $C_2H_4^a$ refer to its dissociation into two triplet methylene groups by stretching the bond distance C−C. However, for singlets at equilibrium distances, it seems reasonable to expect that the distribution of the $\langle\hat{S}^2\rangle$ quantity along the whole molecule presents not too high local spin values and consequently, from a genuine chemical point of view, the lower values found in the spin-free treatment can be regarded as a favorable tendency. This behavior is followed by all systems included in Table 1, the light ones (H_2, Li_2 and Be_2), the hydrides of the second row (HF, H_2O and NH_3) and the hydrocarbons (CH_4, C_2H_6, C_2H_4 and C_2H_2), at the reported correlation levels. Another aspect to highlight is that both treatments predict identical signs for counterpart values of the one- and two-center local spins. As has been pointed out in refs 11 and 13 an adequate partitioning of the $\langle\hat{S}^2\rangle$ quantity requires that the atomic spins for atoms at large distances reproduce the spins of the free atomic fragments, as well as to predict zero spins for systems described by closed-shell restricted Hartree−Fock (RHF) wave functions, which would correspond to a pure covalent description. The spin-free algorithm that we have described in section 3 fulfills both requirements, i.e., it leads to suitable spin values at the dissociation limits and provides values $\langle\hat{S}^2\rangle_A = 0$ and $\langle\hat{S}^2\rangle_{AB} = 0$ for RHF wave functions (see eqs 13 and 14) because all the elements of the matrices u and Λ are zero for that type of wave functions.[16,19] Moreover, in the unrestricted Hartree−Fock (UHF) case the elements of those matrices are nonzero and a simple algebra shows that eqs 5 and 10 are transformed to an identical expression.

Tables 2 and 3 show results of local spin evaluations within the spin-free treatment for species (molecules and radicals) doublets and triplets at the experimental equilibrium distances, except for systems H_2^a and Li_2^a (in Table 3) which refer to the lowest triplet states at distances near the dissociation limit. These results have also been obtained from eqs 13 and 14 since they are valid for any quantum number S. As can be seen in Table 2, the radicals hydroxyl, cyano and amino present high values of the one-center contribution $\langle\hat{S}^2\rangle_A$ in the atoms oxygen, carbon, and nitrogen, respectively, indicating that the unpaired electron which originates the doublet spin symmetry is located on those atoms. The NO molecule shows a distribution of the spin cloud between the nitrogen and oxygen atoms although the value $\langle\hat{S}^2\rangle_N$ is

Table 1. Local Spins of One- And Two-Centers ($\langle \hat{S}^2 \rangle_A$ and $\langle \hat{S}^2 \rangle_{AB}$) Arising from the Treatments Spin-Free (eqs 13 and 14) and with Spin (eq 5 in the Atomic Basis Set) for Singlet Systems in the Ground State at Experimental Equilibrium Distances (^{a} near Dissociation Limits)

system	atom/bond	spin-free $\langle \hat{S}^2 \rangle_A$	spin-free $\langle \hat{S}^2 \rangle_{AB}$	with spin $\langle \hat{S}^2 \rangle_A$	with spin $\langle \hat{S}^2 \rangle_{AB}$	basis set/method
H_2	H	0.100		0.116		6-31G/FCI
	HH		−0.100		−0.116	
H_2^a	H	0.743		0.744		6-31G/FCI
	HH		−0.743		−0.744	
Li_2	Li	0.204		0.210		STO-3G/FCI
	LiLi		−0.204		−0.210	
Li_2^a	Li	0.750		0.750		STO-3G/FCI
	LiLi		−0.750		−0.750	
Be_2	Be	0.125		0.127		STO-3G/FCI
	BeBe		−0.125		−0.127	
Be_2^a	Be	0.000		0.000		STO-3G/FCI
	BeBe		0.000		0.000	
C_2H_4	C	0.477		0.544		6-31G/CISD
	H	0.058		0.067		
	CC		−0.365		−0.411	
	CH		−0.098		−0.108	
	C···H		0.042		0.041	
	HH		0.008		0.008	
	H···H		−0.005		−0.003	
	H···H		−0.006		−0.005	
$C_2H_4^a$	C	1.884		1.875		6-31G/CISD
	H	0.020		0.015		
	CC		−1.850		−1.847	
	C···H		−0.038		−0.038	
	CH		0.019		0.023	
	HH		0.000		0.000	
	H···H		0.000		0.000	
	H···H		0.000		0.000	
HF	F	0.050		0.059		6-31G/CISD
	H	0.050		0.059		
	FH		−0.050		−0.059	
H_2O	O	0.121		0.141		6-31G/CISD
	H	0.055		0.064		
	OH		−0.060		−0.070	
	HH		0.005		0.006	
NH_3	N	0.226		0.257		6-31G/CISD
	H	0.059		0.068		
	NH		−0.075		−0.086	
	HH		0.008		0.009	
CH_4	C	0.428		0.470		6-31G/CISD
	H	0.066		0.077		
	CH		−0.107		−0.118	
	HH		0.014		0.014	
C_2H_6 (staggered)	C	0.361		0.400		6-31G/CISD
	H	0.059		0.068		
	CC		−0.130		−0.136	
	CH		−0.094		−0.104	
	C···H		0.017		0.016	

Table 1. Continued

system	atom/bond	spin-free $\langle \hat{S}^2 \rangle_A$	spin-free $\langle \hat{S}^2 \rangle_{AB}$	with spin $\langle \hat{S}^2 \rangle_A$	with spin $\langle \hat{S}^2 \rangle_{AB}$	basis set/method
	H···H		−0.003		−0.003	
	HH		0.012		0.012	
C_2H_2	C	0.603		0.699		6-31G/CISD
	H	0.049		0.055		
	CC		−0.558		−0.646	
	C···H		−0.036		−0.037	
	CH		−0.081		−0.090	
	HH		−0.003		−0.002	

considerably higher than the $\langle \hat{S}^2 \rangle_O$ one, which agrees with the well-known structural features of that molecule. The doublet radicals CH and CH_3 (in Table 2) and the triplet one CH_2 (in Table 3) also show a clear localization of the unpaired electrons on the carbon atom. In the series of radicals ethyl, vinyl, and ethynyl the main localization of unpaired electrons appears on the carbon atom linked to less hydrogen atoms, denominated as $C^{(2)}$ in Table 2, which is markedly larger than on the other carbon atom $C^{(1)}$. The application of this methodology to the study of the allyl radical leads to show that the carbon atoms $C^{(1)}$ and $C^{(3)}$ (Table 2) are equivalent, presenting a higher $\langle \hat{S}^2 \rangle_A$ value in these atoms than in the $C^{(2)}$ one. This behavior is well-known in this species and explained in terms of the resonance of double bond between the atoms $C^{(1)}$ and $C^{(2)}$ and between the atoms $C^{(2)}$ and $C^{(3)}$. In this radical, the two-center local spin $\langle \hat{S}^2 \rangle_{C_{(1)}C_{(3)}}$ turns out to be 0.247 which is a positive and non-negligible value; this fact can be interpreted in terms of delocalization of the unpaired electron. The presence of this feature, that is, positive non-negligible values for the two-center local spins, has also been found in the triplet homonuclear diatomic molecules O_2 and C_2 as well as in the B_2H_2 molecule (Table 3). The explanation of these values must be done again in terms of delocalization of unpaired electrons. The rest of the triplet systems described in Table 3, NF, NH, and C_2H_4 exhibit local spin features in agreement with those presented in Table 2 and consequently deserve similar comments. For the two triplets reported in Table 3 at the dissociation limit, our treatment describes values of one-center contribution $\langle \hat{S}^2 \rangle_A = 0.750$ for both H_2^a and Li_2^a molecules. These results coincide with those reported for these systems in Table 1 (singlet states), leading again to right $\langle \hat{S}^2 \rangle$ values for the dissociated atomic fragments. However, the values of two-center contributions $\langle \hat{S}^2 \rangle_{AB} = 0.250$ found for both molecules allow a right $\langle \hat{S}^2 \rangle = 2$ for the global triplet states described.

In Table 4, we report numerical values of local spins in order to check the dependence on the electronic correlation of this methodology. In that Table, we describe results arising from both treatments (spin-free and with spin) for the singlet systems HF, NH_3 and C_2H_6, using the configuration interaction (CI) technique at several levels; single and double excitations (CISD); single, double, and triple excitations (CISDT) and single, double, triple, and quadruple excitations (CISDTQ). In the case of the ethane molecule, we have kept frozen (without excitation) 26 of the 30 orbitals forming the 6-31G basis set (the 7 lowest occupied molecular orbitals and the 19 highest unoccupied molecular orbitals) in the procedure denoted frozen I, and 18 orbitals (the 3 lowest occupied molecular orbitals and the 15 highest

Table 2. Local Spins of One- And Two-Centers ($\langle\hat{S}^2\rangle_A$ and $\langle\hat{S}^2\rangle_{AB}$) Arising from the Spin-Free Treatment (eqs 13 and 14) for Doublet Systems at Experimental Equilibrium Distances

system	atom/bond	spin-free		basis set/method
		$\langle\hat{S}^2\rangle_A$	$\langle\hat{S}^2\rangle_{AB}$	
OH	O	0.874		6-31G/CISD
	H	0.063		
	OH		−0.094	
NO	N	0.670		6-31G/CISD
	O	0.319		
	NO		−0.119	
CN	C	1.141		6-31G/CISD
	N	0.452		
	CN		−0.421	
NH$_2$	N	1.060		6-31G/CISD
	H	0.069		
	NH		−0.117	
	HH		0.009	
CH	C	0.912		6-31G/CISD
	H	0.081		
	CH		−0.122	
CH$_3$	C	1.368		6-31G/CISD
	H	0.069		
	CH		−0.151	
	HH		0.013	
$C^{(1)}H_3-C^{(2)}H_2$	$C^{(1)}$	0.368		6-31G/CISD
	$C^{(2)}$	1.226		
	$H_{(CH_3)}$	0.076		
	$H_{(CH_2)}$	0.063		
	CC		−0.194	
	$CH_{(CH_3)}$		−0.097	
	$CH_{(CH_2)}$		−0.128	
	$HH_{(CH_3)}$		0.013	
	$HH_{(CH_2)}$		0.010	
$C^{(1)}H_2=C^{(2)}H$	$C^{(1)}$	0.503		6-31G/CISD
	$C^{(2)}$	1.251		
	$H_{(CH_2)}$	0.068		
	$H_{(CH)}$	0.067		
	CC		−0.469	
	$CH_{(CH_2)}$		−0.104	
	$CH_{(CH)}$		−0.100	
	HH		0.011	
$C^{(1)}H\equiv C^{(2)}$	$C^{(1)}$	0.639		6-31G/CISD
	$C^{(2)}$	1.425		
	H	0.054		
	CC		−0.646	
	CH		−0.090	
$C^{(1)}H_2=C^{(2)}H-C^{(3)}H_2$	$C^{(1)}$	0.753		6-31G/CISD
	$C^{(2)}$	0.392		
	$C^{(3)}$	0.753		
	$H_{(CH_2)}$	0.051		
	$H_{(CH)}$	0.051		
	$C^{(1)}C^{(2)}$		−0.296	

Table 2. Continued

system	atom/bond	spin-free		basis set/method
		$\langle\hat{S}^2\rangle_A$	$\langle\hat{S}^2\rangle_{AB}$	
	$C^{(2)}C^{(3)}$		−0.296	
	$C^{(1)}C^{(3)}$		0.247	
	$CH_{(CH_2)}$		−0.094	
	$CH_{(CH)}$		−0.083	
	HH		0.008	

Table 3. Local Spins of One- And Two-Centers ($\langle\hat{S}^2\rangle_A$ and $\langle\hat{S}^2\rangle_{AB}$) Arising from the Spin-Free Treatment (eqs 13 and 14) for Triplet Systems at Experimental Equilibrium Distances (^{a} near Dissociation Limits)

system	atom/bond	spin-free		basis set/method
		$\langle\hat{S}^2\rangle_A$	$\langle\hat{S}^2\rangle_{AB}$	
H_2^a	H	0.750		6-31G/FCI
	HH		0.250	
Li_2^a	Li	0.750		STO-3G/FCI
	LiLi		0.250	
O_2	O	0.760		6-31G/CISD
	OO		0.240	
NF	N	1.879		6-31G/CISD
	F	0.141		
	NF		−0.010	
NH	N	2.277		6-31G/CISD
	H	0.082		
	NH		−0.180	
C_2	C	0.761		6-31G/CISD
	CC		0.239	
B_2H_2	B	0.979		6-31G/CISD
	H	0.082		
	BB		0.245	
	BH		−0.123	
	B···H		−0.030	
	HH		−0.001	
CH$_2$	C	2.604		6-31G/CISD
	H	0.083		
	CH		−0.196	
	HH		0.007	
C$_2$H$_4$ (triplet)	C	1.352		6-31G/CISD
	H	0.064		
	CC		0.072	
	CH		−0.146	
	C···H		0.005	
	HH		0.012	
	H···H		−0.002	
	H···H		−0.003	

unoccupied molecular orbitals) in the procedure denominated frozen II. As has been pointed out above, in absence of correlation that is, for RHF wave functions, formulas 5, 13 and 14 predict zero values for local spins of one- and two-center which is

Table 4. Local Spins of One- And Two-Centers ($<\hat{S}^2>_A$ and $<\hat{S}^2>_{AB}$) Arising from the Treatments Spin-Free (eqs 13 and 14) and with Spin (eq 5 in the Atomic Basis Set) at Several Correlation Levels, With the 6-31G Basis Sets, At Experimental Equilibrium Distances

		atom/	spin-free		with spin	
System	correlation level	bond	$<\hat{S}^2>_A$	$<\hat{S}^2>_{AB}$	$<\hat{S}^2>_A$	$<\hat{S}^2>_{AB}$
HF	CISD	F	0.050		0.059	
		H	0.050		0.059	
		HF		−0.050		−0.059
	CISDT	F	0.052		0.060	
		H	0.052		0.060	
		HF		−0.052		−0.060
	CISDTQ	F	0.056		0.064	
		H	0.056		0.064	
		HF		−0.056		−0.064
NH$_3$	CISD	N	0.226		0.257	
		H	0.059		0.068	
		NH		−0.075		−0.086
		HH		0.008		0.009
	CISDT	N	0.234		0.264	
		H	0.061		0.071	
		NH		−0.078		−0.088
		HH		0.008		0.009
C$_2$H$_6$ (staggered)	CISD (frozen I)	C	<0.001		<0.001	
		CC		<0.001		<0.001
	CISD (frozen II)	C	0.145		0.174	
		CC		<0.001		0.007
	CISD	C	0.361		0.400	
		CC		−0.130		−0.136

a suitable chemical requirement.[11,13] However, as can be observed in Table 4, the presence of correlation increases the absolute values of local spins in both procedures, although this effect turns out to be slightly less marked in the results arising from the spin-free treatment.

5. CONCLUSION

In this work, we have described a simple and direct partitioning of the expectation value $<\hat{S}^2>$ corresponding to an N-electron system into one- and two-center terms, according to a Mulliken scheme. Our treatment, which utilizes spin-free quantities, can be applied to states of any spin symmetry S and is valid for both independent and correlated particle models of wave functions. This procedure constitutes an improvement on the previously reported treatments since it is independent of the S_z substate, fulfilling the physical requirement of uniqueness for the components of the spin multiplet. Another achievement of our approach, from a computational point of view, is that it avoids the use of the spin blocks of the second-order reduced density matrix, which are not usually available in most standard codes. The results arising from several singlet state systems show lower local spin values compared with those from other reported methods (with spin) at the used correlation levels, although these differences are not too large. We have applied our treatment to selected closed- and open-shell systems and the obtained results are chemically meaningful in all studied cases. They show a

correct behavior in limit situations; adequate atomic spin values at the dissociation limits, in agreement with those of the respective free atoms, and zero values for all one-center and two-center local spins for closed-shell RHF wave functions. Our results and those of other treatments show dependence on the electronic correlation level, although that dependence is slightly lower in our proposal than in the S_z-dependent methods.

■ APPENDIX A

Table 5. Local Spins of One- And Two-Centers ($<\hat{S}^2>_A$ and $<\hat{S}^2>_{AB}$) Arising from eq 5 (in the Atomic Basis Sets) for the Lowest Triplet HeH$^+$ System

system	atom/bond	$<\hat{S}^2>_A$	$<\hat{S}^2>_{AB}$	basis set/method
HeH$^+$ [a] ($S_z = 0$)	He	0.700		aug-cc-pVDZ/FCI
	H	0.870		
	HeH		0.215	
HeH$^+$ [a] ($|S_z| = 1$)	He	0.815		aug-cc-pVDZ/FCI
	H	0.985		
	HeH		0.100	
HeH$^+$ [b] ($S_z = 0$)	He	0.828		aug-cc-pVDZ/FCI
	H	0.696		
	HeH		0.238	
HeH$^+$ [b] ($|S_z| = 1$)	He	0.861		aug-cc-pVDZ/FCI
	H	0.729		
	HeH		0.205	
HeH$^+$ [c] ($S_z = 0$)	He	0.763		aug-cc-pVDZ/FCI
	H	0.734		
	HeH		0.251	
HeH$^+$ [c] ($|S_z| = 1$)	He	0.758		aug-cc-pVDZ/FCI
	H	0.729		
	HeH		0.256	

[a] R(HeH) = 1.117 au. [b] R(HeH) = 2.235 au. [c] R(HeH) = 4.47 au.

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