Local spins: improved Hilbert-space analysis

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Abstract

The decomposition of the expectation value of the spin squared operator for a general wave function has been carried out in the framework of the Hilbert-space analysis. The one and two-center components fulfill all physical requirements imposed to date. An inherent ambiguity of the Hilbert-space decomposition of a two-electron quantity is also discussed in detail. The formalism of effective atomic densities has allowed us to derive in a simple manner appropriate expressions for the decomposition of $\langle \hat{S}^2 \rangle$ in the framework of Hilbert space analysis that are consistent with Mulliken Population Analysis and related quantities.

1 Introduction

The concept of local spin emerges in a quite natural fashion when describing the electronic structure of systems with diradical character such as Non-Kekulé molecules or transition state structures of chemical reactions. Heisenberg Hamiltonian models also invoke the concept of local spin in order to assess the nature of spin-spin interactions between magnetic centers of magnetic systems. Often, the spin properties of a molecule can be characterized by the spin density. There are, however, cases where the overall system is a singlet (where there is no spin density), but for which the existence of some local spin is assumed. In the last years there has been a growing interest in recovering local spins from the analysis of the wavefunction of ab initio calculations.[1–15] Different schemes have been proposed in the literature, most of which are rooted on the decomposition of the expectation value of the spin squared operator into atomic and diatomic contributions, for both single determinant and correlated wave functions. Because the partitioning of the single physical quantity $\langle \hat{S}^2 \rangle$, which in the case of singlet wavefunctions is *zero*, into components is not unique, a number of physical requirements[4,9,15] have been introduced:

(i) one should get no spins whatever for the covalent systems described by a closed shell RHF wave function using doubly filled orbitals,

(ii) if the wave function is properly dissociating, then the asymptotic values of the atomic spins obtained for the atoms at large distances should coincide with the corresponding values of the free atoms,

(iii) in an open-shell system the overall $\langle \hat{S}^2 \rangle$ does not depend on the actual $\hat{S}_z$ projection of the electronic state (multiplet) considered, so one may request to have $\langle \hat{S}^2 \rangle$ components that do not depend on $\hat{S}_z$ either,

(iv) no two-center terms should appear in the case of single-electron systems (or ROHF systems with a single unpaired electron).

In a previous paper[15] we showed that the following general expression

$$
\begin{aligned}
\langle \hat{S}^2 \rangle &= a \int u(\vec{r}_1) d\vec{r}_1 - (1-2a) \iint \left[\Gamma(\vec{r}_1, \vec{r}_2) - \tfrac{1}{2}\rho^s(\vec{r}_1;\vec{r}_2)\rho^s(\vec{r}_2;\vec{r}_1) \right] d\vec{r}_1 d\vec{r}_2 \\
&\quad - \frac{1}{2} \iint \left[\Gamma(\vec{r}_1, \vec{r}_2; \vec{r}_2, \vec{r}_1) - \tfrac{1}{2}\rho^s(\vec{r}_1;\vec{r}_1)\rho^s(\vec{r}_2;\vec{r}_2) \right] d\vec{r}_1 d\vec{r}_2 \qquad (1)
\end{aligned}
$$

is the natural starting point to derive atomic and diatomic components of $\langle \hat{S}^2 \rangle$, where a is a parameter that defines a family of different decompositions that all satisfy requirements (i) to (iii). This equation is written in terms of the density of effectively unpaired electrons, $u(\vec{r})$, defined by Takatsuka[16] as

$$
u(\vec{r}) = 2\rho(\vec{r}) - \int \rho(\vec{r};\vec{r}')\rho(\vec{r}';\vec{r}) d\vec{r}', \qquad (2)
$$

the spin-density matrix,

$$
\rho^s(\vec{r};\vec{r}') = \rho^\alpha(\vec{r};\vec{r}') - \rho^\beta(\vec{r};\vec{r}'), \qquad (3)
$$

and the spin-less cumulant of the second order density matrix, $\Gamma(\vec{r}_1, \vec{r}_2; \vec{r}'_1, \vec{r}'_2)$, which vanishes for single-determinant wave functions and can be defined as the

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sum of the usual (spin-dependent) cumulants as

$$\Gamma(\vec{r}_1,\vec{r}_2;\vec{r}_1',\vec{r}_2') = \sum_{\sigma,\sigma'} \Gamma^{\sigma\sigma'\sigma\sigma'}(\vec{r}_1,\vec{r}_2;\vec{r}_1',\vec{r}_2') \tag{4}$$

where

$$\Gamma^{\sigma\sigma'\sigma\sigma'}(\vec{r}_1,\vec{r}_2;\vec{r}_1',\vec{r}_2') = \rho_2^{\sigma\sigma'\sigma\sigma'}(\vec{r}_1,\vec{r}_2;\vec{r}_1',\vec{r}_2') - \tag{5}$$
$$\rho^\sigma(\vec{r}_1,\vec{r}_1{}')\rho^{\sigma'}(\vec{r}_2,\vec{r}_2') - \delta_{\sigma\sigma'}[\rho^\sigma(\vec{r}_1,\vec{r}_2')\rho^\sigma(\vec{r}_2,\vec{r}_1')].$$

In order to find the proper value of parameter a we introduced requirement (iv), based upon the behaviour of single-electron systems.[15] In this limiting case, the density of distribution of the $\langle \hat{S}^2 \rangle$ for a single electron must be $3/4$ times the electron density, $\langle \hat{S}^2 \rangle = \frac{3}{4} \int \rho(\vec{r})d\vec{r}$. For single-electron systems, or for restricted open-shell descriptions with a single unpaired electron (in that case $\rho(\vec{r})$ corresponds to that of the singly occupied molecular orbital) this requirement is fulfilled *if and only if* one chooses $a = 3/4$.[15]

Consequently, the starting general equation to tackle a proper decomposition of $\langle \hat{S}^2 \rangle$ is the following:

$$\langle \hat{S}^2 \rangle = \frac{3}{4} \int u(\vec{r}_1)d\vec{r}_1 + \frac{1}{2} \iint \left[\Gamma(\vec{r}_1,\vec{r}_2) - \tfrac{1}{2}\rho^s(\vec{r}_1;\vec{r}_2)\rho^s(\vec{r}_2;\vec{r}_1) \right] d\vec{r}_1 d\vec{r}_2$$
$$- \frac{1}{2} \int \int \left[\Gamma(\vec{r}_1,\vec{r}_2;\vec{r}_2,\vec{r}_1) - \tfrac{1}{2}\rho^s(\vec{r}_1;\vec{r}_1)\rho^s(\vec{r}_2;\vec{r}_2) \right] d\vec{r}_1 d\vec{r}_2. \tag{6}$$

In Ref. 15 we obtained one and two-center contributions for a general wave function in the framework of the 3D-space analysis, *i.e.,* for "fuzzy atoms"[17] and

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Bader's atomic domains.[18] In this paper we wish to undertake the decomposition in the context of the so-called "Hilbert-space analysis".[19] The motivation is twofold: first, aside its conceptual relevance, the Hilbert-space decomposition does not require atomic numerical integrations, contrary to the 3D-space analysis; thus it is exact (is free of the numerical errors of that integration). Also, the significant reduction in the computational cost of the decomposition may be relevant for very large systems, especially as compared to 3D-space methods with complicated atomic basins of Bader's analysis. However, there is an apparent ambiguity in decomposing two-electron quantities in the framework of Hilbert-space analysis, which to date has not received due attention. In this paper we also wish to analyze in more detail this problem, which is particularly relevant in the case of the decomposition of $\langle \hat{S}^2 \rangle$. That ambiguity will be exposed in the next section. Then, we will briefly describe the formalism of effective atomic densities,[20] which will allow us to derive in a straightforward manner the most appropriate expressions for the decomposition of $\langle \hat{S}^2 \rangle$ in the framework of Hilbert space analysis. Finally, some numerical results at correlated level will be presented and discussed.

2   Alternative summation schemes in the Hilbert-space analysis

The decomposition of physical quantities into atomic and diatomic contributions is rooted on the identification of an atom within the molecule. Since practical quantum chemistry mostly uses atom-centered basis sets, the atom may be identi-

fied with its nucleus and the subspace spawned by the set of atomic basis functions centered on it. The simplest example of application of such Hilbert-space analysis is Mulliken population analysis,[21] perhaps the most familiar method to determine the number of electrons associated with an atom. Mulliken's gross population of atom A is defined as:

$$N_A = \sum_{\mu \in A} \sum_{\nu} D_{\mu\nu} S_{\nu\mu} = \sum_{\mu \in A} (\mathbf{DS})_{\mu\mu}, \tag{7}$$

where the notation $\mu \in A$ indicates that the summation runs over all atomic basis functions centered on atom A. We recall in this context that matrix $\mathbf{DS}$ is the proper finite basis representation of the first-order density matrix if an overlapping basis set ($\mathbf{S} \neq \mathbf{I}$) is used.[22]

In a similar manner, the Mayer-Wiberg (closed-shell for simplicity) bond order,[23] B_{AB}, between atoms A and B is defined as

$$B_{AB} = \sum_{\mu \in A} \sum_{\sigma \in B} (\mathbf{DS})_{\mu\sigma} (\mathbf{DS})_{\sigma\mu}. \tag{8}$$

Inspecting the expression on Eq. (7), one can see that the overlap integrals enter it in a somewhat non-symmetric manner: one of subscript (μ) is serving for subdividing the quantity into atomic contributions, while another (ν) is a "dummy" index, for which summation over the whole basis is performed—it is used to form the matrix-product $\mathbf{DS}$. This difference may be connected with the fact that for overlapping basis sets matrix $\mathbf{DS}$ is twice the projection matrix performing the projection of any vector $\mathbf{d}$ of LCAO coefficients on the subspace

of the occupied molecular orbitals as **DSd**.[22] The same distinction appears also in Eq. (8) of the Mayer-Wiberg bond order. In the case of real orbitals, one could get exactly the same Mulliken atomic populations also in the form $\sum_{\mu \in A}(\mathbf{SD})_{\mu\mu}$, *i.e.,* by using matrix **SD** which performs the analogous projection of the *row-vectors* $\mathbf{d}^{\dagger}$ as $\mathbf{d}^{\dagger}\mathbf{SD}$. While in the first case the systematization of the terms according to the individual atoms corresponds to the subscript coming form the "ket" part of the overlap integral, in the second one it corresponds to the subscript coming from its "bra" part. It seems logical to stick to one of these possibilities (we prefer the first one), and use it in all types of analyses. Thus the splitting of the terms in the expression of the bond order index Eq. (8) corresponds to the subscripts of the overlap integrals coming from the "kets".

In principle, if an expression contains products with two overlap matrices, then a subdivision into atomic and diatomic contributions by taking one subscript from "bra" and another from "ket" is also possible. In the case of the bond order, that leads to a modified definition of the bond order index[24] as

$$B'_{AB} = \sum_{\mu \in A} \sum_{\nu \in B} (\mathbf{SDS})_{\mu\nu} D_{\nu\mu} \tag{9}$$

As the bond order is a component of the integral of the exchange density, formally both definitions could be acceptable: they represent different decompositions of that integral into a sum of one- and two-center contributions. However, there is a serious argument, favoring the definition of Eq. (8). The modified definition Eq. (9) gives results that are much less "chemical" than those given by the origi-

nal one: it cannot, for instance, recover the integer values for first-row diatomics (e.g., 3 for N_2) if a minimal basis set is used, as does the original definition of Eq. (8). Another argument again such type of "bra"-"ket" mixing is the high degree or arbitrariness that would be introduced in the case of e.g. Generalized Population Analysis,[25] typically used to detect patters of multicenter bonding, where the expressions may contain three, four or more overlap matrices. Furthermore, it has been shown[26] that one can introduce a particular mapping between the atomic overlap matrices of the atomic orbitals and the conventional overlap matrix, that permits to find a one-to-one correspondence between the Hilbert-space and the more general 3D-space analyses expressions of quantities like bond orders, atomic valences or energy components. Such a general mapping is not possible for expressions involving subdivision of the terms according to both "bra" and"ket" subscripts.

These considerations are of interest in the present context because in the recent paper by Alcoba et $al.$[9] a decomposition of $\langle \hat{S}^2 \rangle$ is performed in a manner that one index of the overlap matrix is assigned according to the term coming from the "bra" and another coming from the "ket". (These authors distinguish between them by using both subscripts and superscripts, which, however, do not represent covariant and contravariant indices.) Therefore, their decomposition is consistent only with the use of the alternative bond order formula Eq. (9). It has recently been discovered that this type of decomposition has also been used by some of us[7] as a results of a programming error: two subscripts have been interchanged by a mistake in the treatments of the cumulants. Coincidentally, with

the original treatment of the subscripts of the formulas of Ref. 7 one would get completely unphysical values for the $\langle \hat{S}^2 \rangle$. In fact, experience has shown that this type of "interchanged" subscripts gives results much less sensitive to the choice of parameter a. (The value $a = 1/2$ was used in Ref. 9, while the formulae in Ref. 7 corresponded to $a = 3/8$.) We will see here that no such problems occur in general for the case of the preferable value of $a = 3/4$.

3 Effective atomic density matrices formalism

The formalism of the atomic and diatomic effective densities, first introduced in Ref. 20, is based on the *exact* decomposition of one- and two-electron densities into components that can be considered their one-center and one- and two-center contributions, respectively. These atomic and diatomic densities are identified with the contributions of each atom and pairs of atoms to the overall density, and can be used to derive in a common framework atomic populations, bond orders, atomic valences, molecular energy components, *etc.* for any kind of *atom in molecule* definition. In the simplest case, one can define the effective atomic contributions to the electron density, $\rho_A(\vec{r})$, simply fulfilling $\rho(\vec{r}) \equiv \sum_A^N \rho_A(\vec{r})$. The integral over the whole space of this function for atom A quite naturally yields the electron population associated to the atom

$$\int \rho_A(\vec{r}) d\vec{r} = N_A. \tag{10}$$

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The actual numerical value depends upon how $\rho_A(\vec{r})$ is defined. In the framework of 3D-space analysis, $\rho_A(\vec{r})$ can be written in general as

$$\rho_A(\vec{r}) = w_A(\vec{r})\rho(\vec{r}) \qquad (11)$$

where w_A is a non-negative weight function defined for each atom and each point of the 3D space satisfying $\sum_A w_A(\vec{r}) = 1$. The actual definition of *atom in the molecule* ("fuzzy" or disjoint) is contained in the atomic weight functions.

In the case of Hilbert-space analysis, the effective atomic density can be most suitable written in terms of the matrix elements of the LCAO density matrix as

$$\rho_A(\vec{r}) = \sum_{\mu \in A} \sum_{v} D_{\mu v} \chi_v^*(\vec{r}) \chi_\mu(\vec{r}) \qquad (12)$$

It is trivial to see that the integration of Eqn.(12) yields Mulliken's gross population of atom A, in accord with Eq.(7).

In a similar manner, by combining the appropriate effective atomic contributions of the first-order density matrix to build effective diatomic exchange densities:

$$\rho_x^{AB}(\vec{r};\vec{r}') = \frac{1}{2} \left[\rho_A(\vec{r};\vec{r}')\rho_B(\vec{r}';\vec{r}) + \rho_B(\vec{r};\vec{r}')\rho_A(\vec{r}';\vec{r}) \right] \qquad (13)$$

where

$$\rho_A(\vec{r},\vec{r}') = \sum_{\mu \in A} \sum_{v} D_{\mu v} \chi_v^*(\vec{r}) \chi_\mu(\vec{r}') \qquad (14)$$

is the atomic component of the first order spin-less density matrix $\rho(\vec{r},\vec{r}')$. One can easily recover upon integration of Eqn. (13) the expression of Eq.(8) for the

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Mayer-Wiberg (closed-shell) bond order

$$\iint \rho_x^{AB}(\vec{r},\vec{r}')d\vec{r}d\vec{r}' \;=\; \frac{1}{2}\sum_{\mu\in A}\sum_{\nu}D_{\mu\nu}S_{\nu\sigma}\sum_{\sigma\in B}\sum_{\lambda}D_{\sigma\lambda}S_{\lambda\mu} \tag{15}$$

$$+\frac{1}{2}\sum_{\mu\in B}\sum_{\nu}D_{\mu\nu}S_{\nu\sigma}\sum_{\sigma\in A}\sum_{\lambda}D_{\sigma\lambda}S_{\lambda\mu} = \sum_{\mu\in A}\sum_{\sigma\in B}(\mathbf{DS})_{\mu\sigma}(\mathbf{DS})_{\sigma\mu} = B_{AB}$$

and so forth.

One advantage of using the formalism of effective atomic densities is that one can switch from 3D-space to Hilbert-space formulae or *vice versa* simply by taking the appropriate form of the effective densities involved in the calculation. In a recent paper[15] we have put forward an improved general formulae for the decomposition of $\langle \hat{S}^2 \rangle$ applicable for both single-determinant and correlated wave functions . The numerical implementation of the resulting one- and two-center components was originally carried out in the 3D-physical space. Here we will make use of the formalism of the atomic and diatomic effective matrices depicted above to derive in a simple manner the appropriate one and two-center components of $\langle \hat{S}^2 \rangle$ in the framework of Hilbert-space analysis.

This exercise is of particular interest here because of the formal ambiguity affecting Hilbert-space decompositions in the selection of the indices put forward in the previous section. We most definitely recommend to stick to the assignment of subscripts that will be obtained here, which is consistent with both Mulliken population analysis and the original bond order definition Eq. (8).

4 Decomposition of $\langle \hat{S}^2 \rangle$

Within the formalism of the effective atomic densities, the respective one- and two-center contributions to $\langle \hat{S}^2 \rangle$ can be formally written from the general expression of eqn. (6) simply as

$$
\begin{aligned}
\langle \hat{S}^2 \rangle_A = {} & \frac{3}{4} \int u_A(\vec{r}_1) d\vec{r}_1 + \frac{1}{2} \iint \left[\Gamma_{AA}(\vec{r}_1, \vec{r}_2) - \tfrac{1}{2} \rho_A^s(\vec{r}_1; \vec{r}_2) \rho_A^s(\vec{r}_2; \vec{r}_1) \right] d\vec{r}_1 d\vec{r}_2 \\
& - \frac{1}{2} \int \int \left[\Gamma_{AA}(\vec{r}_1, \vec{r}_2; \vec{r}_2, \vec{r}_1) - \tfrac{1}{2} \rho_A^s(\vec{r}_1; \vec{r}_1) \rho_A^s(\vec{r}_2; \vec{r}_2) \right] d\vec{r}_1 d\vec{r}_2 .
\end{aligned}
\tag{16}
$$

and

$$
\begin{aligned}
\langle \hat{S}^2 \rangle_{AB} = {} & \frac{1}{2} \iint \left[\Gamma_{AB}(\vec{r}_1, \vec{r}_2) - \tfrac{1}{2} \rho_A^s(\vec{r}_1; \vec{r}_2) \rho_B^s(\vec{r}_2; \vec{r}_1) \right] d\vec{r}_1 d\vec{r}_2 \\
& - \frac{1}{2} \int \int \left[\Gamma_{AB}(\vec{r}_1, \vec{r}_2; \vec{r}_2, \vec{r}_1) - \tfrac{1}{2} \rho_A^s(\vec{r}_1; \vec{r}_1) \rho_B^s(\vec{r}_2; \vec{r}_2) \right] d\vec{r}_1 d\vec{r}_2 .
\end{aligned}
\tag{17}
$$

where the atomic (in the case of $u(\vec{r})$ and $\rho^s(\vec{r}, \vec{r}')$) and diatomic (in the case of the cumulants, Γ) densities have been conveniently used, instead of their global counterparts in eqn. (6).

In order to be consistent with the definitions of Eqn.(12) in the framework of Hilbert-space analysis, the effective atomic contributions of the density of effectively unpaired electrons and the spin density matrix must be taken as

$$
\rho_A^s(\vec{r}; \vec{r}') = \sum_{\mu \in A} \sum_{\nu} P_{\mu\nu}^s \chi_\nu^*(\vec{r}) \chi_\mu(\vec{r}')
\tag{18}
$$

and

$$u_A(\vec{r}) = \sum_{\mu \in A} \sum_{\nu} \left[2D_{\mu\nu} - (\mathbf{DSD})_{\mu\nu} \right] \chi_\nu^*(\vec{r}) \chi_\mu(\vec{r}), \qquad (19)$$

where we have made use of Eq. (2).

The spin-less cumulant, Γ, being a genuine two-electron quantity, consists of atomic (if $A = B$) and diatomic ($A \neq B$) contributions:

$$\Gamma_{AB}(\vec{r}_1, \vec{r}_2; \vec{r}_1', \vec{r}_2') = \sum_{\mu \in A} \sum_{\sigma \in B} \sum_{\nu,\lambda} \Gamma_{\mu\sigma\nu\lambda} \, \chi_\nu^*(\vec{r}_1) \chi_\lambda^*(\vec{r}_2) \chi_\mu(\vec{r}_1') \chi_\sigma(\vec{r}_2') \qquad (20)$$

where the $\Gamma_{\mu\sigma\nu\lambda}$ are the corresponding matrix elements of the cumulant in the atomic orbital basis.

Substituting Eqns.(18)-(20) into (16) and integrating, one obtains, after some manipulations, the final expression for the atomic components of $\langle \hat{S}^2 \rangle$

$$
\begin{aligned}
\langle \hat{S}^2 \rangle_A \;=\;& \frac{3}{4} \sum_{\mu \in A} \left[2(\mathbf{DS})_{\mu\mu} - (\mathbf{DSDS})_{\mu\mu} \right] \qquad (21) \\
& - \frac{1}{4} \sum_{\mu,\nu \in A} (\mathbf{P}^s\mathbf{S})_{\mu\nu} (\mathbf{P}^s\mathbf{S})_{\nu\mu} + \frac{1}{4} \sum_{\mu,\nu \in A} (\mathbf{P}^s\mathbf{S})_{\mu\mu} (\mathbf{P}^s\mathbf{S})_{\nu\nu} \\
& + \frac{1}{2} \sum_{\mu,\sigma \in A} \sum_{\nu,\lambda} \left(\Gamma_{\mu\sigma\nu\lambda} - \Gamma_{\mu\sigma\lambda\nu} \right) S_{\lambda\sigma} S_{\nu\mu}
\end{aligned}
$$

Similarly, for the diatomic spin components one gets

$$
\begin{aligned}
\langle \hat{S}^2 \rangle_{AB} \;=\;& -\frac{1}{4} \sum_{\mu \in A} \sum_{\nu \in B} (\mathbf{P}^s\mathbf{S})_{\mu\nu} (\mathbf{P}^s\mathbf{S})_{\nu\mu} + \frac{1}{4} \sum_{\mu \in A} \sum_{\nu \in B} (\mathbf{P}^s\mathbf{S})_{\mu\mu} (\mathbf{P}^s\mathbf{S})_{\nu\nu} \quad (22) \\
& + \frac{1}{2} \sum_{\mu \in A} \sum_{\sigma \in B} \sum_{\nu,\lambda} \left(\Gamma_{\mu\sigma\nu\lambda} - \Gamma_{\mu\sigma\lambda\nu} \right) S_{\lambda\sigma} S_{\nu\mu}.
\end{aligned}
$$

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In the single determinant case the cumulants vanish and these formulae reduce to those derived independently in Ref. 27.

Eqns. (13) and (14) of Alcoba *et al.*[9] are similar to our Eqns. (21) and (22). In that paper, however, aside from the fact that $a = 1/2$ was used (and, therefore, other coeficients differ, too), the authors also chose a different convention in the treatment of the cumulant part: one index of the overlap matrix is assigned according to the term coming from the "bra" and another coming from the "ket". From now on we will refer to that different convention as formula with "interchanged" subscripts.

5   Numerical results

We have written a program that performs the decomposition of $\langle \hat{S}^2 \rangle$ described above in the framework of the Hilbert-space analysis. The first- and second-order density matrices have been obtained using a modified version of Gaussian-03 program suite[28] and an auxiliary program[29] that reads and processes CISD and CASSCF outputs. All calculations have been carried out with the geometrical structure of the molecules optimized at the current level of theory.

To assess the numerical effect on the use of the different summation schemes in the Hilbert-space analysis, we have studied the H_2 molecule at the CASSCF(2,4) level for several basis sets. Table 1 gathers the values of $\langle \hat{S}^2 \rangle_H$ for different values of the parameter a within the continuum of definitions and for the two summation schemes. The results obtained using eqn. (21) exhibit from signif-

icant to small basis set dependence, depending upon the choice of the parameter a. In the case $a = 0$, the local spin on the H atom obtained with the largest basis set (cc-pVQZ with cartesian d and f functions) is as large as 0.607, far away from what one should expect for a diamagnetic H_2 at equilibrium distance. Noticeably, when using the same basis set with pure d and f functions the $\langle \hat{S}^2 \rangle_H$ value decreases to 0.389. On the other hand, the results obtained with the "interchanged" index formula show, in general, less dependence on both basis set and the choice of the parameter a.

The local spin obtained with the recommended[15] value $a = 3/4$ and the preferred formulation are close to zero in all cases, in line with the physical expectations. The numbers have virtually no basis set dependence and are also very similar to those obtained in the framework of 3D-space analysis, reported in Ref. 15. Using the alternative formula with "interchanged" indices the values are somewhat too large, as compared with the "conventional" ones.

The recommended decomposition has also been applied to a series of singlet molecules and the results are presented in Table 2. The optimized geometries and the wave functions were obtained at the CISD/6-31G** level of theory (with cartesian d functions). Note that for these systems the overall $\langle \hat{S}^2 \rangle$ value is zero, but small local atomic spins can be induced by correlation fluctuations. One should only expect the presence of significant diatomic contributions in singlet systems if there would be any antiferromagnetic interaction that could be distinguished from covalent bonding.

As anticipated, the molecules of the H_nX series (HF, H_2O, and NH_3) show

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small values of local spin. The only systems with atomic spin contributions larger than 0.1 are homonuclear diatomic Li_2 and Be_2, with $\langle \hat{S}^2 \rangle_{Li} = 0.156$ and $\langle \hat{S}^2 \rangle_{Be} = 0.175$, respectively. These values are consistent with those obtained within the framework of 3D-space analysis.[15] On the other hand, in the series of hydrocarbons the local spin on the C atoms reported here show relevant differences. Within the 3D-space formulation the atomic spin contributions where always below 0.1.[15] In the Hilbert-space framework both CH_4 ($\langle \hat{S}^2 \rangle_C = 0.320$) and C_2H_6 ($\langle \hat{S}^2 \rangle_C = 0.199$) present quite significant local spin on the C atoms. The most striking finding in Table 2 is the negative local spin on the C atom obtained for C_2H_2. Since there is no physical explanation for a negative value of $\langle \hat{S}^2 \rangle_C$, we tried to understand this odd behavior. First of all, it is important to note that at the CASSCF(6,6)/6-31G** level of theory we obtained $\langle \hat{S}^2 \rangle_C = -0.144$, a similar value. Also, the local spin obtained at the CISD/6-31G** level with the 3D-space formulation was 0.083,[15] ruling out the CISD wave function as a responsible for the spurious number. In Table 1 above we have illustrated the basis set effects for the simplest H_2 molecule. Thus, in order to see the effect of the basis set upon the local spin for the acetylene, we have computed the $\langle \hat{S}^2 \rangle_C$ values at the CISD/6-31G** optimized geometry using several basis sets. The results are gathered in Table 3. The $\langle \hat{S}^2 \rangle_C$ is negative for the 6-31G, 6-31G**, 6-311G**, and cc-pVTZ basis sets, while remains positive for the STO-3G and 6-311G basis sets. For this peculiar molecule, a non-nuclear attractor is found for the STO-3G and cc-pVTZ basis sets, having no apparent effect on the local spin and bond indices values. Moreover, since negative values appear for both small and relatively large basis

sets with and without polarizations functions it is difficult to draw any general conclusion from the data. For comparision, the local spin on C atoms using a 3D-space formulation of ref.[15] have been computed and are also included in Table 3 ($\langle \hat{S}^2 \rangle_C^{3D}$ values). In this case, all $\langle \hat{S}^2 \rangle_C^{3D}$ values are small and positive, and one can see a systematic lowering of them upon inclusion of polarization functions.

In this context it is worth to note that rather odd numbers have been obtained in the literature when combining Hilbert-space analysis techniques and genuine two-electron quantities from correlated wave functions. For instance, Vyboishchikov *et al.*[30] found unphysically positive correlation contributions for diatomic energies at the CID level of theory. On the other hand, the bond order indices that in the correlated case make use of the actual pair density (the so-called delocalization index, DI,[31–35]) have also been matter of debate as, for the simplest case of H_2 described with Weinbaum's classical correlated wave function, the DI gives just 0.39.[35] An alternative formulation formally constructed from the first-order density matrix , the so-called Mayer-Wiberg bond order of eqn.(8)[23,35] was proposed as a more suitable quantity to be connected with bond orders. Both definitions coincide for single-determinant wave functions, thus deviations from both indices are directly related with correlation effects. In Table 3 we have also included the DI and Mayer-Wiberg bond indices for the C-C bond in acetylene with different basis sets. Whereas all B_{CC} values are close to 3, as one would expect for a formal triple bond, the DI_{CC} values are very small (below 1.0) and even unphysically negative in some cases. Moreover, we have performed the DI_{CC} calculations in the framework of the 3D-space, and in all cases the values are positive (yet slightly

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lower than the respective B$_{CC}$ values). One can conclude once again that in some cases one can get spurious results when decomposing quantities that explicitly include the second-order density matrix in the framework of the Hilbert-space analysis.

6 Conclusions

We have carried out the decomposition of the expectation value of the spin operator for a general wave function in the framework of the Hilbert-space analysis that fulfill all the requirements imposed to date. We have shown that there is and ambiguity affecting Hilbert- space decompositions in the selection of the indices where the atoms are centered. We definitely recommend to stick to the assignment of subscripts that is consistent with Mulliken population analysis and original Mayer-Wiberg bond orders. It has been also pointed out that there are cases where one can get spurious results when performing Hilbert-space decompositions on quantities that contains the second-order density matrix.

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Table 1: CASSCF(2,4) atomic $\langle \hat{S}^2 \rangle_A$ values for the H_2 molecule at optimized geometries for several basis sets and values of the parameter a.

Decomposition scheme	a	cc-pVDZ	cc-pVTZ	cc-pVQZ	cc-pVTZ (6d)	cc-pVQZ (6d 10f)
Equation (21)	0	0.402	0.277	0.389	0.305	0.607
	3/8	0.219	0.156	0.214	0.170	0.325
	1/2	0.158	0.116	0.156	0.125	0.231
	3/4[†]	*0.036*	*0.035*	*0.039*	*0.035*	*0.043*
"Interchanged" indexes	0	0.134	0.115	0.136	0.117	0.171
	3/8	0.097	0.083	0.101	0.084	0.130
	1/2	0.085	0.072	0.089	0.073	0.116
	3/4	0.060	0.051	0.066	0.052	0.089

[†] The recommended value

Table 2: CISD/6-31G** atomic $\langle \hat{S}^2 \rangle_A$ and diatomic $\langle \hat{S}^2 \rangle_{AB}$ values for a set of singlet molecules at optimized geometries.

Molecule		$\langle \hat{S}^2 \rangle_A / \langle \hat{S}^2 \rangle_{AB}$	Molecule		$\langle \hat{S}^2 \rangle_A / \langle \hat{S}^2 \rangle_{AB}$
H_2	H	0.036	C_2H_6	C	0.199
	H-H	-0.036		H	0.024
Li_2	Li	0.156		C-C	-0.122
	Li-Li	-0.156		C-H	-0.069
Be_2	Be	0.175		C..H	0.034
	Be-Be	-0.175		H-H	0.018
HF	H	0.006		H..H	-0.015
	F	0.006	C_2H_4	C	0.056
	H-F	-0.006		H	0.024
H_2O	H	0.013		C-C	-0.094
	O	0.013		C-H	-0.036
	O-H	-0.007		C..H	0.055
	H..H	-0.006		H-H	-0.002
NH_3	N	0.061		H..H$_{cis}$	-0.026
	H	0.019		H..H$_{trans}$	-0.014
	N-H	-0.020	C_2H_2	C	*-0.139*
	H..H	0.000		H	0.019
CH_4	C	0.320		C-C	*0.147*
	H	0.026		C-H	0.048
	C-H	-0.080		C..H	-0.056
	H..H	0.018		H..H	-0.006

Table 3: Atomic $\langle \hat{S}^2 \rangle_C$ components, Mayer bond orders, and delocalization indices of the C-C bond for acetylene molecule computed at CISD level of theory with different basis sets.

Basis set	$\langle \hat{S}^2 \rangle_C$	$\langle \hat{S}^2 \rangle_C^{3D}$	B_{CC}	DI_{CC}
sto-3G	0.012	0.159	2.725	0.502
6-31G	-0.074	0.114	3.092	-0.141
6-31G**	-0.139	0.083	2.918	0.461
6-311G	0.030	0.113	2.868	-0.112
6-311G**	-0.143	0.084	2.709	0.214
cc-pvtz	-0.146	0.078	2.722	-0.615