



Descriptions of local spins in the three-dimensional physical space

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ABSTRACT

This report describes the partitioning of the expectation value of the spin-squared operator $\langle \hat{S}^2 \rangle$ corresponding to an N -electron system in the three-dimensional physical space, according to the Bader and fuzzy atom approaches. Numerical determinations performed in selected open-shell systems at Hartree-Fock and density functional theory levels confirm the reliability of the local spins obtained. A comparison between these results and their counterpart ones arising from the partitioning in the Hilbert space is analyzed in detail.

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1. Introduction

During the last decade there has been a considerable interest in studying the partitioning of the expectation value of the spin-squared operator $\langle \hat{S}^2 \rangle$ corresponding to an N -electron system. This interest comes from the ability of the local spins (the one- and two-center components resulting from the partitioning of the $\langle \hat{S}^2 \rangle$ quantity) to describe useful structural properties. The one-center local spins allow one to determine the spin state of an atom or group of atoms in a determined molecule while the two-center ones provide the description of magnetic interactions between the atoms which compose the system. Coupling constants can be calculated with the two-center local spins within the well-known Heisenberg Hamiltonian model. In early works [1–3] Clark and Davidson proposed to partition the value $\langle \hat{S}^2 \rangle$ by means of projection operators [4]; this technique and the results that produces have widely been analyzed and discussed in other reports [5,6]. An alternative approach has been proposed to perform the partitioning of the expectation value $\langle \hat{S}^2 \rangle$ by means of a direct procedure [7–9]. Within that approach the quantity $\langle \hat{S}^2 \rangle$ is expressed as a function depending on the elements of the first- and second-order reduced density matrices and those of the atomic overlap matrix. In subsequent steps those matrix elements are gathered according to the nature of the orbitals of the atomic basis set utilized. Technically, this procedure is similar to the well-known Mulliken-type population analysis where the partitioning of a determined property is carried out in the Hilbert space of the atomic basis set.

The main aim of this work is to complement this kind of studies extending the mentioned direct partitioning of the $\langle \hat{S}^2 \rangle$ quantity

in the Hilbert space to the three-dimensional physical space which, to our knowledge, has not yet been tackled. The analyses in the real space have been regarded as more realistic. Hence, it is of theoretical and practical interest to implement this kind of treatments and to know the reliability of the local spins evaluated in the real space to describe genuine chemical behaviors. Another reason to implement this study is to be able to compare results arising from both types of spaces because, as is well known, the Hilbert-space analyses are strongly dependent on the basis sets and they are not very suitable when diffuse functions are used. Two different procedures have been followed in this work for dividing the whole ordinary physical space into spatial domains associated with atoms; that corresponding to the Bader atoms-in-molecules (AIM) theory [10] and the technique of fuzzy atoms [11]. To simplify the mathematical treatment, in the present work we have limited our study to describe local spins in systems represented by one-determinant wave functions. We have mainly focused on open-shell chemical species at restricted open-shell Hartree-Fock (ROHF) level; a paradigmatic system described at unrestricted density functional theory level is also reported.

This Letter has been organized as follows. The second section describes the derivation of formulas which allow one to evaluate one- and two-center local spins in domains of the three-dimensional real space at the ROHF level. The procedure has been applied to the atomic regions of Bader AIM theory and to those defined in the fuzzy atom approach within a unified treatment. The third section reports the computational details and the results found for some selected open-shell systems as well as their corresponding discussion and comparison with those obtained from the analysis in the Hilbert space. A basis-set dependence study in these results is also included in this section. Finally, in the last section we summarize the concluding remarks and future perspectives of this work.

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2. The partitioning of $\langle \hat{S}^2 \rangle$ in the three-dimensional space

The elements of the first- and second-order reduced density matrices corresponding to an N -electron system described by a determined wave function Ψ will be denoted by ${}^1D_{j\sigma}^{i\sigma}$ and ${}^2D_{j\sigma\sigma'}^{i\sigma k\sigma'}$, respectively. In this notation i, j, k, l, \dots stand for the orbitals of an orthonormal basis set and σ and σ' are the spin coordinates ($\sigma, \sigma' = \alpha, \beta$). The relationship between those matrix elements can be formulated as [12]

$${}^2D_{j\sigma\sigma'}^{i\sigma k\sigma'} = \frac{1}{2} {}^1D_{j\sigma}^{i\sigma} {}^1D_{j\sigma'}^{k\sigma'} - \frac{1}{2} {}^1D_{j\sigma'}^{i\sigma} {}^1D_{j\sigma}^{k\sigma'} + \frac{1}{2} \Gamma_{j\sigma\sigma'}^{i\sigma k\sigma'} \quad (1)$$

where $\Gamma_{j\sigma\sigma'}^{i\sigma k\sigma'}$ are the elements of the cumulant matrix of the second-order reduced density matrix (its statistically irreducible part).

The expectation value of the spin-squared operator \hat{S}^2 , $\langle \hat{S}^2 \rangle = \langle \Psi | \hat{S}^2 | \Psi \rangle$, corresponding to the state Ψ , has been expressed as [8]

$$\langle \hat{S}^2 \rangle = \frac{1}{2} \sum_{ij} (P^s)_j^i (P^s)_i^j - \sum_{ij} \Gamma_{ij}^{ij} + \frac{1}{4} \sum_{ij} (P^s)_i^i (P^s)_j^j - \frac{1}{2} \sum_{ij} \Gamma_{ji}^{ij} \quad (2)$$

where $(P^s)_j^i$ are the elements of the spin density matrix, $(P^s)_j^i = {}^1D_{j\alpha}^{i\alpha} - {}^1D_{j\beta}^{i\beta}$, and $\Gamma_{ij}^{ik} = \sum_{\sigma, \sigma'} \Gamma_{j\sigma\sigma'}^{i\sigma k\sigma'}$.

In the case of wave functions of Slater determinant type all the matrix elements $\Gamma_{j\sigma\sigma'}^{i\sigma k\sigma'}$ are zero (see Eq. (1)) and consequently their sum Γ_{ij}^{ik} also does. Hence, Eq. (2) is transformed into

$$\langle \hat{S}^2 \rangle = \frac{1}{2} \sum_{ij} (P^s)_j^i (P^s)_i^j + \frac{1}{4} \sum_{ij} (P^s)_i^i (P^s)_j^j \quad (3)$$

or alternatively

$$\langle \hat{S}^2 \rangle = \frac{1}{2} \sum_{i,j,k,l} (P^s)_j^i (P^s)_l^k \delta_{il} \delta_{kj} + \frac{1}{4} \sum_{i,j,k,l} (P^s)_j^i (P^s)_l^k \delta_{ij} \delta_{kl} \quad (4)$$

in which the Kronecker deltas δ_{ij} , δ_{kl} , etc. have been introduced.

We will formulate the Kronecker deltas in a general way as [13,14]

$$\delta_{ij} = \langle ij | j \rangle = \sum_A S_j^i(A) \quad (5)$$

in which $\langle ij | j \rangle$ are the standard overlap integrals (where the integration is performed over the whole space) which are partitioned according to the $S_j^i(A)$ quantities related with the atomic domains of the centers A . These quantities can be formulated within the scheme of the Bader AIM theory [10]

$$S_j^i(A) = \langle ij | j \rangle_A \quad (6)$$

where $\langle ij | j \rangle_A$ are the overlap integrals over the Bader atomic domain associated with the nucleus A . Alternatively, the quantities $S_j^i(A)$ can also be formulated following the fuzzy atom approach [11] in which

$$S_j^i(A) = \langle i | w_A(\mathbf{r}) | j \rangle \quad (7)$$

where a non-negative continuous weight function $w_A(\mathbf{r})$ is introduced for each nucleus A . The weight functions provide a measure of the degree in which a determined point of the space \mathbf{r} is considered to belong to atom A . The weights $w_A(\mathbf{r})$ fulfill the conditions

$$w_A(\mathbf{r}) \geq 0 \quad (8)$$

and

$$\sum_A w_A(\mathbf{r}) = 1 \quad (9)$$

The introduction of the Kronecker deltas in Eq. (4) according to Eq. (5) allows one to express the $\langle \hat{S}^2 \rangle$ quantity as a sum of one-center $\langle \hat{S}^2 \rangle_A$ and two-center terms $\langle \hat{S}^2 \rangle_{AB}$

$$\langle \hat{S}^2 \rangle = \sum_A \langle \hat{S}^2 \rangle_A + \sum_{A \neq B} \langle \hat{S}^2 \rangle_{AB} \quad (10)$$

where

$$\langle \hat{S}^2 \rangle_A = \frac{1}{2} \sum_{i,j,k,l} (P^s)_j^i (P^s)_l^k \left[S_i^j(A) S_j^k(A) + \frac{1}{2} S_j^i(A) S_l^k(A) \right] \quad (11)$$

and

$$\langle \hat{S}^2 \rangle_{AB} = \frac{1}{2} \sum_{i,j,k,l} (P^s)_j^i (P^s)_l^k \left[S_i^j(A) S_j^k(B) + \frac{1}{2} S_j^i(A) S_l^k(B) \right] \quad (12)$$

Eqs. (11) and (12) constitute a unified treatment of the three-dimensional partitionings of the expectation value $\langle \hat{S}^2 \rangle$ given by formula (3), which reproduces the AIM and fuzzy atom approaches formulating the $S_j^i(A)$ matrix elements by means of Eqs. (6) and (7), respectively. They are counterpart of those reported in Ref. [7] where the partitioning in the Hilbert space was proposed and are valid for any one-determinant wave function. These formulas adopt their simplest expressions in the case of ROHF wave functions described by a high-spin Slater determinant $S_z = S$; if we use the Hartree-Fock basis set all the elements $(P^s)_j^i$ are zero except the diagonal elements corresponding to the singly occupied (s occ) orbitals whose value is the unity. Hence, those formulas are transformed into

$$\langle \hat{S}^2 \rangle_A = \frac{1}{2} \sum_i^{s \text{ occ}} \sum_k^{s \text{ occ}} \left[S_k^i(A) S_i^k(A) + \frac{1}{2} S_i^i(A) S_k^k(A) \right] \quad (13)$$

and

$$\langle \hat{S}^2 \rangle_{AB} = \frac{1}{2} \sum_i^{s \text{ occ}} \sum_k^{s \text{ occ}} \left[S_k^i(A) S_i^k(B) + \frac{1}{2} S_i^i(A) S_k^k(B) \right] \quad (14)$$

Formulas (13) and (14) constitute the one-center and two-center components of the partitioning of the $\langle \hat{S}^2 \rangle$ quantity at the ROHF level of theory in the three-dimensional space. In this Letter we mainly regard this simplest case although some calculations at unrestricted level have also been tackled.

3. Numerical determinations and discussion

We have gathered in Table 1 the numerical results of local spins of one- and two-centers (the quantities $\langle \hat{S}^2 \rangle_A$ and $\langle \hat{S}^2 \rangle_{AB}$, respectively) for several systems in the ground state with doublet and triplet spin symmetries (except the $C_2(^3\Sigma_g^+)$ system which is an excited state). These numerical calculations were performed at the experimental equilibrium geometries [15–17] at the ROHF level using the 6-31G basis sets. The overlap integrals $S_j^i(A)$ calculated over the domains of the AIM theory were evaluated with the GAUSSIAN code [18] except for the C_2 molecule in which those integrals were calculated with the PSI 3.3 [19] and PROAIM [20] packages. The integrals $\langle i | w_A(\mathbf{r}) | j \rangle$ (see formula (7)) were obtained with a modified version of the code cited in Ref. [21], which follows a Becke integration scheme [22] based on the weight function $w_A(\mathbf{r})$ proposed by this author. The atomic radii used for determining the $w_A(\mathbf{r})$ weights were those employed in previous works [13,14,23].

Columns 3 and 5 in Table 1 describe the results arising from the partitioning of the quantity $\langle \hat{S}^2 \rangle$ in the three-dimensional space by means of the AIM and fuzzy atom approaches, respectively. Moreover, in order to provide a suitable comparison between these results and those obtained from other procedures, we have also included (in column 7) the results arising from a partitioning performed in the Hilbert space defined by the atomic orbitals reported in Ref. [8], which are Mulliken-type population analysis results. In all the cases (see columns 4, 6 and 8) we report expectation values

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

System	Atom [Bond]	AIM		Fuzzy		Hilbert space	
		$\langle \hat{S}^2 \rangle_A$ [$\langle \hat{S}^2 \rangle_{AB}$]	$\langle \hat{S}^2 \rangle_A^c$	$\langle \hat{S}^2 \rangle_A$ [$\langle \hat{S}^2 \rangle_{AB}$]	$\langle \hat{S}^2 \rangle_A^c$	$\langle \hat{S}^2 \rangle_A$ [$\langle \hat{S}^2 \rangle_{AB}$]	$\langle \hat{S}^2 \rangle_A^c$
NO($^2\Pi$)	N	0.386	0.488	0.379	0.482	0.419	0.513
	O	0.060	0.161	0.063	0.165	0.048	0.142
	[NO]	[0.152]	-	[0.154]	-	[0.142]	-
CH($^2\Pi$)	C	0.709	0.723	0.702	0.718	0.750	0.750
	H	0.001	0.014	0.001	0.016	0.000	0.000
	[CH]	[0.020]	-	[0.024]	-	[0.000]	-
CH ₃ ($^2A_2''$)	C	0.628	0.667	0.594	0.643	0.750	0.750
	H	0.001	0.014	0.001	0.019	0.000	0.000
	[CH]	[0.019]	-	[0.025]	-	[0.000]	-
	[HH]	[0.001]	-	[0.001]	-	[0.000]	-
H ₂ NO(2B_1)	N	0.040	0.129	0.039	0.127	0.033	0.116
	O	0.435	0.526	0.421	0.515	0.468	0.551
	H	0.000	0.002	0.000	0.006	0.000	0.000
	[NO]	[0.132]	-	[0.128]	-	[0.124]	-
	[NH]	[0.001]	-	[0.002]	-	[0.000]	-
	[OH]	[0.002]	-	[0.006]	-	[0.000]	-
	[HH]	[0.000]	-	[0.000]	-	[0.000]	-
	[XH]	[0.008]	-	[0.000]	-	[0.000]	-
O ₂ ($^3\Sigma_g^-$)	O	0.500	0.750	0.500	0.750	0.500	0.750
	[OO]	[0.500]	-	[0.500]	-	[0.500]	-
CH ₂ (3B_1)	C	1.737	1.800	1.680	1.756	1.944	1.958
	H	0.002	0.035	0.004	0.044	0.000	0.007
	[CH]	[0.063]	-	[0.076]	-	[0.014]	-
	[HH]	[0.002]	-	[0.004]	-	[0.000]	-
C ₂ ($^3\Sigma_g^+$)	C	0.500	0.749	0.500	0.750	0.500	0.750
	[CC]	[0.499]	-	[0.500]	-	[0.500]	-
HBBH($^3\Sigma_g^-$)	B	0.280	0.514	0.478	0.727	0.500	0.750
	H	0.006	0.056	0.000	0.011	0.000	0.000
	X	0.011	0.078	-	-	-	-
	[BB]	[0.280]	-	[0.478]	-	[0.500]	-
	[BH]	[0.040]	-	[0.011]	-	[0.000]	-
	[B··H]	[0.040]	-	[0.011]	-	[0.000]	-
	[HH]	[0.006]	-	[0.000]	-	[0.000]	-
	[BX]	[0.054]	-	-	-	-	-
	[B··X]	[0.054]	-	-	-	-	-
	[XX]	[0.011]	-	-	-	-	-
	[XH]	[0.008]	-	-	-	-	-
[X··H]	[0.008]	-	-	-	-	-	

of the canonical spin-squared population $\langle \hat{S}^2 \rangle_A^c = \langle \hat{S}_z \rangle_A (\langle \hat{S}_z \rangle_A + 1)$ corresponding to each atomic center A which are reference values [24]. Those $\langle \hat{S}_z \rangle_A$ values have been calculated, in the cases of partitioning in the three-dimensional space, as

$$\langle \hat{S}_z \rangle_A = \frac{1}{2} \sum_i \sum_j (P^s)_j^i S_i(A) \quad (15)$$

which arises from the partitioning of the trace of the spin density matrix according to the procedure described in the previous section.

A survey of the results reported in Table 1 shows that the two partitionings performed in the three-dimensional space present similar values of the one-center quantities $\langle \hat{S}^2 \rangle_A$, although the AIM approach leads to slightly higher values than the fuzzy atom procedure, except in the HBBH($^3\Sigma_g^-$) molecule. Likewise, in the systems studied the one-center values obtained from the partitioning in the Hilbert space turn out to be a little bit higher than those found in the three-dimensional spaces at least in the centers where the presence of unpaired electrons is expected (see e.g. the values for the oxygen atom $\langle \hat{S}^2 \rangle_O$, in the H₂NO(2B_1) system). Moreover, the results show that in all the situations the values found for the one-center quantities $\langle \hat{S}^2 \rangle_A$ are lower than their corresponding canonical ones $\langle \hat{S}^2 \rangle_A^c$ which agrees with our previous results

[8]. These differences $\langle \hat{S}^2 \rangle_A^c - \langle \hat{S}^2 \rangle_A$ have been interpreted as the diminishing of the spin excess on the active centers due to spin delocalization among the whole molecule [8,24]. In relation with the two-center quantities $\langle \hat{S}^2 \rangle_{AB}$ the three partitionings lead to very similar values, although a greater diffusion of the spin cloud can be detected in the three-dimensional space partitionings. Again, the system HBBH($^3\Sigma_g^-$) presents a peculiar behavior regarding the low value found for the $\langle \hat{S}^2 \rangle_{BB}$ quantity in the AIM procedure when compared with its counterpart values found in the fuzzy and Hilbert space partitionings. The anomalous values found for the local spins $\langle \hat{S}^2 \rangle_A$ and $\langle \hat{S}^2 \rangle_{AB}$ in the HBBH($^3\Sigma_g^-$) system in the AIM approach must be interpreted in terms of non-nuclear attractors or pseudoatoms which are local maxima of electron density out of nuclear positions [10,25–27]. In fact, we have detected in our calculations the presence of two non-nuclear attractors symmetrically situated between the two boron atoms, which have been denoted as X in Table 1. The existence of these non-nuclear attractors increases the diffusion of the spin populations leading to lower values for the quantities $\langle \hat{S}^2 \rangle_B$ and $\langle \hat{S}^2 \rangle_{BB}$. As can be seen in the Table, the fuzzy atom approach in which these devices do not appear produces values of $\langle \hat{S}^2 \rangle_B$ and $\langle \hat{S}^2 \rangle_{BB}$ closer to those found in the Hilbert space partitioning.

The basis-set dependence of the local spin values obtained from this methodology has been studied in the NO molecule. We have chosen that system because the incomplete localization of its unpaired electron is well established in the genuine chemical knowledge of this molecule [1,24]. The results, calculated with several basis sets at the experimental geometry, have been gathered in Table 2. As can be seen in that Table the shortest basis set, that STO-3G, produces the most dispersed values. It leads to lower $\langle \hat{S}^2 \rangle_N$ values than the other sets while the $\langle \hat{S}^2 \rangle_O$ values are higher in that mentioned set. Likewise, the two-center values $\langle \hat{S}^2 \rangle_{NO}$ are also higher. For the rest of the basis sets, again local spin values arising from both three-dimensional space partitionings are very close. As expected, the major differences between the numerical values from the different basis sets are found in the Hilbert space partitioning which agrees with the behavior observed in the classic population analyses performed over other quantities as the electronic density, the energy, etc. These results also show that the use of extended basis sets as the 6-31+G (d) does not change significantly the values of local spins in the three-dimensional space partitionings.

In Table 3 we report results of local spins for the fragment Mn_2O_2 within the coordination complex $Mn_2O_2(NH_3)_8$, which is a prototype of multicenter transition metal molecule in which anti-ferromagnetic coupling is of interest. To avoid too high computational expenses we have limited the description of this system to the fuzzy and Hilbert space schemes. In this molecule the calculations have been made at the level of density functional theory (DFT) by means of the UB3LYP functional with the 3-21G basis set, using the above mentioned codes. We describe two states of this molecule; the antiferromagnetically coupled (broken-symmetry) state with $S_z = 0$ ($\langle \hat{S}^2 \rangle = 4.965$), which corresponds to 5 α d electrons on one Mn atom and 5 β d electrons on the other one, and the high spin or ferromagnetically coupled state with 5 α d electrons localized on each Mn atom ($S_z = 5$; $\langle \hat{S}^2 \rangle = 30.075$).

Table 2

Results of local spins of one- and two-centers ($\langle \hat{S}^2 \rangle_A$ and $\langle \hat{S}^2 \rangle_{AB}$) arising from ROHF single determinant wave functions and their corresponding $\langle \hat{S}^2 \rangle_A^c = \langle \hat{S}_z \rangle_A (\langle \hat{S}_z \rangle_A + 1)$ in the NO molecule, using several basis sets.

Basis set	Atom [Bond]	AIM		Fuzzy		Hilbert space	
		$\langle \hat{S}^2 \rangle_A$	$\langle \hat{S}^2 \rangle_A^c$	$\langle \hat{S}^2 \rangle_A$	$\langle \hat{S}^2 \rangle_A^c$	$\langle \hat{S}^2 \rangle_A$	$\langle \hat{S}^2 \rangle_A^c$
		$[\langle \hat{S}^2 \rangle_{AB}]$		$[\langle \hat{S}^2 \rangle_{AB}]$		$[\langle \hat{S}^2 \rangle_{AB}]$	
STO-3G	N	0.324	0.436	0.327	0.439	0.342	0.452
	O	0.088	0.201	0.087	0.200	0.079	0.189
	[NO]	[0.169]	–	[0.168]	–	[0.164]	–
3-21G	N	0.371	0.476	0.365	0.471	0.395	0.494
	O	0.066	0.170	0.068	0.174	0.057	0.156
	[NO]	[0.156]	–	[0.158]	–	[0.149]	–
6-31G	N	0.386	0.488	0.379	0.482	0.419	0.513
	O	0.060	0.161	0.063	0.165	0.048	0.142
	[NO]	[0.151]	–	[0.154]	–	[0.142]	–
D95V	N	0.382	0.484	0.375	0.479	0.418	0.513
	O	0.062	0.164	0.064	0.168	0.048	0.143
	[NO]	[0.153]	–	[0.155]	–	[0.142]	–
cc-pVDZ	N	0.376	0.480	0.372	0.477	0.411	0.507
	O	0.064	0.167	0.065	0.169	0.051	0.147
	[NO]	[0.155]	–	[0.156]	–	[0.144]	–
6-31G (d)	N	0.380	0.482	0.377	0.480	0.416	0.511
	O	0.062	0.165	0.064	0.167	0.049	0.144
	[NO]	[0.154]	–	[0.154]	–	[0.143]	–
D95V (d)	N	0.378	0.481	0.377	0.480	0.420	0.514
	O	0.063	0.166	0.064	0.167	0.047	0.141
	[NO]	[0.154]	–	[0.155]	–	[0.141]	–
6-31+G (d)	N	0.381	0.484	0.380	0.481	0.427	0.520
	O	0.062	0.164	0.063	0.166	0.045	0.138
	[NO]	[0.153]	–	[0.154]	–	[0.139]	–

Table 3

Local spin results for the fragment Mn_2O_2 within the compound $Mn_2O_2(NH_3)_8$ arising from wave functions at DFT level (UB3LYP functional) with basis set 3-21G.

State	Atom [Bond]	Fuzzy		Hilbert space	
		$\langle \hat{S}^2 \rangle_A$	$\langle \hat{S}^2 \rangle_A^c$	$\langle \hat{S}^2 \rangle_A$	$\langle \hat{S}^2 \rangle_A^c$
		$[\langle \hat{S}^2 \rangle_{AB}]$		$[\langle \hat{S}^2 \rangle_{AB}]$	
$S_z = 0$ $\langle \hat{S}^2 \rangle = 4.965$	Mn	5.492	5.707	6.079	5.831
	O	0.008	0.000	0.012	0.000
	[MnO]	[0.034]	–	[0.034]	–
	[MnMn]	[–3.739]	–	[–3.947]	–
	[OO]	[0.001]	–	[0.002]	–
$S_z = 5$ $\langle \hat{S}^2 \rangle = 30.075$	Mn	5.603	5.814	7.576	8.314
	O	0.004	0.012	0.006	0.013
	[MnO]	[0.055]	–	[0.001]	–
	[MnMn]	[3.879]	–	[6.388]	–
	[OO]	[0.006]	–	[0.007]	–

For all the calculations the used geometry was that optimized with the high spin state within the D_{2h} symmetry. The numerical values reported in that Table indicate that the state $S_z = 0$ presents a similar behavior to that found in the simpler molecules described in Table 1, i.e. the values $\langle \hat{S}^2 \rangle_{Mn}$ and $\langle \hat{S}^2 \rangle_{MnMn}$ are a little lower (in absolute value) in the fuzzy atom procedure. This behavior is confirmed in the values found in high spin state, particularly for the $\langle \hat{S}^2 \rangle_{MnMn}$ quantity, which is considerably higher in the Hilbert space treatment. In both broken-symmetry and high spin states, the canonical values are closer to their corresponding $\langle \hat{S}^2 \rangle_{Mn}$ in the fuzzy atom approach which may be interpreted as a better estimation of the spin localization in that approach than in the Hilbert space treatment. It can also be pointed out that both Hilbert space and fuzzy atom approaches identify through the sign of the $\langle \hat{S}^2 \rangle_{MnMn}$ quantity the broken-symmetry state. The comparison between the results found for both states shows higher values

for the high spin state which is reasonable in a chemical point of view. It may also be noted high delocalization of spin density towards the NH_3 ligands mainly in that $S_z = 5$ state.

4. Concluding remarks and perspectives

In this report we have proposed the evaluation of local spins by means of partitionings in the three-dimensional space of the expectation value $\langle \hat{S}^2 \rangle$ corresponding to an N -electron system described by a single determinant wave function. Two approaches have been utilized, that derived from the use of spatial domains of the AIM theory and that arisen from the fuzzy atom method. Both procedures have been formulated within a unique mathematical framework, which turns out to be very useful for computational purposes. The results show the reliability of the three-dimensional partitioning for detecting local spins in good agreement with the genuine chemical knowledge and with the partitioning in the Hilbert space. No significant differences have been found in the results obtained from the two three-dimensional partitionings although the presence of non-nuclear attractors in the AIM theory hampers the interpretation of results in this method. The study on the basis-set dependence performed in the NO molecule reveals a slight lower dependence of the results arising from the three-dimensional space compared with those from the Hilbert space, at least for medium size basis sets. The next challenge is to go beyond the single determinant case, extending these treatments in the real space to a general wave function. This task is currently being carried out in our laboratories.

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