Local spin: A treatment beyond single determinant wave functions

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ABSTRACT

This Letter describes a partitioning of the expectation value $\langle \widehat{S}^2 \rangle$ of an N-electron system (molecule, ion, radical, etc.) into one- and two-center contributions. The proposal is valid for both independent and correlated particle models of the wave function. Our procedure provides local spin results which are physically reasonable for closed and open shell systems. Numerical results of the electronic spin population analyses of selected systems in the Hilbert space of atomic orbitals, arising from both single determinant wave functions and multideterminantal ones are analyzed and compared.

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1. Introduction

The decomposition of the expectation value of the N-electron spin-squared operator $\widehat{S}^2$ into one-center and two-center components has received a considerable attention in the last years; likewise a great effort has been dedicated to the study of local spins within a molecule [1–8]. The interest of this concept, comparable to the partial charge one, arises from its ability to characterize the spin state of an atom or a molecular fragment embedded in a molecular system, which provides an important insight into electronic structures. Besides, the local spin operators allow one to evaluate the spin couplings between two molecular fragments in the well-known Heisenberg Hamiltonian model that is used to describe magnetic interactions. This kind of studies is of paramount importance in the understanding of systems containing unpaired electrons or open shell molecules, which play a relevant role in several areas of chemistry (catalysis and organic syntheses), biochemistry (reactive sites of enzymes), design of new materials (devices to store information) and other disciplines.

Clark and Davidson have proposed a procedure to decompose the $\langle \widehat{S}^2 \rangle$ quantity corresponding to an N-electron system that utilizes projection operators associated with atomic centers or larger fragments within a molecule [1–3]. In this framework, the total spin operator $\widehat{S}$ is expressed as a sum of atomic operators, $\widehat{S}_{atomic}$; the expectation values of the scalar products of two of these operators allow one to evaluate the one-center and two-center contributions to the total quantity $\langle \widehat{S}^2 \rangle$. Although this technique has proven to be very useful in studies of population analyses [9], its application to the case of the decomposition of the $\langle \widehat{S}^2 \rangle$ quantity leads to results difficult to interpret e.g. it can assign nonzero local

spins in systems described by doubly occupied orbitals [4,7]. An alternative approach has recently been reported by Mayer [7]. The first step of this procedure consists in calculating the total expectation value $\langle \widehat{S}^2 \rangle$ and then to partition it into one-center and two-center contributions according to determined criteria. Although this procedure seems to overcome these drawbacks for interpreting results [8], its formulation is restricted to the use of single Slater determinant wave functions. In view of its apparent better suitability, in this Letter we use this last approach to develop a general procedure that goes beyond single Slater determinant wave functions, so that it can be applied to any independent particle or correlated wave function.

We have organized this Letter as follows. The second section describes the expressions of the local spins derived from the structure of the second-order reduced density matrix elements corresponding to any given wave function. The procedure can be applied to closed shell or open shell systems of a determined spin S and generalizes to any wave function the previous single Slater determinant treatment. The third section reports the computational aspects and the numerical results found for some selected open and closed shell molecular systems, in ground and excited states. A discussion of the results obtained at Hartree-Fock and configuration interaction levels is also reported in this section. Finally, in the last section we point out the remarks and conclusions of this work.

2. The partitioning of $\langle \widehat{S}^2 \rangle$

We will refer to an N-electron system described by a determined wave function, Ψ. The elements of the first- and second-order reduced density matrices corresponding to that state will be denoted by $^1D_{j^\sigma}^{i^\sigma}$ and $^2D_{j^\sigma l^{\sigma'}}^{i^\sigma k^{\sigma'}}$, respectively, in which $i, j, k, l, \ldots$ are orbitals of an orthogonal basis set and σ and σ' are the spin coordinates ($\sigma, \sigma' = \alpha, \beta$). The elements $^2D_{j^\sigma l^{\sigma'}}^{i^\sigma k^{\sigma'}}$ have been formulated as [10]

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

where $\Gamma_{j^\sigma l^{\sigma'}}^{i^\sigma k^{\sigma'}}$ are the elements of the cumulant of the second-order reduced density matrix.

A spin-free version of the elements of the second-order reduced density matrix, $^2D_{jl}^{ik} = \sum_{\sigma,\sigma'}{}^2D_{j^\sigma l^{\sigma'}}^{i^\sigma k^{\sigma'}}$, can be obtained substituting in Eq. (1) $^1D_{j^\alpha}^{i^\alpha} = \frac{1}{2}\left(^1D_j^i + {}^1D_j^{(s)i}\right)$ and $^1D_{j^\beta}^{i^\beta} = \frac{1}{2}\left(^1D_j^i - {}^1D_j^{(s)i}\right)$ [11]

$$^2D_{jl}^{ik} = \frac{1}{2}\,^1D_j^i\,^1D_l^k - \frac{1}{4}\,^1D_l^i\,^1D_j^k - \frac{1}{4}\,^1D_l^{(s)i}\,^1D_j^{(s)k} + \frac{1}{2}\Gamma_{jl}^{ik} \tag{2}$$

in which $^1D_j^i = \sum_\sigma{}^1D_{j^\sigma}^{i^\sigma}$ are the elements of the spin-free first-order reduced density matrix; $^1D_j^{(s)i} = {}^1D_{j^\alpha}^{i^\alpha} - {}^1D_{j^\beta}^{i^\beta}$ are the elements of the spin density matrix and $\Gamma_{jl}^{ik} = \sum_{\sigma,\sigma'}\Gamma_{j^\sigma l^{\sigma'}}^{i^\sigma k^{\sigma'}}$. The elements $^2D_{jl}^{ik}$ and $^1D_j^i$ are independent of the spin substates of quantum number S_z corresponding to the state Ψ, as well as those of the sum $-\frac{1}{4}\,^1D_l^{(s)i}\,^1D_j^{(s)k} + \frac{1}{2}\Gamma_{jl}^{ik}$ in Eq. (2). However, the terms $^1D_l^{(s)i}\,^1D_j^{(s)k}$ and Γ_{jl}^{ik} separately, are S_z-dependent. In fact, the sum $-\frac{1}{4}\,^1D_l^{(s)i}\,^1D_j^{(s)k} + \frac{1}{2}\Gamma_{jl}^{ik}$ is the spin-free version of the cumulant of the second-order reduced density matrix [12–15].

The expectation value of the $\widehat{S}^2$ operator, corresponding to the state Ψ, $\langle\widehat{S}^2\rangle = \langle\Psi|\widehat{S}^2|\Psi\rangle$ can be calculated by means of the spin-free second-quantized expression of the operator $\widehat{S}^2$ [16]

$$\langle\widehat{S}^2\rangle = N - \frac{N^2}{4} - \sum_{ik}{}^2D_{ki}^{ik} \tag{3}$$

As is well-known, the trace of the second-order reduced density matrix is

$$\sum_{ik}{}^2D_{ik}^{ik} = \frac{N(N-1)}{2} \tag{4}$$

A simple manipulation of Eqs. (3) and (4) leads to

$$\langle\widehat{S}^2\rangle = \frac{3N^2}{4} - 2\sum_{ik}{}^2D_{ik}^{ik} - \sum_{ik}{}^2D_{ki}^{ik} \tag{5}$$

The substitution of the elements $^2D_{ik}^{ik}$ and $^2D_{ki}^{ik}$ in Eq. (5) according to Eq. (2) allows us to express the expectation value $\langle\widehat{S}^2\rangle$ as

$$\langle\widehat{S}^2\rangle = \frac{1}{2}\sum_{i,k}{}^1D_k^{(s)i}\,^1D_i^{(s)k} - \sum_{i,k}\Gamma_{ik}^{ik} + \frac{1}{4}\sum_{i,k}{}^1D_i^{(s)i}\,^1D_k^{(s)k} - \frac{1}{2}\sum_{i,k}\Gamma_{ki}^{ik} \tag{6}$$

Formula (6) can directly be rewritten for the case of a nonorthogonal basis set such as that defined by the atomic functions centered in each atom $\mu, \nu, \lambda, \gamma, \ldots$, resulting

$$\langle\widehat{S}^2\rangle = \frac{1}{2}\sum_{\mu,\nu}(^1D^{(s)}\mathbb{S})_\nu^\mu(^1D^{(s)}\mathbb{S})_\mu^\nu - \sum_{\mu,\nu,\lambda,\gamma}\mathbb{S}_\lambda^\mu\Gamma_{\mu\gamma}^{\lambda\nu}\mathbb{S}_\nu^\gamma$$
$$+ \frac{1}{4}\sum_{\mu,\nu}(^1D^{(s)}\mathbb{S})_\mu^\mu(^1D^{(s)}\mathbb{S})_\nu^\nu - \frac{1}{2}\sum_{\mu,\nu,\lambda,\gamma}\mathbb{S}_\lambda^\mu\Gamma_{\gamma\mu}^{\lambda\nu}\mathbb{S}_\nu^\gamma \tag{7}$$

in which $\mathbb{S}$ denotes the overlap matrix.

As has been mentioned in the Introduction, one of the objectives of this Letter is to extent the approach reported for single Slater determinant wave functions [7] to a general wave function. The $\langle\widehat{S}^2\rangle$ formulation given in Eq. (7) has a general character so that it turns out to be valid for any single determinant or multideterminantal wave function, of closed or open shell type. In fact, in the case that the wave function is a single Slater determinant all the elements $\Gamma_{\mu\gamma}^{\lambda\nu}$ are zero and consequently expression (7) coincides with formula (8) in Ref. [7]. In other words, the appearance of the terms $\sum_{\mu,\nu,\lambda,\gamma}\mathbb{S}_\lambda^\mu\Gamma_{\mu\gamma}^{\lambda\nu}\mathbb{S}_\nu^\gamma$ and $\frac{1}{2}\sum_{\mu,\nu,\lambda,\gamma}\mathbb{S}_\lambda^\mu\Gamma_{\gamma\mu}^{\lambda\nu}\mathbb{S}_\nu^\gamma$ in formula (7) arises from the use of a wave function beyond a single Slater determinant. We must also highlight that according to formula (7) the $\langle\widehat{S}^2\rangle$ quantity is expressed by sums of terms of type $\left[\frac{1}{2}(^1D^{(s)}\mathbb{S})_\nu^\mu(^1D^{(s)}\mathbb{S})_\mu^\nu - \sum_{\lambda\gamma}\mathbb{S}_\lambda^\mu\Gamma_{\mu\gamma}^{\lambda\nu}\mathbb{S}_\nu^\gamma\right]$ and $\left[\frac{1}{4}(^1D^{(s)}\mathbb{S})_\mu^\mu(^1D^{(s)}\mathbb{S})_\nu^\nu -\right.$ $\frac{1}{2}\sum_{\lambda\gamma}\mathbb{S}_\lambda^\mu\Gamma_{\gamma\mu}^{\lambda\nu}\mathbb{S}_\nu^\gamma]$, which, as has been pointed out above, are S_z-independent.

The partitioning of the $\langle\widehat{S}^2\rangle$ quantity into one-center terms, $\langle\widehat{S}^2\rangle_A$, and two-center terms, $\langle\widehat{S}^2\rangle_{AB}$, is performed assigning the atomic orbitals $\mu, \nu, \ldots$ to the nuclei $A, B, \ldots$

$$\langle\widehat{S}^2\rangle = \sum_A\langle\widehat{S}^2\rangle_A + \sum_{A\neq B}\langle\widehat{S}^2\rangle_{AB} \tag{8}$$

The terms $\sum_{\mu,\nu}(^1D^{(s)}\mathbb{S})_\nu^\mu(^1D^{(s)}\mathbb{S})_\mu^\nu$ and $\sum_{\mu,\nu}(^1D^{(s)}\mathbb{S})_\mu^\mu(^1D^{(s)}\mathbb{S})_\nu^\nu$ in Eq. (7) stand for the exchange and direct terms of the spin density contributions respectively, leading to one-center and two-center spin populations according to the indices μ and ν are assigned to identical or different nucleus. However, as has been shown in Refs. [11,17–21], the cumulant terms $\sum_{\mu,\nu,\lambda,\gamma}\mathbb{S}_\lambda^\mu\Gamma_{\mu\gamma}^{\lambda\nu}\mathbb{S}_\nu^\gamma$ and $\sum_{\mu,\nu,\lambda,\gamma}\mathbb{S}_\lambda^\mu\Gamma_{\gamma\mu}^{\lambda\nu}\mathbb{S}_\nu^\gamma$ have a non-pairing nature and must be assigned to one-center contributions. Likewise, in agreement with our experience in determination of bond orders, which have been calculated using a similar methodology [11], we will choose the highest spin projection substate $S_z = S$ to evaluate the elements of the spin density matrix $^1D^{(s)}$ and those of the cumulant matrix. Hence, the one-center $\langle\widehat{S}^2\rangle_A$ and two-center $\langle\widehat{S}^2\rangle_{AB}$ contributions will be expressed as

$$\langle\widehat{S}^2\rangle_A = \frac{1}{2}\sum_{\mu\in A}\sum_{\nu\in A}\left[^1D^{(s)}(S_z=S)\mathbb{S}\right]_\nu^\mu\left[^1D^{(s)}(S_z=S)\mathbb{S}\right]_\mu^\nu$$
$$- \sum_{\mu\in A}\sum_{\nu,\lambda,\gamma}\mathbb{S}_\lambda^\mu\Gamma_{\mu\gamma}^{\lambda\nu}(S_z=S)\mathbb{S}_\nu^\gamma + \frac{1}{4}\sum_{\mu\in A}\sum_{\nu\in A}\left[^1D^{(s)}(S_z=S)\mathbb{S}\right]_\mu^\mu$$
$$\times \left[^1D^{(s)}(S_z=S)\mathbb{S}\right]_\nu^\nu - \frac{1}{2}\sum_{\mu\in A}\sum_{\nu,\lambda,\gamma}\mathbb{S}_\lambda^\mu\Gamma_{\gamma\mu}^{\lambda\nu}(S_z=S)\mathbb{S}_\nu^\gamma \tag{9}$$

and

$$\langle\widehat{S}^2\rangle_{AB} = \frac{1}{2}\sum_{\mu\in A}\sum_{\nu\in B}\left[^1D^{(s)}(S_z=S)\mathbb{S}\right]_\nu^\mu\left[^1D^{(s)}(S_z=S)\mathbb{S}\right]_\mu^\nu$$
$$+ \frac{1}{4}\sum_{\mu\in A}\sum_{\nu\in B}\left[^1D^{(s)}(S_z=S)\mathbb{S}\right]_\mu^\mu\left[^1D^{(s)}(S_z=S)\mathbb{S}\right]_\nu^\nu \tag{10}$$

In the next section we report results arising from formulas (9) and (10) for single Slater determinant and multideterminantal wave functions, in order to study the importance of these effects in view of the spin distribution.

3. Results and discussion

Table 1 reports the results of local spins of one- and two-centers, $\langle\widehat{S}^2\rangle_A$ and $\langle\widehat{S}^2\rangle_{AB}$ respectively, for several systems in the ground and excited states with spin symmetries singlet (H_2, HF, NH_3 and H_2O), doublet (NO, CH, CH_3 and H_2NO) and triplet (O_2, CH_2, C_2 and HBBH linear). The numerical calculations were performed at the experimental equilibrium geometries [22–24] at the restricted Hartree-Fock (RHF) level for closed shell systems and at the restricted open shell Hartree-Fock (ROHF) level for doublet and triplet ones. Besides, we accomplished numerical determinations for all those systems at the level of single and double excitation configuration interaction approximation (CISD), using as reference the RFH states (singlets) and ROHF ones (doublets and triplets). In all the cases the 6-31G basis sets were used. The spin-free first- and second-order reduced density matrices were obtained with the PSI3 package [25] whereas the spin density matrices were calculated for $S_z = S$, in the molecular basis set, by the modified formula reported in Refs. [26,27]

$$^1D_j^{(s)i}(S_z) = \frac{S_z}{S(S+1)}\left[\frac{(N+2)}{2}\,^1D_j^i - 2\sum_k(^2D_{jk}^{ik} + {}^2D_{kj}^{ik})\right] \tag{11}$$

and then transformed into the atomic basis set.

Table 1
Local spins of one- and two-centers ($\langle\widehat{S}^2\rangle_A$ and $\langle\widehat{S}^2\rangle_{AB}$) arising from RHF and ROHF single determinant wave functions, CISD correlated wave functions and their corresponding $\langle\widehat{S}^2\rangle_A^{canonical} = \langle S_z\rangle_A(\langle S_z\rangle_A + 1)$ results using the 6-31G basis sets.

System	State	Theory level			
		Atom [Bond]	Single determinant wave function		Correlated wave function	
			$\langle\widehat{S}^2\rangle_A$ $[\langle\widehat{S}^2\rangle_{AB}]$	$\langle\widehat{S}^2\rangle_A^{canonical}$	$\langle\widehat{S}^2\rangle_A$ $[\langle\widehat{S}^2\rangle_{AB}]$	$\langle\widehat{S}^2\rangle_A^{canonical}$
H_2	$^1\Sigma_g^+$	H	0.000	0.000	0.000	0.000
		[HH]	[0.000]	–	[0.000]	–
HF	$^1\Sigma^+$	F	0.000	0.000	0.000	0.000
		H	0.000	0.000	0.000	0.000
		[FH]	[0.000]	–	[0.000]	–
NH_3	$^1A_1$	N	0.000	0.000	0.000	0.000
		H	0.000	0.000	0.000	0.000
		[NH]	[0.000]	–	[0.000]	–
		[HH]	[0.000]	–	[0.000]	–
H_2O	$^1A_1$	O	0.000	0.000	0.000	0.000
		H	0.000	0.000	0.000	0.000
		[OH]	[0.000]	–	[0.000]	–
		[HH]	[0.000]	–	[0.000]	–
NO	$^2\Pi$	N	0.419	0.513	0.389	0.484
		O	0.048	0.142	0.069	0.164
		[NO]	[0.142]	–	[0.146]	–
CH	$^2\Pi$	C	0.750	0.750	0.810	0.809
		H	0.000	0.000	−0.027	−0.028
		[CH]	[0.000]	–	[−0.017]	–
CH_3	$^2A_2''$	C	0.750	0.750	0.990	0.982
		H	0.000	0.000	−0.034	−0.035
		[CH]	[0.000]	–	[−0.025]	–
		[HH]	[0.000]	–	[0.002]	–
H_2NO	$^2B_1$	N	0.033	0.116	0.068	0.172
		O	0.468	0.551	0.376	0.481
		H	0.000	0.000	−0.002	−0.002
		[NO]	[0.124]	–	[0.157]	–
		[NH]	[0.000]	–	[0.000]	–
		[OH]	[0.000]	–	[−0.001]	–
		[HH]	[0.000]	–	[0.000]	–
O_2	$^3\Sigma_g^-$	O	0.500	0.750	0.548	0.750
		[OO]	[0.500]	–	[0.452]	–
CH_2	$^3B_1$	C	1.944	1.958	2.325	2.329
		H	0.000	0.007	−0.052	−0.050
		[CH]	[0.014]	–	[−0.056]	–
		[HH]	[0.000]	–	[−0.003]	–
C_2	$^3\Sigma_g^+$	C	0.500	0.750	0.526	0.750
		[CC]	[0.500]	–	[0.474]	–
HBBH (linear)	$^3\Sigma_g^-$	B	0.500	0.750	0.463	0.696
		H	0.000	0.000	0.029	0.028
		[BB]	[0.500]	–	[0.457]	–
		[BH]	[0.000]	–	[0.012]	–
		[B...H]	[0.000]	–	[0.013]	–
		[HH]	[0.000]	–	[0.001]	–

Columns 5 and 7 in Table 1 describe expectation values of the canonical spin-squared population $\langle\widehat{S}^2\rangle_A^{canonical} = \langle S_z\rangle_A(\langle S_z\rangle_A + 1)$ corresponding to each atomic center A, which constitute a reference to be compared with those obtained from the direct partitioning of the $\langle\widehat{S}^2\rangle$ quantity [8]. Those $\langle S_z\rangle_A$ have been calculated through the spin density matrix elements corresponding to the highest value of the molecular spin projection $S_z = S$, that is

$$\langle\widehat{S}_z\rangle_A = \frac{1}{2}\sum_{\mu\in A}\left[^1D^{(s)}(S_z = S)\mathbb{S}\right]_\mu^\mu = \frac{1}{2}\left(N_A^\alpha - N_A^\beta\right) \quad (12)$$

where N_A^α and N_A^β stand for the atomic spin-up and spin-down populations on the atomic center A, respectively.

As can be observed in Table 1, zero value is obtained for all one-center and two-center contributions in singlet state systems, in both single determinant and correlated CISD wave functions. This behaviour, which has been predicted in Ref. [7] for closed shell single determinant wave functions, is now confirmed and extended to the multideterminantal correlated case. In fact, for singlet states all

the elements of the spin density matrix are zero and we have shown that the elements $\sum_k\left[\Gamma_{jk}^{ik}(S = 0) + \frac{1}{2}\Gamma_{kj}^{ik}(S = 0)\right]$ also turn out to be zero [28]. Consequently, the quantities $\langle\widehat{S}^2\rangle_A$ and $\langle\widehat{S}^2\rangle_{AB}$ in Eqs. (9) and (10) vanish for that spin symmetry. As expected, the results obtained in open shell systems present a quite different aspect, showing nonzero one- and two-center local spins. A survey of Table 1 shows that it is possible to detect the correlation effects on the local spin, which produces small differences between the values found for the quantities $\langle\widehat{S}^2\rangle_A$ at single determinant and correlated wave function approaches in doublet and triplet state systems. Likewise, slight differences can also be observed between the corresponding two-center contributions $\langle\widehat{S}^2\rangle_{AB}$ at both mentioned approaches in those open shell systems. Besides, the reported $\langle\widehat{S}^2\rangle_A$ values turn out to be consistent in general with the corresponding canonical ones obtained with the $\langle\widehat{S}_z\rangle_A$ parameters calculated through the spin density matrix decomposition of Eq. (12). These results confirm the conclusion reported in Ref. [8] which shows that this canonical decomposition leads to one-center contributions similar, but not identical, to those arising from the partitioning of the total expectation value $\langle\widehat{S}^2\rangle$. It is important to analyze the differences between the local spin populations $\langle\widehat{S}^2\rangle_A$ values arising from Eq. (9) and their corresponding canonical ones reported in Table 1. According to Eq. (9) the quantities $\langle\widehat{S}^2\rangle_A$ contain four components; two of them (the first and third terms of that equation) are functionals of the spin density while the second and fourth terms are related with the irreducible many-body effects [11]. Within the independent particle model the cumulant terms are zero and consequently the difference between the canonical spin and its local spin counterpart is

$$\langle\widehat{S}^2\rangle_A^{canonical} - \langle\widehat{S}^2\rangle_A = \frac{1}{2}\sum_{\mu\in A}\left[^1D^{(s)}(S_z = S)\mathbb{S}\right]_\mu^\mu - \frac{1}{2}\sum_{\mu\in A}$$
$$\times \sum_{\nu\in A}\left[^1D^{(s)}(S_z = S)\mathbb{S}\right]_\nu^\mu\left[^1D^{(s)}(S_z = S)\mathbb{S}\right]_\mu^\nu \quad (13)$$

Eq. (13) can be seen as a deviation from the idempotency of the part of the spin density matrix assigned to a determined center A and consequently as a degree of delocalization of the electron spin cloud corresponding to that center over the whole molecule. Therefore, the more localized electron spin cloud, the better numerical agreement between $\langle\widehat{S}^2\rangle_A^{canonical}$ and $\langle\widehat{S}^2\rangle_A$. In the correlated case, the cumulant terms in Eq. (9) contribute to a higher localization, due to their one-center nature. In fact, as can be observed in Table 1, the numerical value of the differences $\langle\widehat{S}^2\rangle_A^{canonical} - \langle\widehat{S}^2\rangle_A$ are lower for the correlated case than for the single determinant one. Finally, we must note that in certain systems (CH, CH_3, H_2NO and CH_2) some one-center local spin values and their counterpart canonical ones are slightly greater than the molecular spin value $S(S + 1)$ while others take small negative ones, compensating each other. Such spin excesses and deficits are in agreement with experimental results arising from electron spin resonance and may be interpreted in terms of spin polarization and spin delocalization mechanisms [29]. These effects do not appear in the independent particle model case.

4. Concluding remarks

In this Letter we have described a procedure to evaluate local spins which can be applied to any N-electron wave function, for closed or open shell systems. Our proposal, which generalizes previous treatments limited to single determinant wave function, is based on an appropriate management of the cumulant of the second-order reduced density matrix, whose elements are assigned to one-center contributions to the total expectation value $\langle\widehat{S}^2\rangle$. The numerical determinations of spin population analyses performed in the Hilbert space of atomic orbitals confirm the suitabil-

ity of our proposals. Likewise, the differences between the spin population values and the corresponding canonical ones have been interpreted as a degree of delocalization of the spin density in the systems. Our framework can also be applied to partitionings in the three-dimensional physical space, such as the atoms in molecules approach [30] or the fuzzy atoms one [31]. In this direction we are currently working in our laboratories.

Acknowledgements

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