

Towards a unique definition of the local spin

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Abstract

In this work we demonstrate that there is a *continuum* of different formulations for the decomposition of $\langle \hat{S}^2 \rangle$ that fulfill all physical requirements imposed to date. We introduce a new criterion based upon the behaviour of single-electron systems to fix the value of the parameter defining that continuum and thus we put forward a new general formula applicable for both single-determinant and correlated wave functions. The numerical implementation has been carried out in the three-dimensional physical space for several atomic definitions. A series of representative closed-shell and open-shell systems have been used to illustrate the performance of this new decomposition scheme against other existing approaches. Unlike other decompositions of $\langle \hat{S}^2 \rangle$, the new scheme provides very small local-spin values for genuine diamagnetic molecules treated with correlated wave functions, in conformity with the physical expectations.

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1 Introduction

The spin state of an atom or a group of atoms within a molecule is not a quantum mechanical observable. Nevertheless, the concept of local spin is generally invoked when discussing spin-spin interactions between magnetic centers in a molecule with Heisenberg Hamiltonian models or to describe organic molecules with diradical character. For instance, the spin on transition metals of bioinorganic complexes is particularly relevant for experimentalists and can be used for spin-labeling functional groups. In addition, local-spin values could also be used as a stringent test for DFT and DMFT functionals in order to analyze their ability to recover the spin distribution along the molecular space.

In the last years there has been a growing interest in recovering local spins from ab initio wave functions.¹⁻¹⁴ These techniques are aiming to express the expectation value of the \hat{S}^2 operator as a sum of atomic and diatomic contributions:

$$\langle \hat{S}^2 \rangle = \sum_A \langle \hat{S}^2 \rangle_A + \sum_{A,B \neq A} \langle \hat{S}^2 \rangle_{AB}. \quad (1)$$

In 2001 Clark and Davidson¹ proposed a general framework based on the definition of local (atomic) spin operators, \hat{S}_A , obtained by proper projections of the overall spin vector operator. The expectation values of the atomic spin-square operators and diatomic products of spin-operators, namely $\langle \hat{S}_A^2 \rangle$ and $\langle \hat{S}_A \hat{S}_B \rangle$, can be considered as the atomic and diatomic contributions to the overall $\langle \hat{S}^2 \rangle$ value, respectively. Unfortunately, this formalism leads to significant local-spin contributions for genuine closed-shell diamagnetic molecular systems such as the H₂ molecule treated at the RHF level of theory.

Later on, Mayer⁴ proposed an alternative strategy to partition the expectation value of the \hat{S}^2 operator in the spirit of classical population analysis. In the case of *single-determinant* wave functions Mayer obtained expressions for the atomic and diatomic contributions to $\langle \hat{S}^2 \rangle$ depending only on the molecular spin-density matrix, $\rho^s(\vec{r}; \vec{r}')$. Such a decomposition trivially leads to zero atomic spins for any closed-shell restricted wave function. This decomposition was carried out

originally in the framework of the so-called Hilbert-space analysis. The generalization of the formulae to the 3D physical-space analysis was already outlined by Mayer⁴ and has also been very recently explored by Alcoba et al.⁸ using both Bader's QTAIM¹⁵ domains and Becke's "fuzzy" atoms.¹⁶

Many molecular species do not admit single-determinant description. In some singlet systems such as diradicals or in the dissociation process of a molecule, where one can also recognize the existence of local spins, a proper spin description can be only accomplished using multi-determinant wave functions, whose $\langle \hat{S}^2 \rangle$ decomposition is not straightforward. Indeed, in the recent years, a number of different $\langle \hat{S}^2 \rangle$ decomposition schemes, exhibiting different features, have been proposed.^{5-7,9} In the first scheme, proposed by Alcoba et al.,⁵ the components of $\langle \hat{S}^2 \rangle$ were expressed in terms of the total spin-density matrix and therefore zero spins were obtained for every singlet state system. Subsequently, Mayer⁶ proposed an alternative formulation on the basis of several physical requirements: *i*) to obtain zero local spins for closed-shell restricted wave functions, *ii*) proper asymptotics, *i.e.*, in the dissociation limit the atoms/fragments should have the same local $\langle \hat{S}^2 \rangle$ value as the respective free atoms/fragment radicals, *iii*) the formula used for a general wave function should reduce to that used in the single-determinant case if applied to single-determinant wave functions.

In this formulation, the atomic and diatomic components of $\langle \hat{S}^2 \rangle$ were expressed in terms of the value that they would have in the single-determinant case, plus correction terms arising from the deviation of the first-order density matrix from the idempotency, as well as contributions from the cumulant of the second-order density matrix. (Both vanish for single determinant wave functions thus fulfilling requirement *iii*.) These correction terms were distributed between atomic and diatomic contributions in such a way that the local spins obtained for atoms or other fragments at large distances coincide with those of the free atoms. The Hilbert-space realization of the formalism given in ref. 7 corroborated the physical expectations in all cases. For instance, small atomic contributions were obtained for every closed-shell molecule at equilibrium distance, including *e.g.* the carbon atoms of singlet π -conjugated systems such as benzene calculated at the CASSCF level

of theory. At the same time, large local spins were found for the square cyclo-butadiene which is known to be a “molecular antiferromagnet”. Furthermore, the CASSCF dissociation curves of O_2 molecule for both singlet and triplet states lead to atomic atomic local-spin values that tend asymptotically to 2, as expected for the 3P_2 state of the free oxygen atom. Similarly, ethylene dissociates into two triplet methylene radicals, and so forth.

Although it seemed as there was no further freedom to choose another local-spin decomposition scheme, Alcoba et al.⁹ have recently shown that this is not the case. These authors have introduced yet another requirement for the partitioning of $\langle \hat{S}^2 \rangle$ for non-singlet states, according to which the one and two-center components should be independent of the S_z value (in the absence of magnetic field). Their partitioning scheme uses “spin-free” quantities such as the effectively unpaired density matrix¹⁷ and the “spin-free cumulant matrix”, which depend on the spin-free first- and second-order reduced density matrices.^{18,19} Their Hilbert-space local-spin results are similar to but not identical with those obtained by Mayer and Matito in ref. 7, and keep the physical requirement of S_z independence.

In this paper we shall show that there is actually a *continuum* of different formulations that fulfill all physical requirements imposed to date to the decomposition of $\langle \hat{S}^2 \rangle$; and this applies to both single- and multi-determinant wave functions. In order to find the best local-spin decomposition scheme, we impose a new, additional requirement related to the one-electron distribution, that eliminates the ambiguity. The resulting local-spin decomposition it is thus unique and fulfills all physical requirements found so far.

The paper is organized as follows: first we put forward the ambiguities associated with the decomposition of $\langle \hat{S}^2 \rangle$ for any wave function, then we suggest a unique definition of the local spin based on new theoretical considerations and finally we compare the results of the 3D-space realization of our new local-spin definition against previous definitions.

2 Theory

The \hat{S}^2 operator can be written as

$$\hat{S}^2 = \sum_i^N \hat{s}_i^2 + \sum_{i \neq j}^N \hat{s}_i \hat{s}_j. \quad (2)$$

The expectation value for an N -electron system described by a general wave function can be expressed in terms of the spinless first- and second-order density matrices as (see appendix AI for further details)

$$\begin{aligned} \langle \hat{S}^2 \rangle &= \frac{3}{4} \int \rho(\vec{r}_1; \vec{r}_1) d\vec{r}_1 - \frac{1}{4} \int \int \rho_2(\vec{r}_1, \vec{r}_2; \vec{r}_1, \vec{r}_2) d\vec{r}_1 d\vec{r}_2 \\ &\quad - \frac{1}{2} \int \int \rho_2(\vec{r}_1, \vec{r}_2; \vec{r}_2, \vec{r}_1) d\vec{r}_1 d\vec{r}_2 \end{aligned} \quad (3)$$

where the first- and the second-order density matrices are normalized to N and $N(N-1)$ (Note that this normalization is different from that used by Alcoba et al.⁹), respectively. The spinless second-order density matrix is often expressed in terms of the first-order density matrix elements and the so-called 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) as

$$\begin{aligned} \rho_2(\vec{r}_1, \vec{r}_2; \vec{r}'_1, \vec{r}'_2) &= \rho(\vec{r}_1; \vec{r}'_1) \rho(\vec{r}_2; \vec{r}'_2) - \frac{1}{2} \rho(\vec{r}_1; \vec{r}'_2) \rho(\vec{r}_2; \vec{r}'_1) \\ &\quad - \frac{1}{2} \rho^s(\vec{r}_1; \vec{r}'_2) \rho^s(\vec{r}_2; \vec{r}'_1) + \Gamma(\vec{r}_1, \vec{r}_2; \vec{r}'_1, \vec{r}'_2) \end{aligned} \quad (4)$$

where $\rho^s(\vec{r}; \vec{r}')$ is the first-order spin-density matrix, defined as the difference between the alpha and beta components of the first-order density matrix

$$\rho^s(\vec{r}; \vec{r}') = \rho^\alpha(\vec{r}; \vec{r}') - \rho^\beta(\vec{r}; \vec{r}'). \quad (5)$$

The spinless cumulant $\Gamma(\vec{r}_1, \vec{r}_2; \vec{r}'_1, \vec{r}'_2)$ represents the sum of the four respective spin-dependent cumulants, and differs from the entity (Λ) that Alcoba et al.⁹ called ‘‘spin-free cumulant’’.

Substituting eq. (4) into eq. (3) one gets

$$\begin{aligned} \langle \hat{S}^2 \rangle &= \frac{3}{4} \int \rho(\vec{r}_1) d\vec{r}_1 - \frac{3}{8} \iint \rho(\vec{r}_1; \vec{r}_2) \rho(\vec{r}_2; \vec{r}_1) d\vec{r}_1 d\vec{r}_2 + \frac{1}{8} \iint \rho^s(\vec{r}_1; \vec{r}_2) \rho^s(\vec{r}_2; \vec{r}_1) d\vec{r}_1 d\vec{r}_2 \\ &+ \frac{1}{4} \int \rho^s(\vec{r}_1) d\vec{r}_1 \int \rho^s(\vec{r}_2) d\vec{r}_2 - \frac{1}{4} \iint \Gamma(\vec{r}_1, \vec{r}_2) d\vec{r}_1 d\vec{r}_2 - \frac{1}{2} \iint \Gamma(\vec{r}_1, \vec{r}_2; \vec{r}_2, \vec{r}_1) d\vec{r}_1 d\vec{r}_2 \end{aligned} \quad (6)$$

where $\rho(\vec{r}_1) \equiv \rho(\vec{r}_1; \vec{r}_1)$ and $\Gamma(\vec{r}_1, \vec{r}_2) \equiv \Gamma(\vec{r}_1, \vec{r}_2; \vec{r}_1, \vec{r}_2)$.

The effectively unpaired electron density, $u(\vec{r})$, defined by Takatsuka¹⁷ as

$$u(\vec{r}) = 2\rho(\vec{r}) - \int \rho(\vec{r}; \vec{r}') \rho(\vec{r}'; \vec{r}) d\vec{r}' \quad (7)$$

can be used to transform eq. (6) to the form

$$\begin{aligned} \langle \hat{S}^2 \rangle &= \frac{3}{8} \int u(\vec{r}_1) d\vec{r}_1 - \frac{1}{4} \iint \left[\Gamma(\vec{r}_1, \vec{r}_2) - \frac{1}{2} \rho^s(\vec{r}_1; \vec{r}_2) \rho^s(\vec{r}_2; \vec{r}_1) \right] d\vec{r}_1 d\vec{r}_2 \\ &- \frac{1}{2} \iint \left[\Gamma(\vec{r}_1, \vec{r}_2; \vec{r}_2, \vec{r}_1) - \frac{1}{2} \rho^s(\vec{r}_1; \vec{r}_1) \rho^s(\vec{r}_2; \vec{r}_2) \right] d\vec{r}_1 d\vec{r}_2. \end{aligned} \quad (8)$$

The spin density, the cumulants and $u(\vec{r})$ vanish for restricted single-determinant wave functions and, therefore, for such wave functions, the decomposition of eq. (8) leads to identically zero spin components, thus fulfilling the requirement *i*. This is not the case for the expression (6), since the first and second terms on the r.h.s. can be decomposed into non-zero one-center and one- and two-center contributions, respectively, although their sum vanishes. In fact, the natural decomposition of eq. (6) into one and two-center terms leads to Clark and Davidson's formulae.³ Moreover, Alcobra et al.⁹ pointed out that since $\rho(\vec{r}_1)$ and $\rho_2(\vec{r}_1, \vec{r}_2)$ are spin-independent quantities, by virtue of eq. (4), the sum

$$\Gamma(\vec{r}_1, \vec{r}_2; \vec{r}'_1, \vec{r}'_2) - \frac{1}{2} \rho^s(\vec{r}_1; \vec{r}'_2) \rho^s(\vec{r}_2; \vec{r}'_1) \quad (9)$$

must be spin-independent too (It is essentially their "spin-free cumulant"). Also, they showed

that (in the normalization used here)

$$\int \left[\Gamma(\vec{r}_1, \vec{r}_2) - \frac{1}{2} \rho^s(\vec{r}_1; \vec{r}_2) \rho^s(\vec{r}_2; \vec{r}_1) \right] d\vec{r}_2 = -\frac{1}{2} u(\vec{r}_1). \quad (10)$$

On this basis, they suggested the following general expression for $\langle \hat{S}^2 \rangle$

$$\langle \hat{S}^2 \rangle = \frac{1}{2} \int u(\vec{r}_1) d\vec{r}_1 - \frac{1}{2} \iint \left[\Gamma(\vec{r}_1, \vec{r}_2; \vec{r}_2, \vec{r}_1) - \frac{1}{2} \rho^s(\vec{r}_1; \vec{r}_1) \rho^s(\vec{r}_2; \vec{r}_2) \right] d\vec{r}_1 d\vec{r}_2. \quad (11)$$

Both expression (8) and Alcoba's (11) are natural starting points to derive $\langle \hat{S}^2 \rangle$ components that fulfill the imposed requirement to be independent of the S_z projection. Upon integration over the whole space both expressions are equivalent. However, the calculation of the one- and two-electron integrals over one- and two-center atomic domains leads to different contributions. In fact, one can freely modulate the relative weight of the first two terms on the r.h.s. of eq. (8) with a parameter a and get a general expression like

$$\begin{aligned} \langle \hat{S}^2 \rangle = & a \int u(\vec{r}_1) d\vec{r}_1 - (1 - 2a) \iint \left[\Gamma(\vec{r}_1, \vec{r}_2) - \frac{1}{2} \rho^s(\vec{r}_1; \vec{r}_2) \rho^s(\vec{r}_2; \vec{r}_1) \right] d\vec{r}_1 d\vec{r}_2 \\ & - \frac{1}{2} \iint \left[\Gamma(\vec{r}_1, \vec{r}_2; \vec{r}_2, \vec{r}_1) - \frac{1}{2} \rho^s(\vec{r}_1; \vec{r}_1) \rho^s(\vec{r}_2; \vec{r}_2) \right] d\vec{r}_1 d\vec{r}_2 \end{aligned} \quad (12)$$

which leads to different decompositions of $\langle \hat{S}^2 \rangle$ that fulfill requirements *i – iii*. (The two equations discussed above correspond to the values $a = 3/8$ and $a = 1/2$, respectively.) On this scenario, one should find a sound argument permitting to choose the proper value of a , and thus the most satisfactory decomposition of $\langle \hat{S}^2 \rangle$.

3 Atomic and diatomic spin components

The decomposition of physical quantities into one and two-center contributions is rooted on the identification of an atom within the molecule. In the 3D-space analysis the atom is identified by a region of the physical space or atomic domain and its nucleus. Atomic and diatomic contributions

can be simply obtained by integration over the corresponding atomic domains Ω_A as

$$\begin{aligned}\int f(\vec{r})d\vec{r} &= \sum_A \int w_A(\vec{r})f(\vec{r})d\vec{r} \\ \int f(\vec{r}_1, \vec{r}_2)d\vec{r}_1d\vec{r}_2 &= \sum_{A,B} \iint w_A(\vec{r}_1)w_B(\vec{r}_2)f(\vec{r}_1, \vec{r}_2)d\vec{r}_1d\vec{r}_2\end{aligned}\quad (13)$$

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 one- and two-electron terms of (12) can be thus naturally decomposed into one- and two-center contributions, respectively, as shown in eq. (13), to obtain

$$\begin{aligned}\langle \hat{S}^2 \rangle_A &= a \int w_A(\vec{r}_1)u(\vec{r}_1)d\vec{r}_1 - (1-2a) \iint w_A(\vec{r}_1)w_A(\vec{r}_2) \\ &\quad \times \left[\Gamma(\vec{r}_1, \vec{r}_2) - \frac{1}{2}\rho^s(\vec{r}_1; \vec{r}_2)\rho^s(\vec{r}_2; \vec{r}_1) \right] d\vec{r}_1d\vec{r}_2 \\ &\quad - \frac{1}{2} \iint w_A(\vec{r}_1)w_A(\vec{r}_2) \left[\Gamma(\vec{r}_1, \vec{r}_2; \vec{r}_2, \vec{r}_1) - \frac{1}{2}\rho^s(\vec{r}_1; \vec{r}_1)\rho^s(\vec{r}_2; \vec{r}_2) \right] d\vec{r}_1d\vec{r}_2\end{aligned}\quad (14)$$

and

$$\begin{aligned}\langle \hat{S}^2 \rangle_{AB} &= -(1-2a) \iint w_A(\vec{r}_1)w_B(\vec{r}_2) \left[\Gamma(\vec{r}_1, \vec{r}_2) - \frac{1}{2}\rho^s(\vec{r}_1; \vec{r}_2)\rho^s(\vec{r}_2; \vec{r}_1) \right] d\vec{r}_1d\vec{r}_2 \\ &\quad - \frac{1}{2} \iint w_A(\vec{r}_1)w_B(\vec{r}_2) \left[\Gamma(\vec{r}_1, \vec{r}_2; \vec{r}_2, \vec{r}_1) - \frac{1}{2}\rho^s(\vec{r}_1; \vec{r}_1)\rho^s(\vec{r}_2; \vec{r}_2) \right] d\vec{r}_1d\vec{r}_2.\end{aligned}\quad (15)$$

Eqns. (14) and (15) can be written more conveniently by using the matrix representations \mathbf{D} , \mathbf{P}^s , Γ of the first-order density matrix, spin-density and second-order density matrices, respectively, in terms of the molecular orbitals—and the atomic overlap matrix \mathbf{S}^A (see appendix AII for further details). By using the definition of the effectively unpaired electron density, eq. (7), the atomic contribution of the spin squared operator can be written as

$$\begin{aligned}\langle \hat{S}^2 \rangle_A &= a \left(2\text{Tr}(\mathbf{D}\mathbf{S}^A) - \text{Tr}(\mathbf{D}\mathbf{S}^A\mathbf{D}) \right) + \left(\frac{1}{2} - a \right) \text{Tr}(\mathbf{P}^s\mathbf{S}^A\mathbf{P}^s\mathbf{S}^A) \\ &\quad - (1-2a) \sum_{ijkl} \Gamma_{ijkl} S_{ki}^A S_{lj}^A - \frac{1}{2} \sum_{ijkl} \Gamma_{ijkl} S_{li}^A S_{kj}^A + \frac{1}{4} \text{Tr}(\mathbf{P}^s\mathbf{S}^A)^2.\end{aligned}\quad (16)$$

Similarly, the diatomic terms can be expressed as follows

$$\begin{aligned} \langle \hat{S}^2 \rangle_{AB} &= \left(\frac{1}{2} - a \right) \text{Tr} \left(\mathbf{P}^s \mathbf{S}^A \mathbf{P}^s \mathbf{S}^B \right) - (1 - 2a) \sum_{ijkl} \Gamma_{ijkl} S_{ik}^A S_{jl}^B \\ &\quad - \frac{1}{2} \sum_{ijkl} \Gamma_{ijkl} S_{il}^A S_{jk}^B + \frac{1}{4} \text{Tr} \left(\mathbf{P}^s \mathbf{S}^A \right) \text{Tr} \left(\mathbf{P}^s \mathbf{S}^B \right). \end{aligned} \quad (17)$$

4 Selection of parameter a

The expressions above illustrate what we referred in the introduction as a *continuum* of closely related decompositions of $\langle \hat{S}^2 \rangle$ into atomic and diatomic components, which for any value of a satisfy all the physical requirements introduced. For instance, Alcoba's formulation⁹ is based on the expression where $a = 1/2$, whereas Mayer's original spin-dependent expression⁷ for correlated wave functions can be easily rewritten in a form where $a = 3/8$ (plus some terms depending on the spin-density that sum up to zero but can lead to changes in the one- and two-center components for non-singlets).

Clearly, the requirements introduced so far for the decomposition of $\langle \hat{S}^2 \rangle$ are not sufficient. It is necessary to introduce some additional external requirement, based on some physico-chemical considerations, which permits to choose between these possibilities. This can be done by considering how these formulae behave if there is only a *single electron* in the system.

The value $\langle \hat{S}^2 \rangle = 3/4$ is an *intrinsic* property of the electron, so if one locates an electron in the space with the density (probability density) $\rho(\vec{r})$, that means that one locates a spin $\langle \hat{S}^2 \rangle = 3/4$ with that probability, too. Therefore, the density of distribution of the $\langle \hat{S}^2 \rangle$ for a single electron is 3/4 times the electron density:

$$\langle \hat{S}^2 \rangle = \frac{3}{4} \int \rho(\vec{r}) dr \quad (18)$$

which is the only term on the r.h.s. of Eq.s (3) and (6) which does not disappear if there is only one electron in the system. Therefore, for a single electron the atomic components of $\langle \hat{S}^2 \rangle$ should be equal to the respective gross electron populations multiplied by 3/4. (No overlap populations

may be considered in this case because that would result in a spurious self-coupling of the spin of the given electron with itself.) Now, it is easy to see that in the special case of a single electron, function $u(\vec{r})$ equals $\rho(\vec{r})$ as a consequence of the idempotency of the first order density matrix. Therefore Eq. (12) reproduces Eq. (18) in the case of a single electron system if, and only if, one chooses $a = 3/4$. Interestingly, $a = 3/4$ is also the only value for which $\langle \hat{S}^2 \rangle_A$ is always positive in a general FCI wave function of a minimal-basis-set H_2 model (see appendix AII for further details). Another interesting conclusion drawn from this model system for $a = 3/4$ is that one can anticipate small $\langle \hat{S}^2 \rangle_A$ values at equilibrium distances of singlet molecules, except for true diradicals or systems with strong multireferencial character.

Finally, since for single-determinant wave functions the cumulants are zero by definition, in that case Eqs. (16) and (17) can be expressed solely in terms of the spin-density matrix elements as

$$\langle \hat{S}^2 \rangle_A = a \text{Tr} \left(\mathbf{P}^s \mathbf{S}^A \mathbf{P}^s - \mathbf{P}^s \mathbf{S}^A \mathbf{P}^s \mathbf{S}^A \right) + \frac{1}{2} \text{Tr} \left(\mathbf{P}^s \mathbf{S}^A \mathbf{P}^s \mathbf{S}^A \right) + \frac{1}{4} \text{Tr} \left(\mathbf{P}^s \mathbf{S}^A \right)^2 \quad (19)$$

and

$$\langle \hat{S}^2 \rangle_{AB} = \left(\frac{1}{2} - a \right) \text{Tr} \left(\mathbf{P}^s \mathbf{S}^A \mathbf{P}^s \mathbf{S}^B \right) + \frac{1}{4} \text{Tr} \left(\mathbf{P}^s \mathbf{S}^A \right) \text{Tr} \left(\mathbf{P}^s \mathbf{S}^B \right). \quad (20)$$

The original single-determinant formulation of Mayer,⁴ also used by Alcoba et al. in ref. 8, corresponds to the particular case where $a = 0$. It is easy to see that the most recent general formula proposed by Alcoba et al.,⁹ with $a = 1/2$, reduces for the single-determinant case to an expression where for the diatomic terms one has $\langle \hat{S}^2 \rangle_{AB} = \langle \hat{S}_z^2 \rangle_{AB}$, which is to say, the x and y components of the \hat{S}^2 operator would not contribute to the diatomic spin interactions.

Based on the considerations described above we suggest the choice $a = 3/4$ and hence the following alternative formulation to be used for single-determinant wave functions

$$\langle \hat{S}^2 \rangle_A = \frac{3}{4} \text{Tr} \left(\mathbf{P}^s \mathbf{S}^A \mathbf{P}^s \right) - \frac{1}{4} \text{Tr} \left(\mathbf{P}^s \mathbf{S}^A \mathbf{P}^s \mathbf{S}^A \right) + \frac{1}{4} \text{Tr} \left(\mathbf{P}^s \mathbf{S}^A \right)^2 \quad (21)$$

and

$$\langle \hat{S}^2 \rangle_{AB} = -\frac{1}{4} \text{Tr}(\mathbf{P}^s \mathbf{S}^A \mathbf{P}^s \mathbf{S}^B) + \frac{1}{4} \text{Tr}(\mathbf{P}^s \mathbf{S}^A) \text{Tr}(\mathbf{P}^s \mathbf{S}^B). \quad (22)$$

It is easy to see that in the case of a single electron or in that of an ROHF system with a single unpaired electron, eq. 22 vanishes, thus avoiding spurious self-coupling of the single electron. In the next section we provide also some numerical evidence supporting the choice $a = 3/4$.

5 Numerical results

We have implemented the decompositions of $\langle \hat{S}^2 \rangle$ described above in the framework of 3D-space analysis for a variety of atomic definitions, namely Becke,¹⁶ Becke- ρ ,²⁰ Hirshfeld,²¹ Hirshfeld-Iterative²² and QTAIM¹⁵ (see appendix AII). The first- and second-order density matrices have been obtained using a modified version of Gaussian-03²³ and an auxiliary program²⁴ that reads and processes CISD and CASSCF outputs. All calculations have been carried out at the optimized geometry of the molecule at the current level of theory.

First of all, in Table I we compare the values of $\langle \hat{S}^2 \rangle_A$ calculated for H₂ at the equilibrium geometry at the CASSCF(2,4) level for several basis sets and atomic definitions. As expected for a 3D-space analysis, the contributions (in this case atomic spin-squared values) are rather basis set independent. The effect of the atomic definition on the values of $\langle \hat{S}^2 \rangle_A$ depends upon the particular choice for the parameter a . In the case of $a = 0$, the formula that reduces to the original Mayer’s scheme for the single-determinant case, the values obtained for “fuzzy” atom definitions such as Becke and Hirshfeld are ca. twice those obtained for QTAIM. The differences decrease for $a = 3/8$, which conforms with Mayer’s general formula⁶ for singlets, and $a = 1/2$, which corresponds to Alcoba’s formulation.⁹ In the case of $a = 3/4$ the values of $\langle \hat{S}^2 \rangle_A$ are very small, as expected for a diamagnetic molecule, and are very similar for all basis sets and atomic definitions. The Hilbert-space results (not shown) exhibit large basis set dependence. Interestingly, these effects are minimal right when using $a = 3/4$, and for that case the values obtained are very similar to

those reported in Table 1. The implementation and numerical realization in the case of Hilbert-space analysis will be discussed elsewhere.

The effect of the atomic definitions in 3D-space analysis can be more relevant when different type of atoms are present in the molecule, since the relative atomic sizes have a major influence on the values originating from the decomposition of any physical quantity. In Table II we report the atomic and diatomic spin components obtained for the NO molecule at the UHF/cc-pVTZ level of theory using $a = 3/4$. It can be seen that the differences between the atomic definitions are small and the overall picture is not modified. The molecule is a doublet and, even though the atomic contributions are significant (roughly 0.5 for N and 0.25 for O atoms), the diatomic contribution is essentially zero in all cases. This is a clear indication that there is essentially a single unpaired electron in the system, causing a minor spin-polarization only, and no spurious self-coupling appears. Since the effect of the particular atomic definition is very small, hereafter we report only the values obtained using the Hirshfeld-Iterative scheme.

The one- and two-center contributions of $\langle \hat{S}^2 \rangle$ obtained for a collection of representative singlet systems are gathered in Table III. The optimized geometries and the wave functions were obtained at the CISD/6-31G** level of theory (six 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. A local-spin analysis is only useful if the genuine antiferromagnetic interactions of localized spins can be clearly distinguished from the electron pairing of alpha and beta spins associated with bond formation. All molecules in Table III are well described with single-determinant wave functions (except perhaps Li_2 and Be_2), therefore one should expect very small atomic and diatomic spin contributions. The atomic and diatomic spin values we obtain here are significantly smaller than those reported by Alcoba, arising from Hilbert-space analysis. The results indicate that among all values of the parameter a , the choice $a = 3/4$ provides the smallest atomic spin values. For instance, in the case of acetylene a significant, and rather unphysical, $\langle \hat{S}^2 \rangle_A$ value of 0.339 on the C atom is obtained for $a = 0$, whereas for $a = 3/4$ the value decreases to the much more reasonable 0.09. Interestingly, in the case of the less conventional Li_2 and Be_2 molecules the trend

is the opposite.

We have also considered open-shell doublet and triplet molecules described at the UHF level, in order to assess the effect of the parameter a on the single-determinant description. The one- and two-center contributions of $\langle \hat{S}^2 \rangle$ using Hirshfeld-Iterative atomic definitions are collected on Tables IV and V, respectively. The optimized geometries and wave functions were obtained at the UHF/cc-pVTZ level of theory. The overall $\langle \hat{S}^2 \rangle$ value is also reported, since significant spin contamination is present in some cases like the CN or CH radicals. Note that the case of $a = 0$ corresponds to the original formulation of Mayer⁴ for single-determinant wave functions, whereas $a = 1/2$ would correspond to the “spin-free” formulation introduced by Alcoba.⁹

In the case of doublet systems, the differences in the atomic spin contributions for different values of the parameter a are smaller than for the singlets. The sign of diatomic contributions often changes going from $a = 0$ to the preferred $a = 3/4$ value but, except in the case of NO and CN radicals, the spin is essentially localized on one atom and therefore the diatomic contributions are very small. Interestingly, the atomic spin contribution on the H atoms for radicals like OH, CH, CH₃ or NH₂ is essentially zero when $a = 0$, yet there is significant (between 0.022 and 0.072) diatomic contribution involving the H atom. This rather puzzling picture changes with $a = 3/4$, where the local spin on H atom increases but the diatomic contribution between the atoms is essentially zero, again in accordance with the model of a single unpaired electron which is significantly delocalized. In the case of CH and CN radicals there is a significant spin contamination that results in atomic spin contributions larger than the value of 3/4 of a single localized electron. In both cases, the local spin on the C atoms is larger than 1, in line with an overall $\langle \hat{S}^2 \rangle$ values of 1.106 and 1.075, respectively. The diatomic contribution in the case of CN is significant and negative (up to -0.23), indicating some degree of antiferromagnetic coupling between the centers. However, it is difficult to draw conclusions from a wave function with such amount of spin contamination.

The results for a set of molecules in their lowest triplet state are collected in Table V. The UHF wave function exhibits small spin contamination for all molecules. In contrast to the rather small differences found for the doublets, the local-spin contributions depend considerably on the

value of the parameter a in the case of homonuclear diatomic molecules, especially for Li_2 and O_2 . Note that for $a = 3/4$ the atomic spin contribution on Li and O atoms is larger than the value of a localized electron ($3/4$), whereas for $a = 1/2$ the atomic spin is very close to that number. In fact, it can be easily seen that in the case of Li_2 described at the ROHF level of theory, the value $a = 1/2$ yields exactly $\langle \hat{S}^2 \rangle_A = 3/4$ and $\langle \hat{S}^2 \rangle_{AB} = 1/4$ at any interatomic distance and for any atomic definition. On the other hand, the results for the NF, NH and CH_2 molecules are consistent with the presence of two unpaired electrons located on the N and C atoms, respectively, with negligible diatomic contributions.

Finally, Figure 1 displays the $\langle \hat{S}^2 \rangle_A$ values as a function of the parameter a along the dissociation curve of several homonuclear diatomic molecules, namely H_2 , N_2 and O_2 , in their lowest-lying singlet state described with a proper full-valence CASSCF wave function. As stated above, at the dissociation limit the atomic spin values tend to the value of the corresponding free atoms, i.e. $3/4$, $15/4$ and 2 in the case of H, N and O atoms, respectively, for all values of a . In the case of N_2 , at very short interatomic distances (ca. 0.8 \AA), a small negative value of -0.012 has been obtained for $\langle \hat{S}^2 \rangle_A$ of the N atom; such a small value can be attributed to the integration error associated to any 3D-space analysis and is not considered to be of any special relevance.

6 Conclusions

We have shown that there is a *continuum* of different formulations for the decomposition of $\langle \hat{S}^2 \rangle$ that fulfill all physical requirements imposed to date. We have presented a new criterion based upon the behaviour of single-electron systems and a simple two-electron model by which the value of the parameter defining that continuum can be properly fixed, and based on this a new general formula applicable for both single-determinant and correlated wave functions has been introduced. The scheme has been realized in the three-dimensional physical space and implemented for Bader's QTAIM and a number of "fuzzy" atom definitions. We provide numerical data for a set of representative closed-shell and open-shell systems and for the dissociation curves of several diatomic

molecules. The results have been compared with other existing formulations. Contrary to the most recent results, very small local-spin values are obtained for genuine diamagnetic molecules treated at the correlated level, in conformity with the physical expectations.

7 Appendices

AI. Expectation value of the \hat{S}^2 operator

The \hat{S}^2 operator can be written as a sum of one- and two-electron operators acting on the spin coordinates of an N -electron wave function

$$\hat{S}^2 = \sum_i^N [\hat{s}_x^2(i) + \hat{s}_y^2(i) + \hat{s}_z^2(i)] + \sum_{i \neq j}^N [\hat{s}_x(i)\hat{s}_x(j) + \hat{s}_y(i)\hat{s}_y(j) + \hat{s}_z(i)\hat{s}_z(j)]. \quad (23)$$

The action of the different individual one-electron spin operators over the corresponding alpha and beta one-electron spin functions yields the well-know relations (in a.u.)

$$\begin{aligned} \hat{s}_x |\alpha\rangle &= \frac{1}{2} |\beta\rangle & \hat{s}_y |\alpha\rangle &= \frac{i}{2} |\beta\rangle & \hat{s}_z |\alpha\rangle &= \frac{1}{2} |\alpha\rangle \\ \hat{s}_x |\beta\rangle &= \frac{1}{2} |\alpha\rangle & \hat{s}_y |\beta\rangle &= -\frac{i}{2} |\alpha\rangle & \hat{s}_z |\beta\rangle &= -\frac{1}{2} |\beta\rangle. \end{aligned} \quad (24)$$

The expectation value of a symmetric sum of Hermitian one-electron operators of the form $h_1 = \sum_i^N h(i)$ for an antisymmetric wave function $|\Psi\rangle$ can be written in terms of the corresponding one-electron reduced density matrix (1-RDM). In the case of the one-electron part of eqn. (23), one can make use of the appropriate relations of eqn. (24) and integrate over the spin coordinates to obtain

$$\begin{aligned}
\langle \Psi | \sum_i^N \hat{s}_i^2 | \Psi \rangle &= \sum_{\sigma, \sigma'}^{\alpha, \beta} \int [\hat{s}_x^2(s_1) + \hat{s}_y^2(s_1) + \hat{s}_z^2(s_1)] \rho^{\sigma\sigma'}(\vec{r}'_1; \vec{r}_1) \Big|_{\vec{x}'_1 = \vec{x}_1} d\vec{x}_1 = \\
&\frac{3}{4} \sum_{\sigma}^{\alpha, \beta} \int \rho^{\sigma\sigma}(\vec{r}_1; \vec{r}_1) d\vec{r}_1 \equiv \frac{3}{4} \int [\rho^{\alpha}(\vec{r}_1) + \rho^{\beta}(\vec{r}_1)] d\vec{r}_1 = \frac{3}{4} \int \rho(\vec{r}_1) d\vec{r}_1
\end{aligned} \tag{25}$$

where $\vec{x} = (\vec{r}, s)$ stands for the spatial and spin coordinates of the electron.

In the case of a sum of two-electron operators, the expectation value can be expressed quite analogously through the second-order reduced density matrix (2-RDM)

$$\langle \Psi | \sum_{i \neq j}^N \hat{h}(i, j) | \Psi \rangle = \sum_{\substack{\sigma'_1, \sigma'_2 \\ \sigma_1, \sigma_2}}^{\alpha, \beta} \iint \hat{h}(\vec{x}_1, \vec{x}_2) \rho_2^{\sigma'_1 \sigma'_2 \sigma_1 \sigma_2}(\vec{r}'_1, \vec{r}'_2; \vec{r}_1, \vec{r}_2) \Big|_{\substack{\vec{x}'_1 = \vec{x}_1 \\ \vec{x}'_2 = \vec{x}_2}} d\vec{x}_1 d\vec{x}_2. \tag{26}$$

Let us consider first the two-electron contribution of eqn. (23) involving \hat{s}_z -type operators. In this case, since the alpha and beta spin functions are eigenfunctions of the one-electron \hat{s}_z operators, only those terms of the 2-RDM do not vanish after integration over the spin coordinates, for which $\sigma_1 = \sigma'_1$ and $\sigma_2 = \sigma'_2$, leading to the expression

$$\begin{aligned}
\langle \Psi | \sum_{i \neq j}^N \hat{s}_z(i) \hat{s}_z(j) | \Psi \rangle &= \sum_{\substack{\sigma'_1, \sigma'_2 \\ \sigma_1, \sigma_2}}^{\alpha, \beta} \iint \hat{s}_z(s_1) \hat{s}_z(s_2) \rho_2^{\sigma'_1 \sigma'_2 \sigma_1 \sigma_2}(\vec{r}'_1, \vec{r}'_2; \vec{r}_1, \vec{r}_2) \Big|_{\substack{\vec{x}'_1 = \vec{x}_1 \\ \vec{x}'_2 = \vec{x}_2}} d\vec{x}_1 d\vec{x}_2 = \\
&= \frac{1}{4} \iint \rho_2^{\alpha\alpha\alpha\alpha}(\vec{r}_1, \vec{r}_2; \vec{r}_1, \vec{r}_2) d\vec{r}_1 d\vec{r}_2 + \frac{1}{4} \iint \rho_2^{\beta\beta\beta\beta}(\vec{r}_1, \vec{r}_2; \vec{r}_1, \vec{r}_2) d\vec{r}_1 d\vec{r}_2 \\
&\quad - \frac{1}{4} \iint \rho_2^{\alpha\beta\alpha\beta}(\vec{r}_1, \vec{r}_2; \vec{r}_1, \vec{r}_2) d\vec{r}_1 d\vec{r}_2 - \frac{1}{4} \iint \rho_2^{\beta\alpha\beta\alpha}(\vec{r}_1, \vec{r}_2; \vec{r}_1, \vec{r}_2) d\vec{r}_1 d\vec{r}_2.
\end{aligned} \tag{27}$$

As for the terms involving either \hat{s}_x - or \hat{s}_y -type operators, each such operator flips the spin function on which it acts; therefore only those terms of the 2-RDM do not vanish upon integration

over the spin coordinates, for which $\sigma_1 \neq \sigma'_1$ and $\sigma_2 \neq \sigma'_2$:

$$\begin{aligned} \langle \Psi | \sum_{i \neq j}^N \hat{s}_x(i) \hat{s}_x(j) | \Psi \rangle &= \sum_{\substack{\alpha, \beta \\ \sigma'_1, \sigma'_2 \\ \sigma_1, \sigma_2}} \iint \hat{s}_x(s_1) \hat{s}_x(s_2) \rho_2^{\sigma'_1 \sigma'_2 \sigma_1 \sigma_2}(\vec{r}'_1, \vec{r}'_2; \vec{r}_1, \vec{r}_2) \Big|_{\substack{\vec{x}'_1 = \vec{x}_1 \\ \vec{x}'_2 = \vec{x}_2}} d\vec{x}_1 d\vec{x}_2 = \\ &= \frac{1}{4} \iint \rho_2^{\alpha \beta \beta \alpha}(\vec{r}_1, \vec{r}_2; \vec{r}_1, \vec{r}_2) d\vec{r}_1 d\vec{r}_2 + \frac{1}{4} \iint \rho_2^{\beta \alpha \alpha \beta}(\vec{r}_1, \vec{r}_2; \vec{r}_1, \vec{r}_2) d\vec{r}_1 d\vec{r}_2. \end{aligned} \quad (28)$$

It is easy to see that exactly the same terms originate from the contribution of the \hat{s}_y -type operator.

Adding up eqns. (25), (27) and twice (28) one obtains

$$\begin{aligned} \langle \hat{S}^2 \rangle &= \frac{3}{4} \int \rho(\vec{r}_1; \vec{r}_1) d\vec{r}_1 + \frac{1}{4} \iint \rho_2^{\alpha \alpha \alpha \alpha}(\vec{r}_1, \vec{r}_2; \vec{r}_1, \vec{r}_2) d\vec{r}_1 d\vec{r}_2 + \frac{1}{4} \iint \rho_2^{\beta \beta \beta \beta}(\vec{r}_1, \vec{r}_2; \vec{r}_1, \vec{r}_2) d\vec{r}_1 d\vec{r}_2 \\ &- \frac{1}{4} \iint \rho_2^{\alpha \beta \alpha \beta}(\vec{r}_1, \vec{r}_2; \vec{r}_1, \vec{r}_2) d\vec{r}_1 d\vec{r}_2 - \frac{1}{4} \iint \rho_2^{\beta \alpha \beta \alpha}(\vec{r}_1, \vec{r}_2; \vec{r}_1, \vec{r}_2) d\vec{r}_1 d\vec{r}_2 \\ &+ \frac{1}{2} \iint \rho_2^{\alpha \beta \beta \alpha}(\vec{r}_1, \vec{r}_2; \vec{r}_1, \vec{r}_2) d\vec{r}_1 d\vec{r}_2 + \frac{1}{2} \iint \rho_2^{\beta \alpha \alpha \beta}(\vec{r}_1, \vec{r}_2; \vec{r}_1, \vec{r}_2) d\vec{r}_1 d\vec{r}_2. \end{aligned} \quad (29)$$

Moreover, since the 2-RDM satisfies

$$\rho_2^{\sigma_1 \sigma_2 \sigma_1 \sigma_2}(\vec{r}_1, \vec{r}_2; \vec{r}_1, \vec{r}_2) = -\rho_2^{\sigma_1 \sigma_2 \sigma_2 \sigma_1}(\vec{r}_1, \vec{r}_2; \vec{r}_2, \vec{r}_1) \quad (30)$$

one can add and subtract the terms $\frac{1}{2} \iint \rho_2^{\alpha \alpha \alpha \alpha}(\vec{r}_1, \vec{r}_2; \vec{r}_1, \vec{r}_2) d\vec{r}_1 d\vec{r}_2$ and $\frac{1}{2} \iint \rho_2^{\beta \beta \beta \beta}(\vec{r}_1, \vec{r}_2; \vec{r}_1, \vec{r}_2) d\vec{r}_1 d\vec{r}_2$ to eqn. (29) and make use of eqn. (30) to obtain a final formula for $\langle \hat{S}^2 \rangle$ conveniently expressed in terms of the spinless first- and second-order density matrices as

$$\langle \hat{S}^2 \rangle = \frac{3}{4} \int \rho(\vec{r}_1; \vec{r}_1) d\vec{r}_1 - \frac{1}{4} \iint \rho_2(\vec{r}_1, \vec{r}_2; \vec{r}_1, \vec{r}_2) d\vec{r}_1 d\vec{r}_2 - \frac{1}{2} \iint \rho_2(\vec{r}_1, \vec{r}_2; \vec{r}_2, \vec{r}_1) d\vec{r}_1 d\vec{r}_2 \quad (31)$$

where

$$\begin{aligned} \rho_2(\vec{r}_1, \vec{r}_2; \vec{r}_1, \vec{r}_2) &= \rho_2^{\alpha \alpha \alpha \alpha}(\vec{r}_1, \vec{r}_2; \vec{r}_1, \vec{r}_2) + \rho_2^{\beta \beta \beta \beta}(\vec{r}_1, \vec{r}_2; \vec{r}_1, \vec{r}_2) + \rho_2^{\alpha \beta \alpha \beta}(\vec{r}_1, \vec{r}_2; \vec{r}_1, \vec{r}_2) \\ &+ \rho_2^{\beta \alpha \beta \alpha}(\vec{r}_1, \vec{r}_2; \vec{r}_1, \vec{r}_2). \end{aligned} \quad (32)$$

AII. 3D-space analysis

In the classical Hilbert-space atomic partition each atom is identified by its nucleus and the subspace of the basis atomic orbitals centered on it. In the 3D-space analysis the atom is identified by a region of the physical space or atomic domain (and its nucleus, of course). If the atomic domains are disjoint, then the decomposition of a physical quantity into atomic contributions can be simply carried out by integration over the corresponding atomic domains Ω_A as

$$\begin{aligned}\int f(\vec{r})d\vec{r} &= \sum_A \int_{\Omega_A} f(\vec{r})d\vec{r} \\ \int f(\vec{r}_1, \vec{r}_2)d\vec{r}_1d\vec{r}_2 &= \sum_{A,B} \int_{\Omega_A} \int_{\Omega_B} f(\vec{r}_1, \vec{r}_2)d\vec{r}_1d\vec{r}_2,\end{aligned}\quad (33)$$

where one can see that a one and two-electron quantities quite naturally decompose into one-center and one- and two-center contributions, respectively.

One may, however, consider also so called “fuzzy” atomic domains, having no strict boundaries. In order to treat the most different schemes in a common framework, one can introduce a non-negative weight function $w_A(\vec{r})$ for each atom and each point of the 3D space satisfying the requirement

$$\sum_A w_A(\vec{r}) = 1 \quad (34)$$

In the case of the “fuzzy” atoms, the value of $w_A(\vec{r})$ is large in the vicinity of the nucleus of atom A and quickly becomes negligible outside. In the special case of disjoint atomic domains, such as those of Bader’s Atoms in Molecules theory,¹⁵ $w_A(\vec{r}) = 1$ for points inside the atomic domain of A and $w_A(\vec{r}) = 0$ outside of it.

Then, the decomposition of a physical quantity into atomic contributions can be performed by inserting the identity (34) one or two times for the one and two-electron integrals, respectively

$$\begin{aligned}\int f(\vec{r})d\vec{r} &= \sum_A \int w_A(\vec{r})f(\vec{r})d\vec{r} \\ \int f(\vec{r}_1, \vec{r}_2)d\vec{r}_1d\vec{r}_2 &= \sum_{A,B} \iint w_A(\vec{r}_1)w_B(\vec{r}_2)f(\vec{r}_1, \vec{r}_2)d\vec{r}_1d\vec{r}_2.\end{aligned}\quad (35)$$

In the past we have made use of the simplest Becke’s atoms¹⁶ to show how several quantities such as bond orders, overlap populations or energy components can be obtained for “fuzzy” atoms.²⁵ The shape of such Becke atoms is determined by a “stiffness parameter” and by a set of fixed atomic radii that define the relative size of the atomic basins. One can also use the position of the minima of the total density along the internuclear axis²⁶ for each pair of atoms to determine the ratio of the atomic radii. Such a scheme, referred as Becke- ρ in ref. 20 can be considered as a good and efficient adaptation of some ideas of Bader’s theory.

Hirshfeld²¹ defined another way to partition the molecular space using promolecular densities. Lately, the iterative-Hirshfeld approach,²² improving over classical Hirshfeld’s, has been suggested. In both schemes the atomic weight of atom A at a given point in the space is determined by the ratio

$$w_A(\vec{r}) = \frac{\rho_A^0(\vec{r})}{\sum_B \rho_B^0(\vec{r})} \quad (36)$$

where $\rho_A^0(\vec{r})$ represents a promolecular density of the atom A .

In the classical Hirshfeld the resulting shape of the atoms in the molecule are strongly dependent on the choice of the promolecular state of the atom. The improved Hirshfeld-Iterative scheme corrects this problem by an iterative process to obtain promolecular atomic densities that integrate to the same (usually fractional) number of electrons as do the atoms in the molecule.

We have made use of all “fuzzy” atom definitions mentioned above, as well as Bader’s atomic domains, to obtain the one- and two-center contributions of $\langle \hat{S}^2 \rangle$. In this paper we show that different atomic definitions induce only minor qualitative differences in the results.

Instead of using the formulae (35) to the first order density matrix, the spin-density matrix or

the cumulant, one can express them in terms of the molecular (or natural) orbitals as

$$\rho(\vec{r}; \vec{r}') = \sum_{ij} D_{ij} \phi_j^*(\vec{r}) \phi_i(\vec{r}'), \quad (37)$$

$$\rho^s(\vec{r}, \vec{r}') = \sum_{ij} P_{ij}^s \phi_j^*(\vec{r}) \phi_i(\vec{r}'), \quad (38)$$

$$\Gamma_2(\vec{r}_1, \vec{r}_2; \vec{r}'_1, \vec{r}'_2) = \sum_{ijkl} \Gamma_{ijkl} \phi_k^*(\vec{r}_1) \phi_l^*(\vec{r}_2) \phi_i(\vec{r}'_1) \phi_j(\vec{r}'_2) \quad (39)$$

and reduce the integrations to calculating the atomic overlap matrix

$$S_{ij}^A = \int w_A(\vec{r}) \phi_i^*(\vec{r}) \phi_j(\vec{r}) d\vec{r}. \quad (40)$$

in the basis of molecular orbitals.

AIII. The H₂ model

A highly desirable requirement for the decomposition scheme of $\langle \hat{S}^2 \rangle$ is that the one-center contributions should be non-negative. Let us consider the H₂ molecule with minimal basis at the full-CI level. The molecular orbitals are determined from symmetry considerations and the ground state wave function can be written as $\Psi = \sqrt{1 - c_1^2} \Psi_0 + c_1 \Psi_1$, where Ψ_0 and Ψ_1 are the ground-state and double-excited Slater determinants, respectively. For this model system, taking $S_{12}^A = -S_{12}^B = \frac{1}{2}$ for the atomic overlap matrix element (the exact value at the dissociation limit), eq. (16) can be expressed as

$$\langle \hat{S}^2 \rangle_A = 4ac_1^2(1 - c_1^2) + \left(\frac{3}{2} - 2a \right) c_1 \sqrt{1 - c_1^2}. \quad (41)$$

In Figure 2 we plot $\langle \hat{S}^2 \rangle_A$ vs. c_1 for several values of the parameter a . At the dissociation limit of the ground state, $\left(c_1 = -\sqrt{\frac{1}{2}} \right)$ all curves tend to the proper value $\langle \hat{S}^2 \rangle_A = 3/4$. Similarly, all curves predict zero local spin for Hartree-Fock wave functions ($c_1 = 0$). However, only for the

special case of $a = 3/4$ are all values of $\langle \hat{S}^2 \rangle_A$ positive for any value of the mixing coefficient c_1 .

Another interesting property in the case of $a = 3/4$ is that the second term in eq. (41)—which is linear in the coefficient c_1 as c_1 tends to zero—vanishes. Note that this is the leading term in singlet systems that are well-described with a single closed-shell determinant wave function, as the first term on the r.h.s. would be quadratic in c_1 . This shows that very small local-spin values are thus obtained for genuine diamagnetic molecules, if the preferred value $a=3/4$ is used, in accordance with the physical expectations.

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Tables and Figures

Table 1: CASSCF(2,4) atomic $\langle \hat{S}^2 \rangle_A$ values for the H₂ molecule at optimized geometries for several atomic definitions and values of the parameter a .

Atom in Molecule	a	cc-pVDZ	cc-pVTZ	cc-pVQZ
Becke	0	0.109	0.111	0.109
	3/8	0.072	0.073	0.073
	1/2	0.059	0.060	0.061
	3/4	0.034	0.034	0.036
Hirshfeld	0	0.122	0.124	0.122
	3/8	0.079	0.080	0.080
	1/2	0.064	0.065	0.066
	3/4	0.035	0.036	0.038
QTAIM	0	0.059	0.060	0.058
	3/8	0.044	0.044	0.045
	1/2	0.039	0.039	0.040
	3/4	0.028	0.029	0.031

Table 2: Comparison of the one- and two-center local-spin values for the NO molecule at the UHF/cc-pVTZ level using different Atoms in Molecules definitions and $a=3/4$.

Molecule	Atom/ Atom pair	Becke	Becke- ρ	Hirshfeld	Hirshfeld Iterative	QTAIM
NO	N	0.540	0.497	0.531	0.527	0.547
	O	0.232	0.272	0.241	0.244	0.229
	N, O	-0.003	-0.002	-0.002	-0.002	-0.005

Table 3: One- and two-center local-spin values for singlet systems at the CISD/6-31g** level for different values of the parameter a .

Molecule	Atom/ Atom pair	$a = 0$	$a = 3/8$	$a = 1/2$	$a = 3/4$
H ₂	H	0.054	0.041	0.037	0.029
	H,H	-0.054	-0.041	-0.037	-0.029
Li ₂	Li	0.091	0.116	0.125	0.141
	Li,Li	-0.091	-0.116	-0.125	-0.141
Be ₂	Be	0.122	0.136	0.141	0.150
	Be,Be	-0.122	-0.136	-0.141	-0.150
HF	H	0.030	0.024	0.022	0.018
	F	0.030	0.024	0.022	0.019
	H,F	-0.030	-0.024	-0.022	-0.019
H ₂ O	H	0.029	0.025	0.023	0.021
	O	0.072	0.053	0.046	0.034
	O,H	-0.036	-0.026	-0.023	-0.017
	H,H	0.007	0.002	0.000	-0.004
NH ₃	N	0.115	0.083	0.073	0.051
	H	0.030	0.026	0.025	0.023
	N,H	-0.038	-0.028	-0.024	-0.017
	H,H	0.004	0.001	0.000	-0.003
CH ₄	C	0.177	0.124	0.106	0.071
	H	0.039	0.033	0.030	0.026
	C,H	-0.044	-0.031	-0.027	-0.018
	H,H	0.002	-0.001	-0.001	-0.003
C ₂ H ₆	C	0.198	0.124	0.100	0.051
	H	0.038	0.031	0.029	0.024
	C,C	-0.057	-0.036	-0.029	-0.015
	C,H	-0.044	-0.028	-0.023	-0.013
	C...H	-0.003	-0.001	0.000	0.001
	H,H	0.002	0.000	-0.001	-0.003
C ₂ H ₄	H...H	0.003	0.000	-0.001	-0.003
	C	0.261	0.169	0.138	0.077
	H	0.037	0.032	0.030	0.026
	C,C	-0.175	-0.109	-0.087	-0.044
	C,H	-0.037	-0.027	-0.024	-0.017
	C...H	-0.007	-0.003	-0.002	0.000
	H,H	0.002	-0.001	-0.002	-0.004
	H...H _{cis}	0.003	0.000	-0.001	-0.003
	H...H _{trans}	0.001	-0.001	-0.001	-0.002
	C ₂ H ₂	C	0.339	0.215	0.173
H		0.033	0.029	0.028	0.026
C,C		-0.304	-0.185	-0.146	-0.067
C,H		-0.027	-0.026	-0.026	-0.025
C...H		-0.008	-0.003	-0.002	0.001
H,H		0.003	0.000	0.000	-0.002

Table 4: One- and two-center local-spin values for doublet systems at the UHF/cc-pVTZ level for different values of the parameter a .

Molecule	Atom/ Atom pair	$\langle \hat{S}^2 \rangle$	$a = 0$	$a = 3/8$	$a = 1/2$	$a = 3/4$
OH	O	0.756	0.712	0.726	0.731	0.740
	H		0.001	0.015	0.019	0.028
	O,H		0.021	0.008	0.003	-0.006
NO	N	0.767	0.475	0.449	0.370	0.317
	O		0.087	0.166	0.192	0.244
	N,O		0.155	0.076	0.050	-0.002
CN	C	1.075	1.084	1.147	1.168	1.211
	N		0.199	0.262	0.283	0.325
	C,N		-0.104	-0.167	-0.188	-0.230
NH ₂	N	0.759	0.649	0.681	0.691	0.712
	H		0.001	0.018	0.024	0.035
	N,H		0.026	0.010	0.005	-0.005
	H,H		0.001	0.000	0.000	0.000
CH	C	1.106	0.955	1.000	1.015	1.045
	H		0.007	0.052	0.067	0.098
	C,H		0.072	0.027	0.012	-0.018
CH ₃	C	0.761	0.544	0.601	0.620	0.658
	H		0.003	0.025	0.032	0.046
	C,H		0.033	0.014	0.007	-0.005
	H,H		0.002	0.001	0.000	-0.001

Table 5: One- and two-center local-spin values for triplet systems at the UHF/cc-pVTZ level for different values of the parameter a .

Molecule	Atom/ Atom pair	$\langle \hat{S}^2 \rangle$	$a = 0$	$a = 3/8$	$a = 1/2$	$a = 3/4$
Li ₂	Li	1.988	0.497	0.683	0.745	0.870
	Li,Li		0.497	0.311	0.248	0.124
O ₂	O	2.042	0.540	0.713	0.770	0.886
	O,O		0.481	0.308	0.250	0.135
NF	N	2.024	1.607	1.681	1.706	1.756
	F		0.030	0.104	0.129	0.179
	N,F		0.193	0.119	0.094	0.044
NH	N	2.015	1.846	1.885	1.898	1.925
	H		0.005	0.044	0.057	0.084
	N,H		0.082	0.043	0.030	0.003
C ₂	C	2.009	0.677	0.735	0.754	0.793
	C,C		0.327	0.269	0.250	0.211
CH ₂	C	2.016	1.612	1.696	1.724	1.780
	H		0.006	0.052	0.067	0.097
	C,H		0.095	0.053	0.039	0.010
	H,H		0.006	0.003	0.002	0.000

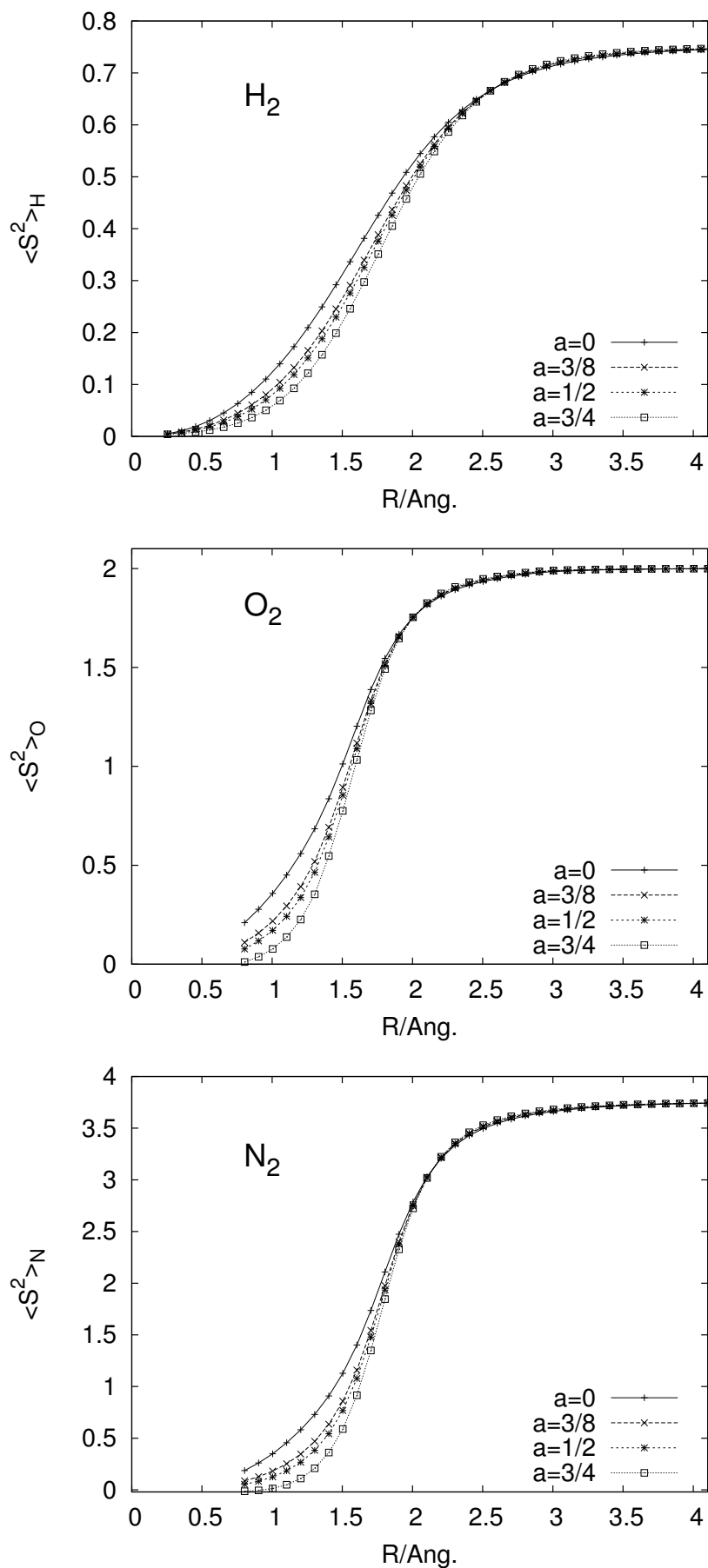


Figure 1: Change of $\langle \hat{S}^2 \rangle_A$ along the dissociation of H₂, N₂ and O₂ molecules calculated at the full valence CASSCF level with cc-pVTZ basis set for different values of the parameter a .

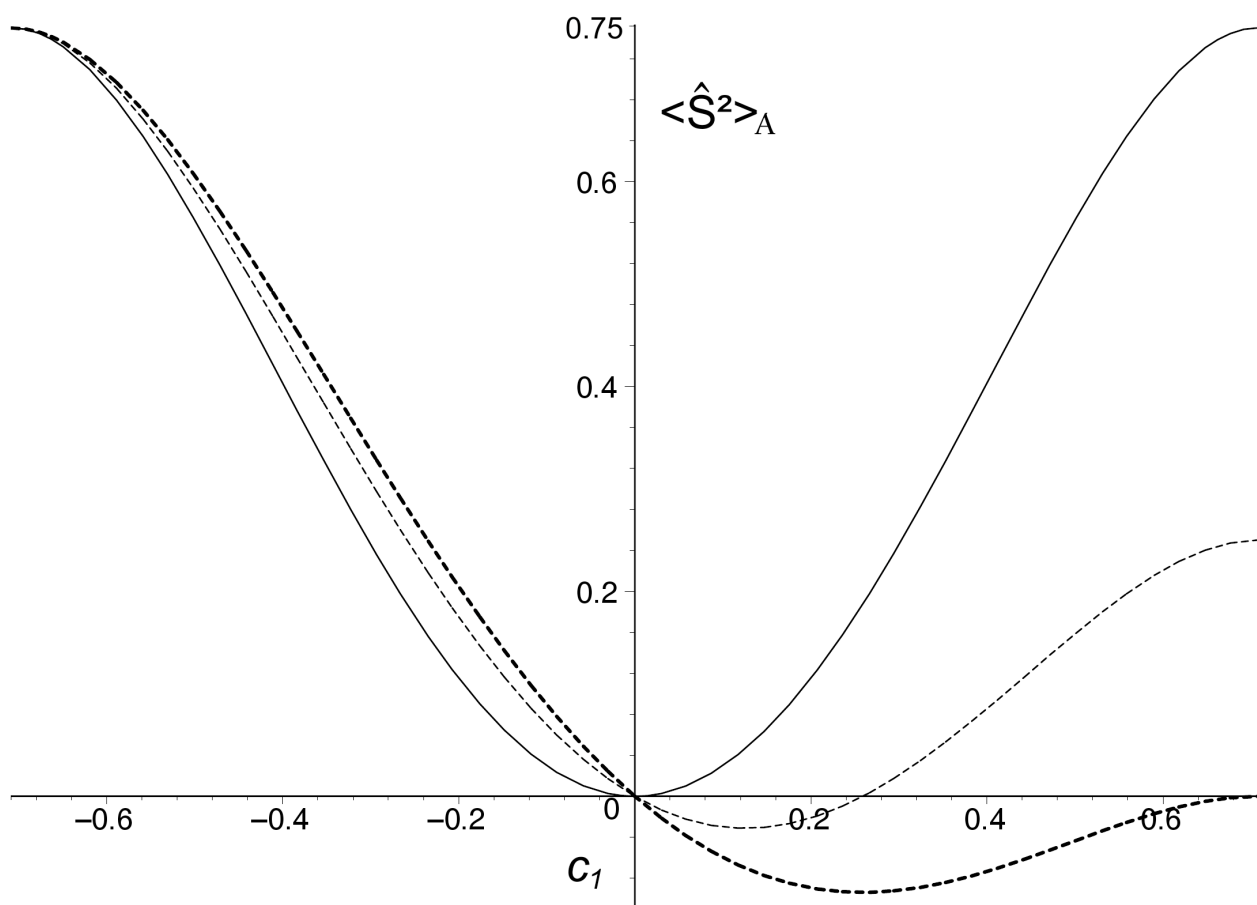


Figure 2: Change of $\langle \hat{S}^2 \rangle_A$ with respect to the mixing coefficient c_1 for a 2x2 FCI H_2 model for different values of parameter a . Solid line $a = 3/4$, dotted line $a = 1/2$, thick dotted line $a = 3/8$.