

Relationships between Cumulant and Spin-Density Matrices: Application to the Decomposition of Spin

Alicia Torre,[†] Diego R. Alcoba,[‡] Luis Lain,^{*,†} and Roberto C. Bochicchio[†]

Departamento de Química Física, Facultad de Ciencia y Tecnología, Universidad del País Vasco, Apdo. 644 E48080 Bilbao, Spain and Departamento de Física, Facultad de Ciencias Exactas y Naturales, Universidad de Buenos Aires, Ciudad Universitaria, 1428, Buenos Aires, Argentina

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This paper reports the derivation of a relationship between some elements of the cumulant matrix of the second-order reduced density matrix and the elements of the spin-density matrix. This relationship turns out to be very useful to determine local spins through the partitioning of the spin expectation value $\langle \hat{S}^2 \rangle$ of an N -electron system. The procedure enables expression of both one- and two-center contributions only in terms of one-electron matrix elements, the elements of the spin-density matrix. We report numerical determinations of local spins in the Hilbert space of atomic orbitals in selected molecules and radicals in triplet and doublet states.

1. Introduction

As is well-known, any determination of a two-electron property, beyond the one-particle approximation, requires the use of the second-order reduced density matrix, although its utilization is very often cumbersome. One of the most useful managements of this matrix consists in expressing its elements in terms of Grassmann products of elements of its corresponding first-order reduced density matrix plus elements of its cumulant matrix.^{1,2} Cumulants were introduced in statistics a very long time ago, but during the past decade the cumulant matrices of the reduced density matrices have been widely studied and used in many-electron theory. These matrices, which have also been named irreducible parts of the reduced density matrices,³ possess the interesting property of being additively separable (extensive). An appropriate treatment of the cumulant matrices has allowed one to reconstruct successfully reduced density matrices of second and higher orders.^{4–9} The cumulant matrices are also related with other important tools as the Green's functions, used in quantum field theory,¹⁰ and with the matrix of effectively unpaired electrons,^{11–14} used in studies of population analyses of closed- and open-shell systems.

On the other hand, partitionings of molecular properties into contributions associated with atoms or groups of atoms that constitute a molecule have played an important role in chemistry and related areas, since they provide an intuitive insight in terms of building blocks. The partitioning of the number of electrons of a determined molecular system, known as population analysis, is perhaps the most widely studied property and its achievements have been obtained through many approaches and procedures.^{15–19} The decompositions of the molecular energy and of the first- and second-order reduced density matrices of an N -electron system^{20–29} have allowed one to describe the nature and features of chemical bondings and to assess bonding strengths among atoms.

Another property whose partitioning has been studied is the expectation value of the N -electron spin-squared operator \hat{S}^2 .^{30–39} The interest of this decomposition lies in its ability to assign portions of the total molecular electron spin to individual atoms or molecular fragments. These determinations allow one to predict the spin state of an atom or fragment embedded in a molecule as well as other properties, as the spin–spin coupling constants between two fragments within the Heisenberg Hamiltonian model.

In a recent paper³⁸ we have described a partitioning of the $\langle \hat{S}^2 \rangle$ quantity corresponding to an N -electron system, in the Hilbert space of atomic orbitals, at the level of multideterminantal correlated wave functions. This study has allowed us to compare results derived from correlated and uncorrelated wave functions. The reported formulas depend on the cumulant matrix of the two-electron reduced density matrix, which is also a two-electron tool. In this article we show that it is possible to describe such a partitioning only in terms of the spin-density, which is a one-electron device. This achievement is based on the derivation of a relationship between some elements of the cumulant matrix of the second-order reduced density matrix and the elements of the spin-density matrix corresponding to the substate of maximum projection $S_z = S$. This relationship makes the expressions that describe the local spins turn out to be independent of two-electron terms and consequently more appropriate from a computational point of view.

We have organized the paper as follows. In the second section we show the relationship between the matrix elements of the cumulant of the second-order reduced density matrix in the substate $S_z = S$ and those of the spin-density matrix of that substate. The third section describes the basic aspects of the partitioning of the $\langle \hat{S}^2 \rangle$ quantity into one-center and two-center contributions, providing local spin formulas in terms of one-electron tools. In the fourth section we report some numerical determinations performed in selected triplet and doublet systems as well as the computational details. Finally, in the last section we summarize the remarks and conclusions of this work.

* To whom correspondence should be addressed. Fax: +34-946013500. E-mail: qfplapel@lg.ehu.es.

[†] Universidad del País Vasco.

[‡] Universidad de Buenos Aires. Fellow of the Consejo Nacional de Investigaciones Científicas (CONICET) Argentina.

2. Relationships between Cumulant and Spin-Density Matrix Elements

We will express the expectation value of the \hat{S}^2 operator corresponding to an N -electron system in a determined state Ψ , by means of the relationship^{40,41}

$$\langle \hat{S}^2 \rangle = -\frac{N(N-4)}{4} - \sum_{ik} ({}^2D)_{ki}^{ik} \quad (1)$$

in which $({}^2D)_{ki}^{ik}$ are some elements of the spin-free second-order reduced density matrix of that state. Taking into account the value of the trace of that matrix, $\sum_{ik} ({}^2D)_{ik}^{ik} = \binom{N}{2}$, eq 1 can straightforwardly be written as

$$\langle \hat{S}^2 \rangle = \frac{3N^2}{4} - 2 \sum_{ik} ({}^2D)_{ik}^{ik} - \sum_{ik} ({}^2D)_{ki}^{ik} \quad (2)$$

In the following, i, j, k, l, \dots will be orbitals of an orthogonal basis set, and σ and σ' are the spin coordinates ($\sigma, \sigma' = \alpha, \beta$). The elements of the second-order reduced density matrix, $({}^2D)_{j\sigma'k\sigma}^{\alpha\alpha}$, those of the first-order reduced density matrix, $({}^1D)_{j\sigma}^{\alpha\alpha}$, and the elements of the cumulant matrix of the second-order reduced density matrix, $(\Gamma)_{j\sigma'k\sigma}^{\alpha\alpha}$, are related by²

$$({}^2D)_{j\sigma'k\sigma}^{\alpha\alpha} = \frac{1}{2}({}^1D)_{j\sigma}^{\alpha\alpha}({}^1D)_{k\sigma'}^{\alpha\alpha} - \frac{1}{2}({}^1D)_{k\sigma}^{\alpha\alpha}({}^1D)_{j\sigma'}^{\alpha\alpha} + \frac{1}{2}(\Gamma)_{j\sigma'k\sigma}^{\alpha\alpha} \quad (3)$$

A spin-free version of eq 3 can be obtained taking into account $({}^2D)_{jl}^{ik} = \sum_{\sigma, \sigma'} ({}^2D)_{j\sigma'k\sigma}^{\alpha\alpha}$, $({}^1D)_j^i = \sum_{\sigma} ({}^1D)_{j\sigma}^{\alpha\sigma}$, $(\Gamma)_{jl}^{ik} = \sum_{\sigma, \sigma'} (\Gamma)_{j\sigma'k\sigma}^{\alpha\alpha}$, $({}^1D)_{j\sigma}^{\alpha\alpha} = (1/2)[({}^1D)_j^i + (P^s)_j^i]$ and $({}^1D)_{j\sigma}^{\beta\beta} = (1/2)[({}^1D)_j^i - (P^s)_j^i]$, resulting^{28,29,38}

$$({}^2D)_{jl}^{ik} = \frac{1}{2}({}^1D)_j^i({}^1D)_l^k - \frac{1}{4}({}^1D)_j^i({}^1D)_l^k - \frac{1}{4}(P^s)_j^i(P^s)_l^k + \frac{1}{2}(\Gamma)_{jl}^{ik} \quad (4)$$

in which $(P^s)_j^i = ({}^1D)_{j\alpha}^{\alpha\alpha} - ({}^1D)_{j\beta}^{\beta\beta}$ are the elements of the spin-density matrix. Note that although the elements $(P^s)_i^j(P^s)_j^k$ and $(\Gamma)_{jl}^{ik}$ depend on the substate defined by the quantum number S_z of the state Ψ , $({}^2D)_{jl}^{ik}$, $({}^1D)_j^i$, and the sums $[-(1/4)(P^s)_i^j(P^s)_j^k + (1/2)(\Gamma)_{jl}^{ik}]$ are S_z -independent.^{28,38}

The substitution of the elements $({}^2D)_{ik}^{jk}$ and $({}^2D)_{ki}^{ik}$ in eq 2 according to eq 4 and the value of the trace $\sum_i ({}^1D)_i^i = N$ allow one to express the $\langle \hat{S}^2 \rangle$ quantity as

$$\langle \hat{S}^2 \rangle = \frac{1}{2} \sum_{i,k} (P^s)_k^i (P^s)_i^k + \frac{1}{4} \sum_{i,k} (P^s)_i^i (P^s)_k^k - \sum_{i,k} \left[(\Gamma)_{ik}^{ik} + \frac{1}{2} (\Gamma)_{ki}^{ik} \right] \quad (5)$$

As has been mentioned in the Introduction, eq 5 depends on the elements of the two-electron cumulant matrix, whose treatment is cumbersome. In this section we describe a procedure that allows one to express the elements $\sum_k [(\Gamma)_{jk}^{ik} + (1/2)(\Gamma)_{kj}^{ik}]$ in terms of elements of the spin-density matrix, which is of one-electron nature and is easier to handle in both theoretical and computational approaches.

Let us express the matrix elements $(\Gamma)_{jk}^{ik}$ and $(\Gamma)_{kj}^{ik}$ in the orthogonal basis set i, j, k, l, \dots , according to eq 4. Taking into account the well-known relationships $\sum_k ({}^2D)_{jk}^{ik} = [(N-1)/2] ({}^1D)_j^i$ (contraction of the second-order reduced density matrix), $\sum_k ({}^1D)_k^k = N$ (trace of the first-order reduced density matrix) and $\sum_k (P^s)_k^k = 2 S_z$ (trace of the spin-density matrix) we obtain

$$\sum_k \left[(\Gamma)_{jk}^{ik} + \frac{1}{2} (\Gamma)_{kj}^{ik} \right] = \sum_k ({}^2D)_{kj}^{ik} + \frac{N-4}{4} ({}^1D)_j^i + \frac{1}{2} \sum_k (P^s)_k^i (P^s)_j^k + \frac{S_z}{2} (P^s)_j^i \quad (6)$$

The value of the elements $\sum_k ({}^2D)_{kj}^{ik}$ can easily be calculated through its spin components, that is,

$$\begin{aligned} \sum_k ({}^2D)_{kj}^{ik} &= \sum_k [({}^2D)_{k\sigma'j\sigma}^{\alpha\alpha} + ({}^2D)_{k\beta'j\beta}^{\beta\beta} + ({}^2D)_{k\sigma'j\sigma}^{\alpha\beta} + ({}^2D)_{k\beta'j\beta}^{\beta\alpha}]_{S_z=S} \\ &= \left[-\frac{N^\alpha-1}{2} ({}^1D)_{j\alpha}^{\alpha\alpha} - \frac{N^\beta-1}{2} ({}^1D)_{j\beta}^{\beta\beta} + ({}^1D)_{j\beta}^{\alpha\beta} \right]_{S_z=S} \end{aligned} \quad (7)$$

in which since the elements $({}^2D)_{kj}^{ik}$ are spin-free, and we have chosen the substate $S_z = S$ for expressing their spin components. In that equation, the terms $-(N^\alpha-1)/2 ({}^1D)_{j\alpha}^{\alpha\alpha}$ and $-(N^\beta-1)/2 ({}^1D)_{j\beta}^{\beta\beta}$ come from the contraction of the terms $\sum_k ({}^2D)_{k\sigma'j\sigma}^{\alpha\alpha}$ and $\sum_k ({}^2D)_{k\beta'j\beta}^{\beta\beta}$, respectively, whereas the term $[({}^1D)_{j\beta}^{\alpha\beta}]_{S_z=S}$ is equal to $\sum_k [({}^2D)_{k\sigma'j\sigma}^{\alpha\beta} + ({}^2D)_{k\beta'j\beta}^{\beta\alpha}]_{S_z=S}$ for that substate (see Appendix). Obviously N^α and N^β denote the number of α - and β -electrons, respectively, of that mentioned substate.

The substitutions in eq 7 of $N^\alpha = (N/2) + S$ and $N^\beta = (N/2) - S$ as well as $({}^1D)_{j\beta}^{\alpha\beta} = (1/2)[({}^1D)_j^i - (P^s)_j^i]$ allow one to express the elements $\sum_k ({}^2D)_{kj}^{ik}$ as

$$\sum_k ({}^2D)_{kj}^{ik} = -\frac{N-4}{4} ({}^1D)_j^i - \frac{S+1}{2} [(P^s)_j^i]_{S_z=S} \quad (8)$$

which substituted in eq 6 leads to

$$\sum_k \left[(\Gamma)_{jk}^{ik} + \frac{1}{2} (\Gamma)_{kj}^{ik} \right]_{S_z=S} = \frac{1}{2} \left[\sum_k (P^s)_k^i (P^s)_j^k - (P^s)_j^i \right]_{S_z=S} \quad (9)$$

This relationship provides to interpret the expression $\sum_k [(\Gamma)_{jk}^{ik} + (1/2)(\Gamma)_{kj}^{ik}]_{S_z=S}$ as a measure of the deviation of the idempotency of the spin-density matrix P^s due to the correlation effects.

3. Partitioning of $\langle \hat{S}^2 \rangle$: Local Spins

The partitioning of the $\langle \hat{S}^2 \rangle$ quantity can be performed using eq 5. However, for practical reasons it is more useful to express that equation in the basis set of the atomic orbitals μ, ν, \dots , that is

$$\begin{aligned} \langle \hat{S}^2 \rangle &= \frac{1}{2} \sum_{\mu, \nu} (P^s S)_\nu^\mu (P^s S)_\mu^\nu + \frac{1}{4} \sum_{\mu, \nu} (P^s S)_\mu^\mu (P^s S)_\nu^\nu - \\ &\sum_{\mu, \nu, \lambda, \gamma} (S)_\lambda^\mu \left[(\Gamma)_{\mu\nu}^{\lambda\nu} + \frac{1}{2} (\Gamma)_{\gamma\mu}^{\lambda\nu} \right] (S)_\nu^\gamma \end{aligned} \quad (10)$$

where $S_\mu^\mu = \langle \mu | \nu \rangle$ are the elements of the overlap matrix.

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

$$\langle \hat{S}^2 \rangle = \sum_A \langle \hat{S}^2 \rangle_A + \sum_{A \neq B} \langle \hat{S}^2 \rangle_{AB} \quad (11)$$

we assign the atomic orbitals μ, ν, \dots to the nuclei A, B, \dots and we evaluate the densities at the maximum projection substate $S_z = S$, resulting³⁸

$$\langle \hat{S}^2 \rangle_A = \frac{1}{2} \sum_{\mu \in A} \sum_{\nu \in A} (P^s S)_\nu^\mu (P^s S)_\mu^\nu + \frac{1}{4} \sum_{\mu \in A} \sum_{\nu \in A} (P^s S)_\mu^\mu (P^s S)_\nu^\nu - \sum_{\mu \in A} \sum_{\nu, \lambda, \gamma} (S)_\lambda^\mu \left[(\Gamma)_{\mu\gamma}^{\lambda\nu} + \frac{1}{2} (\Gamma)_{\gamma\mu}^{\lambda\nu} \right] (S)_\nu^\gamma \quad (12)$$

and

$$\langle \hat{S}^2 \rangle_{AB} = \frac{1}{2} \sum_{\mu \in A} \sum_{\nu \in B} (P^s S)_\nu^\mu (P^s S)_\mu^\nu + \frac{1}{4} \sum_{\mu \in A} \sum_{\nu \in B} (P^s S)_\mu^\mu (P^s S)_\nu^\nu \quad (13)$$

Formulas 12 and 13 constitute expressions of the local spins corresponding to the one- and two-center terms, respectively, providing the values of the distribution of the $\langle \hat{S}^2 \rangle$ quantity. In agreement with our previous experience,^{25,28,38,43,44} the cumulant terms possess a nonparing nature, consequently they have only been assigned to one-center terms.

An alternative formulation of eq 12 can be obtained if eq 9 is transformed to the atomic basis set and substituted in that equation, providing the calculation of local spin associated with the nuclei A as

$$\langle \hat{S}^2 \rangle_A = \frac{1}{2} \sum_{\mu \in A} \sum_{\nu \in A} (P^s S)_\nu^\mu (P^s S)_\mu^\nu + \frac{1}{4} \sum_{\mu \in A} \sum_{\nu \in A} (P^s S)_\mu^\mu (P^s S)_\nu^\nu - \frac{1}{2} \sum_{\mu \in A} \left[\sum_{\nu} (P^s S)_\nu^\mu (P^s S)_\mu^\nu - (P^s S)_\mu^\mu \right] \quad (14)$$

in which, obviously, all the spin-density matrix elements must be calculated for the substate $S_z = S$. Equation 14 is equivalent to eq 12 but is simpler since it is free of two-electron terms and is computationally more favorable.

Let us now analyze eq 14 in depth. The split of the sum \sum_ν in eq 14 into the functions $\nu \in A$ and $\nu \notin A$ finally leads to

$$\langle \hat{S}^2 \rangle_A = \frac{1}{2} \sum_{\mu \in A} (P^s S)_\mu^\mu \left[1 + \frac{1}{2} \sum_{\nu \in A} (P^s S)_\nu^\nu \right] - \frac{1}{2} \sum_{\mu \in A} \sum_{B \neq A} \sum_{\nu \in B} (P^s S)_\nu^\mu (P^s S)_\mu^\nu \quad (15)$$

The terms $(1/2) \sum_{\mu \in A} (P^s S)_\mu^\mu = (1/2)(N_A^\alpha - N_A^\beta)$ can physically be interpreted as the expectation values $\langle S_z \rangle_A$, consequently the first term of the rhs of eq 15 is the canonical spin-squared population $\langle \hat{S}^2 \rangle_A^{\text{canonical}} = \langle \hat{S}_z \rangle_A (\langle \hat{S}_z \rangle_A + 1)$ of the atomic center A.³⁷ This quantity can be regarded as the gross spin population

TABLE 1: Local Spins of One- and Two-Centers ($\langle \hat{S}^2 \rangle_A$ and $\langle \hat{S}^2 \rangle_{AB}$) and Values of $\langle \hat{S}^2 \rangle_A^{\text{canonical}} = \langle \hat{S}_z \rangle_A (\langle \hat{S}_z \rangle_A + 1)$ in Triplet Systems Obtained at the Level of CISD Correlated Wave Functions with the 6-31G Basis Sets

system	state	atom/ bonding	$\langle \hat{S}^2 \rangle_A$	$\langle \hat{S}^2 \rangle_A^{\text{canonical}}$	$\langle \hat{S}^2 \rangle_{AB}$	
NH	$^3\Sigma^-$	N	1.861	1.859		
		H	0.052	0.050		
		NH				0.044
CH ₂	3B_1	C	2.325	2.329		
		H	-0.052	-0.050		
		CH				-0.057
		HH				0.003
C ₂	$^3\Sigma_g^+$	C	0.526	0.750		
		CC				0.474
NF	$^3\Sigma^-$	N	1.739	1.808		
		F	0.000	0.070		
		NF				0.130
O ₂	$^3\Sigma_g^-$	O	0.548	0.750		
		OO				0.452
HBBH (linear)	$^3\Sigma_g^-$	B	0.463	0.700		
		H	0.029	0.028		
		BB				0.457
		BH				0.012
		B...H				0.013
		HH				0.001
		CH ₂ =CH ₂ (plane)	$^3B_{1u}$	C	0.726	0.703
		H	0.011	0.120		
		CC			0.205	
		CH			0.005	
		C...H			0.005	
		HH			0.000	

of center A (similar to the Mulliken gross atomic population) and allows one to express eq 15 as

$$\langle \hat{S}^2 \rangle_A = [\langle \hat{S}_z \rangle_A (\langle \hat{S}_z \rangle_A + 1)]_{S_z=S} - \frac{1}{2} \sum_{B \neq A} \sum_{\mu \in A} \sum_{\nu \in B} [(P^s S)_\nu^\mu (P^s S)_\mu^\nu]_{S_z=S} \quad (16)$$

The second term of eq 16, that is, $-(1/2) \sum_{B \neq A} \sum_{\mu \in A} \sum_{\nu \in B} (P^s S)_\nu^\mu (P^s S)_\mu^\nu$ is the spin population shared between the nucleus A and the rest of the nuclei; consequently, this term measures the delocalization degree of the electron spin cloud corresponding to a given center over the whole system. As can be observed, all these quantities are expressed by mean of one-electron terms and must be evaluated at the substate $S_z = S$. Equation 16 clearly shows that the $\langle \hat{S}^2 \rangle_A$ values obtained by the present scheme can be interpreted as a measure of $S_A(S_A + 1)$, which is consistent with the values obtained from $\langle S_z \rangle_A$ quantities, that is, $\langle \hat{S}^2 \rangle_A = S_A(S_A + 1) = \langle S_z \rangle_A (\langle S_z \rangle_A + 1)$. However, this measure accounts for the decrease of the spin on the fragment with respect to the canonical spin, due to spin delocalization. This consistency seems to be an important criterion for assessing local spin decomposition approaches as shown in ref 37.

4. Results and Discussion

To test the reliability of our methodology to describe local spins, we have performed numerical determinations in several systems in triplet and doublet spin symmetries. Tables 1 and 2 report results of the local spins $\langle \hat{S}^2 \rangle_A$ (eq 14 or equivalently eq 16), $\langle \hat{S}^2 \rangle_{AB}$ (eq 13) and $\langle \hat{S}^2 \rangle_A^{\text{canonical}}$, corresponding to molecules and radicals in triplet and doublet states, respectively. This procedure avoids the explicit use of eq 12,

TABLE 2: Local Spins of One- and Two-Centers ($\langle \hat{S}^2 \rangle_A$ and $\langle \hat{S}^2 \rangle_{AB}$) and Values of $\langle \hat{S}^2 \rangle_A^{\text{canonical}} = \langle \hat{S}_z \rangle_A (\langle \hat{S}_z \rangle_A + 1)$ in Doublet Systems Obtained at the Level of CISD Correlated Wave Functions with the 6-31G Basis Sets

system	state	atom/bonding	$\langle \hat{S}^2 \rangle_A$	$\langle \hat{S}^2 \rangle_A^{\text{canonical}}$	$\langle \hat{S}^2 \rangle_{AB}$
OH	$^2\Pi$	O	0.723	0.723	
		H	0.013	0.014	
		OH			0.007
NH ₂	2B_1	N	0.769	0.769	
		H	-0.005	-0.005	
		NH			-0.003
		HH			0.001
CH ₃	$^2A''_2$	C	0.989	0.982	
		H	-0.035	-0.035	
		CH			-0.025
		HH			0.002
CN	$^2\Sigma^+$	C	0.827	0.841	
		N	-0.058	-0.043	
		CN			-0.009
C ⁽¹⁾ H ₃ -C ⁽²⁾ H ₂	$^2A'$	C ⁽¹⁾	-0.030	-0.030	
		C ⁽²⁾	0.664	0.680	
		H	0.008	0.021	
		H	0.013	0.015	
		H	0.008	0.008	
		CC			-0.016
		CH _(CH₃)			0.001
		CH _(CH₂)			0.004
C ⁽¹⁾ H ₂ =C ⁽²⁾ H	$^2A'$	C ⁽¹⁾	0.088	0.087	
		C ⁽²⁾	0.558	0.579	
		H	-0.010	-0.003	
		H	-0.007	0.005	
		H	0.003	0.007	
		CC			0.032
		C ⁽²⁾ H			0.004
		HH			0.000
C ⁽¹⁾ H≡C ⁽²⁾	$^2\Sigma^+$	C ⁽¹⁾	-0.086	-0.058	
		C ⁽²⁾	0.829	0.858	
		H	0.007	0.010	
		CC			-0.008
		C ⁽¹⁾ H			0.007
		C ⁽²⁾ H			0.001
C ⁽¹⁾ H ₂ =C ⁽²⁾ H-C ⁽³⁾ H ₂	2A_2	C ⁽¹⁾	0.144	0.288	
		C ⁽²⁾	0.056	0.050	
		C ⁽³⁾	0.144	0.288	
		H	0.001	0.001	
		H	-0.007	0.006	
		H	0.003	0.007	
		C ⁽¹⁾ C ⁽²⁾ /C ⁽²⁾ C ⁽³⁾			0.008
		C ⁽¹⁾ C ⁽³⁾			0.202
		C ⁽¹⁾ H			-0.002
		C ⁽²⁾ H			0.000
HH			0.000		

previously utilized in ref 38, which requires the determinations of two-electron quantities $(\Gamma)_{\mu\nu}^{\lambda\sigma}$. We have included in this work some of the systems reported in that reference just to show that eqs 14 and 12 provide identical results, proving the correctness of the above-reported derivations. The PSI3 package⁴⁵ was used for evaluating the overlap integrals $S_{\mu\nu}^{\lambda\sigma}$ as well as the density matrices required for the calculation of spin-density matrix elements $(P^s)_i^j$ in the molecular orbital basis sets using the Luzanov and Whyman procedure⁴⁶ for the highest projection $S_z = S$. Then in subsequent steps the spin-density matrix was transformed into the atomic basis sets to obtain the matrix elements $(P^s S)_{\mu\nu}^{\lambda\sigma}$ and to evaluate local spins using our own computational implementation. All the calculations were carried out with the 6-31G basis sets at the level of configuration interaction (CI) with single and double excitations (CISD) using as reference the ROHF states. The experimental equilibrium geometries have been used for all the systems⁴⁷ except for the ethyl radical, which has been computed with the geometry optimized at the UHF-

CISD/6-31G* level provided in ref 47 and the ethylene molecule (triplet) described at the geometry reported in ref 48.

As can be observed in Table 1, the values found for the one-center quantities $\langle \hat{S}^2 \rangle_A$ and $\langle \hat{S}^2 \rangle_A^{\text{canonical}}$ are very close in the radical imidogen and also in the radical methylene, whereas the two-center $\langle \hat{S}^2 \rangle_{AB}$ values are very low in both systems. This distribution of the $\langle \hat{S}^2 \rangle$ quantity indicates a clear localization of the unpaired electrons on a determined atomic region, that of N atom and C atom, respectively. The systems nitrogen fluoride and the ethylene (triplet) also show these features, although the values found for two-center spin components are appreciable in these species. The rate among one-center and two-center component values indicates electron localization over the N atom in NF system and spin delocalization over the two identical C atoms in ethylene molecule. However, in this last system, negligible values have been found between the centers carbon and hydrogen or between two hydrogens (linked to identical or distinct carbon atoms). All these results are in agreement with the genuine chemical knowledge of these compounds. The partitioning of the $\langle \hat{S}^2 \rangle$ quantity in the species C₂, O₂, and HBBH (linear), which are also reported in Table 1, is quite different. These last three systems present significant values for both one-center $\langle \hat{S}^2 \rangle_A$ and two-center $\langle \hat{S}^2 \rangle_{AB}$ spin populations, and the difference between the values $\langle \hat{S}^2 \rangle_A$ and $\langle \hat{S}^2 \rangle_A^{\text{canonical}}$ is considerably higher than in the previous commented systems. This fact must be interpreted in terms of a delocalization of the electron spin cloud in the molecules C₂ and O₂. The HBBH compound shows spin localization on the B atoms and a high delocalization limited to the bonding region between the two identical boron atoms, since the values of $\langle \hat{S}^2 \rangle_{AB}$ found in the bonding regions BH (the neighbor hydrogen), B•••H (the furthest hydrogen), and HH are very low. Likewise, the low one-center spin population centered on the hydrogen atoms found excludes the localization of unpaired electrons around these atomic regions.

The results gathered in Table 2 describe the decomposition of the spin $\langle \hat{S}^2 \rangle$ in systems in doublet states. The three first systems described in that table, that is, the radicals hydroxyl, amino, and methyl, present very similar values for the one-center quantities $\langle \hat{S}^2 \rangle_A$ and $\langle \hat{S}^2 \rangle_A^{\text{canonical}}$ whereas the two-center local spins are close to zero for all pairs of atoms. As expected, these results confirm that the unpaired electron is located on the oxygen, nitrogen, and carbon atoms, respectively. In the cyano radical our procedure predicts the localization of the unpaired electron on the carbon atom in agreement with chemical intuition and experimental results. The species ethyl, vinyl, and ethynyl constitute a series of radicals in which the localization of the unpaired electron appears on the carbon atom linked to less hydrogen atoms, which in Table 2 has been denominated as C⁽²⁾. No significant spin population appears on the other carbon atom C⁽¹⁾. Likewise, the spin population assigned to hydrogen atoms is negligible in these compounds and consequently the positions of these atoms within the corresponding radical has not explicitly been indicated in the Table. The two-center spin populations for the bondings CC, CH, and HH also turns out to be negligible, pointing out the localized character of the electron spin cloud in those three compounds. The allyl radical is an interesting system to test this methodology. This compound is an example of resonance stabilized radical, where the double bond may be situated between the carbon atoms C⁽¹⁾C⁽²⁾ or between the carbons C⁽²⁾C⁽³⁾. Hence, spin

delocalization over carbons C⁽¹⁾ and C⁽³⁾ must be expected, due to resonance. The results provided by the partitioning of the $\langle \hat{S}^2 \rangle$ quantity confirm these predictions. The values found for the spin-squared populations over the carbon atoms C⁽¹⁾ and C⁽³⁾ are identical but are considerably higher than that found for the carbon C⁽²⁾. Likewise, the two-center spin populations C⁽¹⁾C⁽²⁾ and C⁽²⁾C⁽³⁾, although very low, are also identical. These results are in perfect agreement with experimental electron spin resonance results.⁴⁹ The difference between the values $\langle \hat{S}^2 \rangle_A$ and $\langle \hat{S}^2 \rangle_A^{\text{canonical}}$ for this system implies the appearance of an appreciable two-center spin population C⁽¹⁾C⁽³⁾ proving the delocalization of the spin cloud over the extreme carbons due to the node of the π electron cloud at the central carbon atom.⁴⁹

5. Concluding Remarks

In this work we have derived a simple relationship between elements of the cumulant matrix of the second-order reduced density matrix and those of the spin-density matrix for the highest spin-projection substate $S_z = S$. This relationship has been applied to perform a partitioning of $\langle \hat{S}^2 \rangle$, in the Hilbert space defined by the atomic orbital basis set, to achieve expression of both one- and two-center components in terms of one-electron quantities. The results obtained in open-shell systems at correlated multideterminantal level confirm the previous predictions of several^{36–38} authors over the suitability of the decomposition of the expectation value of the N -electron spin-squared operator \hat{S}^2 . We are currently working in our laboratories to predict magnetic properties of transition-metal clusters using this methodology. In this sense we note that alternative partitioning schemes to closely match $\langle \hat{S}^2 \rangle_A$ values with local spins as assigned by other chemical considerations, for example, formal oxidation states of centers, are also being investigated. Moreover, we are trying to extend these types of decompositions to other approaches, for example, partitionings that decompose a determined quantity in the three-dimensional physical space instead of the Hilbert space. An appropriate comparison among results arising from different partitioning schemes and working spaces for the $\langle \hat{S}^2 \rangle$ quantity is desirable.

Appendix

Determination of the Matrix Elements

$$\sum_k [({}^2D)_{k\alpha j\beta}^{i\alpha k\beta} + ({}^2D)_{k\beta j\alpha}^{i\beta k\alpha}]$$

The matrix elements $({}^1D)_{j\beta}^{i\beta}$ and $({}^2D)_{k\beta j\alpha}^{i\beta k\alpha}$ corresponding to a state Ψ can be expressed as expectation values of products of fermion operators, respectively

$$({}^1D)_{j\beta}^{i\beta} = \langle \Psi | (i^\beta)^\dagger (j^\beta)^- | \Psi \rangle$$

and

$$\sum_k ({}^2D)_{k\beta j\alpha}^{i\beta k\alpha} = \frac{1}{2} \langle \Psi | \sum_k (i^\beta)^\dagger (k^\alpha)^\dagger (j^\alpha)^- (k^\beta)^- | \Psi \rangle$$

In these expressions $(i^\beta)^\dagger$ and $(j^\alpha)^-$ etc. are the usual creation and annihilation operators corresponding to the spin orbitals i^β and j^α , respectively.

By use of the anticommutation rules of these operators, the last expression can be transformed into

$$\begin{aligned} \sum_k ({}^2D)_{k\beta j\alpha}^{i\beta k\alpha} &= \frac{1}{2} \langle \Psi | \sum_k (i^\beta)^\dagger [\delta_{j\alpha}^{k\alpha} - (j^\alpha)^- (k^\alpha)^\dagger] (k^\beta)^- | \Psi \rangle \\ &= \frac{1}{2} \langle \Psi | \sum_k (i^\beta)^\dagger (k^\beta)^- | \Psi \rangle \delta_{j\alpha}^{k\alpha} - \frac{1}{2} \langle \Psi | (i^\beta)^\dagger (j^\alpha)^- \sum_k (k^\alpha)^\dagger (k^\beta)^- | \Psi \rangle \\ &= \frac{1}{2} \langle \Psi | (i^\beta)^\dagger (j^\beta)^- | \Psi \rangle - \frac{1}{2} \langle \Psi | (i^\beta)^\dagger (j^\alpha)^- S^\dagger | \Psi \rangle \end{aligned}$$

where $\delta_{j\alpha}^{k\alpha}$ are the Kronecker deltas and $S^\dagger = \sum_k (k^\alpha)^\dagger (k^\beta)^-$ is the raising spin operator.⁵⁰

In the case of the highest S_z value, ($S_z = S$), $S^\dagger | \Psi \rangle = 0$ and consequently

$$\sum_k [({}^2D)_{k\beta j\alpha}^{i\beta k\alpha}]_{S_z=S} = \frac{1}{2} \langle \Psi | (i^\beta)^\dagger (j^\beta)^- | \Psi \rangle_{S_z=S} = \frac{1}{2} [({}^1D)_{j\beta}^{i\beta}]_{S_z=S}$$

According to this relationship and taking into account the index permutation rules in the second-order reduced density matrix, one finally obtains

$$\sum_k [({}^2D)_{k\beta j\alpha}^{i\beta k\alpha} + ({}^2D)_{k\alpha j\beta}^{i\alpha k\beta}]_{S_z=S} = [({}^1D)_{j\beta}^{i\beta}]_{S_z=S}$$

which is the relationship used in section 2.⁵¹

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