

# Local spin and open quantum systems: clarifying misconceptions, unifying approaches

A. Martín Pendás\* and E. Francisco\*

*Departamento de Química Física y Analítica. Facultad de Química. Universidad de Oviedo. 33006 Oviedo. Spain.*

E-mail: [ampendas@uniovi.es](mailto:ampendas@uniovi.es)

## Abstract

The theory of open quantum systems (OQSs) is applied to partition the squared spin operator into fragment (local spin) and interfragment (spin-coupling) contributions in a molecular system. An atomic or fragment subsystem is described by a quantum mechanical mixed density operator composed of sectors, characterized by different integer number of electrons that appear with specific probabilities. The fragment spin operators coincide with those defined by Clark and Davidson in their seminal paper on local spins (*J. Chem. Phys.* 2001, **115**, 7382). OQSs provide a unique way to rationalize the non-zero values of local spins found in closed-shell molecules, a fact that has led to propose a large number of modified definitions, which we show suffer from inconsistencies. The OQS viewpoint makes it easy to build models for localized and itinerant spins. These models are used to classify possible local spin arrangements. The role of electron correlation is also studied through the analysis of the Hubbard Hamiltonian in small chains. Local spins result from a game played differently by localized and delocalized electrons. A number of examples exemplifying the ability of the OQS local spin perspective to uncover simple chemical patterns is examined.

# 1 Introduction

No other conceptual framework in the history of human thought has been interpreted in so many mutually exclusive ways as Quantum Mechanics (QM).<sup>1,2</sup> In a way, interpreting QM has become a discipline on its own, and although most practicing physicists simply take Copenhagen’s interpretation for granted and apply the *take the money and run* aphorism, trying to understand what lies deep in a wavefunction is still a way of making a living in Physics. Applying QM to Chemistry adds a new source of noise to this situation. Chemists think locally in real space. However, as soon as two otherwise isolated fragments start to interact with each other locality disappears in the overall state vector. Atoms dissolve on forming molecules, and molecules dissolve on forming molecular aggregates. Yet, chemists know that atoms, functional groups and other entities like bonds or lone pairs persist in molecules, endowing systems with properties that can be subtly tuned.

Extracting local information from global wavefunctions is thus essential to theoretical chemistry. As in QM, many different, again mutually exclusive routes to analyze (i.e. interpret) wavefunctions have been proposed. Sooner or later, these techniques need to cope with how to decompose a quantum mechanical expectation value into its *chemical* constituents, which must be first isolated from the wavefunction. We thus partition binding or reaction energies, giving rise to energy decomposition analyses,<sup>3</sup> the number of electrons of a system into its atoms or fragments, providing what we call population analyses,<sup>4</sup> and so on. Literally dozens of techniques give different answers to these questions. Those answers are then used to guide the synthesis of new materials, for instance.<sup>5</sup>

A particularly relevant issue that has received quite a lot of attention in recent years is the partition of the total electronic spin of a system into fragment and interfragment contributions.<sup>6-18</sup> Although maybe not immediately obvious, much of our current digital technology is based on the control of local magnetic interactions in crystals.<sup>19</sup> These have been interpreted historically through model Hamiltonians, which almost invariably deal with local (i.e. localized) spins. For instance, in the Heisenberg Hamiltonian,  $H = -\sum_{A<B} J_{AB} \hat{\mathbf{S}}_A \cdot \hat{\mathbf{S}}_B$ ,

local spins are associated to magnetic centers that interact in a pairwise manner. In Chemistry, the presence of localized spins leads to radicals, which have been used in very many different ways. When the total spin of the system vanishes,  $\langle \hat{S}^2 \rangle = 0$ , and with it the spin density  $\rho_s(\mathbf{r})$  at each point in space, a partitioning technique for the spin-square operator  $\hat{S}^2$  becomes urgent. This is the case of e.g. antiferromagnets in solid state physics, or of singlet diradicals or polyradicals in chemistry.

Clear as this need is, it was only with the beginning of this century that the problem was first attacked. In a set of papers, Clark and Davidson (CD),<sup>6-8,12</sup> showed how to rigorously partition the electron spin into local contributions by means of projection operators. Aside from the arbitrariness of the atomic projectors, their approach is exact, and it was initially applied with Löwdin's symmetric projections. Since then, CD local spins have been used rather commonly in the physical literature.<sup>20</sup> In chemistry, however, the CD approach was soon criticized,<sup>9</sup> for some extra requirements for a spin partition to be physically meaningful were added that were not satisfied by the local spins of CD. In particular, it was suggested that local atomic spins  $\langle \hat{S}_A^2 \rangle$  of closed-shell wavefunctions should be zero. After all, how could the atomic local spin of an otherwise perfectly diamagnetic single molecule get a non-zero value? Little later, Mayer<sup>11,13,14,16</sup> insisted on this shortcoming of Clark and Davidson approach and proposed an alternative definition that enforced zero local spins for restricted single-determinant wavefunctions (SDW). A rapid succession of proposals followed. Alcoba et al<sup>15,21</sup> generalized Mayer's approach to correlated wavefunctions, but forcing zero local atomic spins even at dissociation, Mayer and Matito<sup>14</sup> solved this inconsistency, and in a final round, Ramos-Cordoba et al (RC)<sup>17</sup> proposed a set of four conditions that any theory of local spins should satisfy. Namely, (i) closed-shell restricted wavefunctions should lead to zero local spins; (ii) local spins should behave properly in asymptotic (i.e. dissociation) limits, tending to the  $\langle \hat{S}^2 \rangle$  value of the isolated fragments; (iii) correlated formulas should tend to single-determinant ones in the absence of correlation; (iv) local spins of one-electron systems should be proportional to the electron population of the center considered. Ramos-Cordoba

et al also showed that a one-parameter linear combination of the expressions proposed by CD and Alcoba et al leads to a continuous family of local spins, from which only one member satisfies the four conditions, together with a non-negativity constraint, simultaneously. Since then, this proposal has been used repeatedly to deal with the quantification of di- and poly-radical character in molecules,<sup>22,23</sup> etc.

Here we show that regardless the choice in the atomic projections, the CD local spins provide a fully rigorous decomposition of  $\langle \hat{S}^2 \rangle$ . To show this, we start by considering atoms in molecules as open quantum systems (OQSs), characterized by well-defined subsystem density operators obtained by tracing out the degrees of freedom of the rest of the system. An atom-in-the-molecule has a fluctuating number of electrons (each possibility gives rise to a so-called sector, equipped with its own set of density matrices). The CD local spins turn out to be weighted sums of squared-spin expectation values that run over all possible sectors and sector spin states.

As an easy to understand example, the H atom in a H<sub>2</sub> molecule *cannot* have a zero local spin. At the single-determinant level, with any symmetry-preserving atomic partitioning, we find either 0, 1, or 2 electrons in it with probabilities 1/4, 1/2, and 1/4, respectively.<sup>24</sup> This results from the 50/50 covalent/ionic mixing enforced by the wavefunction structure. Since  $S$  in these three situations is forced to be 0, 1/2 and 0, respectively, *this leads, inevitably*, to  $\langle \hat{S}_H^2 \rangle = 1/4 \times 0(0 + 1) + 1/2 \times 1/2(1/2 + 1) + 1/4 \times 0(0 + 1) = 3/8$ , which is the CD result. There is no inconsistency here. Much on the contrary, what we find inconsistent is to assign a null local spin value to this H atom. This requisite is summarized by Mayer’s reasoning that the absence of *free* spins *should* lead to null local spins for single-determinants. However, this ignores that the electrons of a Lewis pair delocalize. Actually, they delocalize *freely* over the two atoms for a pure covalent pair. Since we *can* find an isolated electron in our H atom-in-the-molecule, its local spin is not null.

Local spins are thus non-vanishing in general in closed-shell molecules. We will fully unveil their relation to covalency and to the localization and delocalization of electrons,

showing that the OQS point of view tells a fully consistent, rigorous story. This by no means implies that Ramos-Cordoba et al formalism is not useful. In fact, it is compatible with our present findings once we understand where the non-vanishing spins are hidden in their proposal.

The OQS perspective sheds much light on how spin and spin interactions evolve as electrons delocalize and as electron correlation becomes significant. The Heisenberg-like image of a magnetic material, for instance, is rather obvious in localized cases, dissolving as the magnetic electrons delocalize. We think that the Hubbard model may be very useful to identify several local spin regimes, and offer a couple of examples with it.

We start by presenting Clark and Davidson projectors, as well as Löwdin's density matrix formalism. We then turn to show how the sequence of requirements imposed by Mayer led to a number of algebraic operations which are not legitimate in our opinion. In the end, these are the basis of Ramos-Cordoba et al formula, which we also show to provide non-physical results in cases not considered up to now. Then we briefly review the real space open systems formalism, and demonstrate how the CD local spin acquires its full sense after it. A number of academic examples is then examined.

## 2 Local spin formulations

Let us briefly consider the different formulations of the local spin concept, starting from the projection formalism proposed by Clark and Davidson.<sup>6</sup> The total vector spin operator of an  $N$  electron system is defined as the sum of the spins for each electron,  $\hat{\mathbf{S}} = \sum_i^N \hat{\mathbf{S}}_i$ . Now consider a one-electron projection for each atom or fragment  $A$  in which we divide the system, such that  $\sum_A \hat{P}^A = \hat{1}$  and  $\hat{P}^A \hat{P}^B = \delta_{AB} \hat{P}^A$ , and assign a fragment spin operator as  $\hat{\mathbf{S}}_A = \sum_i^N \hat{\mathbf{S}}_i \hat{P}_i^A$ . With this, it is easy to show that  $\hat{\mathbf{S}}_A$  is a proper angular momentum

operator, and with it,

$$\hat{S}^2 = \sum_{A,B} \hat{\mathbf{S}}_A \cdot \hat{\mathbf{S}}_B = \sum_A \hat{S}_A^2 + \sum_A \sum_{B \neq A} \hat{\mathbf{S}}_A \cdot \hat{\mathbf{S}}_B, \quad (1)$$

so that the squared spin operator is a sum of intra- and inter-fragment terms, the latter measuring the coupling of the spins associated to each pair of fragments. To compute the expectation value of each of these terms, we notice that ( $\hat{\mathbf{S}}_A \cdot \hat{\mathbf{S}}_A = \hat{S}_A^2$ )

$$\hat{\mathbf{S}}_A \cdot \hat{\mathbf{S}}_B = \sum_{i,j} \hat{\mathbf{S}}_i \cdot \hat{\mathbf{S}}_j \hat{P}_i^A \hat{P}_j^B = \delta_{AB} \sum_i \hat{S}_i^2 \hat{P}_i^A + \sum_i \sum_{j \neq i} \hat{\mathbf{S}}_i \cdot \hat{\mathbf{S}}_j \hat{P}_i^A \hat{P}_j^B, \quad (2)$$

which is a sum of one- and two-electron operators. Using the one- and two-particle reduced density matrices  $\rho_1$  and  $\rho_2$ ,

$$\langle \hat{\mathbf{S}}_A \cdot \hat{\mathbf{S}}_B \rangle = \frac{3}{4} \delta_{AB} \text{Tr}(\hat{P}_1^A \rho_1) + \text{Tr}(\hat{P}_1^A \hat{P}_2^B \hat{\mathbf{S}}_1 \cdot \hat{\mathbf{S}}_2 \rho_2). \quad (3)$$

In the above expression we have used the fact that the spin of each electron is  $s = 1/2$ . Now it is clear that, since for any fragment partition  $\text{Tr}(\hat{P}_1^A \rho_1) = N_A$ , the fragment's electron population, the first term in Eq. 3 just adds the squares of the spins of the electrons associated to the fragment, while the second takes into account their mutual coupling.

As it can be seen, the approach up to now is completely rigorous and univocal. The only arbitrariness lies in the choice of the fragment projectors. One can use either Fock or real space approaches. For instance, if a local basis set  $\{|\mu\rangle\}$  is used to build the one-electron functions used to construct the wavefunction, then a proper Hermitian Löwdin projector can be defined by using the Löwdin-orthogonalized basis  $|\mu'\rangle = \sum_\nu |\nu\rangle S_{\nu\mu}^{-1}$ :  $\hat{P}^A = \sum_{\mu' \in A} |\mu'\rangle \langle \mu'|$ .<sup>9</sup> Any Fock projector is dependent on the details of the basis set and the way in which one-electron functions are constructed. In exhaustive real space partitionings with fragment regions satisfying  $\bigcup_A \Omega_A = \mathcal{R}^3$ , the projector is simply equal to the standard Heaviside-like indicator function or atomic weight  $\hat{P}^A(\mathbf{r}) = \omega_A(\mathbf{r})$ , where  $\omega_A(\mathbf{r})$  is equal to

one within the  $A$  region and zero outside. Real space projectors lead to expectation values invariant under orbital transformations, and should be favoured. For this reason we will use the following general notation, which is explicit in the case of real space partitions:

$$\begin{aligned}\mathrm{Tr}(\hat{P}_1^A \hat{\rho}_1) &\equiv \int_A \hat{\rho}(\mathbf{x}; \mathbf{x}')|_{\mathbf{x}' \rightarrow \mathbf{x}} d\mathbf{x} \quad \text{and} \\ \mathrm{Tr}(\hat{P}_1^A \hat{P}_2^B \hat{g}_{1,2} \rho_2) &\equiv \int_A \int_B \hat{g}_{\rho_2}(\mathbf{x}_1, \mathbf{x}_2; \mathbf{x}'_1, \mathbf{x}'_2)|_{\substack{\mathbf{x}'_1 \rightarrow \mathbf{x}_1 \\ \mathbf{x}'_2 \rightarrow \mathbf{x}_2}} d\mathbf{x}_1 d\mathbf{x}_2,\end{aligned}$$

where  $\mathbf{x} \equiv \mathbf{r}\sigma$  gathers spin-space electron coordinates, while  $\mathbf{r}$  refers to the spatial-only components. We will use in our examples the partition provided by the quantum theory of atoms in molecules of Bader and coworkers,<sup>25</sup> but our conclusions are completely general.

It only remains to compute the effect of the  $\hat{\mathbf{S}}_1 \cdot \hat{\mathbf{S}}_2$  operator on the two-particle density matrix (2RDM). As we will be showing, several unfortunate misinterpretations around this step lie at the root of the very many different routes taken by different authors. In a collinear spin regime, it was Dirac<sup>26</sup> in 1929 who showed, with the help of very simple arguments, that for two different electron spins,  $\hat{\mathbf{S}}_1 \cdot \hat{\mathbf{S}}_2 = (2\hat{p}_{12}^\sigma - 1)/4$ , where  $\hat{p}_{12}^\sigma$  is a permutation operator that exchanges only the electron spin coordinates of electrons 1 and 2 (i.e. their  $S_z$  projections). It is clear that this operation acts on *pairs of electrons*. Now,

$$\hat{p}_{12}^\sigma \rho_2(\mathbf{r}_1\sigma_1, \mathbf{r}_2\sigma_2; \mathbf{r}'_1\sigma'_1, \mathbf{r}'_2\sigma'_2) = \rho_2(\mathbf{r}_1\sigma_2, \mathbf{r}_2\sigma_1; \mathbf{r}'_1\sigma'_1, \mathbf{r}'_2\sigma'_2) = -\rho_2(\mathbf{r}_2\sigma_1, \mathbf{r}_1\sigma_2; \mathbf{r}'_1\sigma'_1, \mathbf{r}'_2\sigma'_2), \quad (4)$$

where we have used the antisymmetry properties of the 2RDM. Integrating out the spin variables, we can thus write<sup>17</sup>

$$\sum_i \sum_{j \neq i} \langle \hat{\mathbf{S}}_i \cdot \hat{\mathbf{S}}_j \rangle = -\frac{1}{4} \iint \rho_2(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 - \frac{1}{2} \iint \rho_2(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}_2, \mathbf{r}_1) d\mathbf{r}_1 d\mathbf{r}_2. \quad (5)$$

Straightforward manipulation also leads to

$$\langle \hat{\mathbf{S}}_A \cdot \hat{\mathbf{S}}_B \rangle = \frac{3}{4} \delta_{AB} \int_A \rho(\mathbf{r}) d\mathbf{r} - \frac{1}{4} \int_A \int_B \{ \rho_2(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}_1, \mathbf{r}_2) + 2\rho_2(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}_2, \mathbf{r}_1) \} d\mathbf{r}_1 d\mathbf{r}_2, \quad (6)$$

which is Clark and Davidson expression written in density matrix language. Since  $\hat{\mathbf{S}}_A$  is a Hermitian operator, local spins and spin couplings satisfy all rules of well-behaved operators in QM. For instance,  $\langle S_A^2 \rangle \geq 0$ . It can be shown that (see the supporting information (SI)) for a single-determinant description of  $\text{H}_2$  with  $\Psi = |\sigma_g(1)\bar{\sigma}_g(2)|$ ,  $\langle \hat{S}_A^2 \rangle = 3/8$  and  $\langle \hat{\mathbf{S}}_A \cdot \hat{\mathbf{S}}_B \rangle = -3/8$  ( $A \neq B$ ). This fact "*makes a physical interpretation ... in terms of local spins difficult, because closed-shell molecules by definition have no spin excess at any point in space*" for Podewitz et al,<sup>27</sup> an argument which is an invalid extrapolation of the behavior of the spin density, and is a result that "*looks for me intuitively not appealing*" for Mayer.<sup>13</sup>

The path taken by Mayer<sup>11</sup> leading directly to recent local spin expressions starts from Löwdin's representation for  $\hat{S}^2$ ,<sup>28</sup>

$$\hat{S}^2 = -\frac{N(N-4)}{4} + \sum_{i<j} \hat{p}_{ij}^\sigma, \quad (7)$$

who acknowledges Dirac's paper.<sup>26</sup> The first term of this expression condenses the contribution coming from the integration to  $\mathcal{R}^3$  of  $\rho(\mathbf{r})$  in Eq. 6 ( $N \times 3/4$ ), together with the first term in the double integral of Eq. 6 ( $-N(N-1)/4$ ), that gives  $N \times 3/4 - N(N-1)/4 = -N(N-4)/4$ . It thus mixes one-particle and two-particle counts. Adding them is *legitimate* when obtaining a global expectation value, but *it is not* when using fragment projectors, since the number of intra- and inter-fragment electron pairs is not obvious and needs be computed. In other words, writing  $\hat{S}^2 = -\hat{N}^2/4 + \hat{N} + \sum_{i<j} \hat{p}_{ij}^\sigma$  as in Eq. 2 of Ref. 13 should not be allowed in a rigorous local spin definition. Doing so, some two-electron terms (which would end up in  $AB$  spin-coupling contributions) become effectively embedded in the one-electron contributions (which are necessarily absorbed in the local spin, one-center terms).

A different route was followed by Alcoba and coworkers,<sup>15</sup> who used spinless quantities such as the effectively unpaired density matrix  $u$  introduced by Takatsuka, Fueno and



Yamaguchi<sup>29</sup> and later by Staroverov and Davidson,<sup>30-32</sup>

$$u(\mathbf{r}_1; \mathbf{r}'_1) = 2\rho(\mathbf{r}_1; \mathbf{r}'_1) - \int \rho(\mathbf{r}_1; \mathbf{r}_2)\rho(\mathbf{r}_2; \mathbf{r}'_1)d\mathbf{r}_2. \quad (8)$$

The  $u$  diagonal density has been repeatedly used as a local (or global, when integrated) measure of the number of unpaired electrons, an interpretation which is made clear after an expansion in terms of spinless natural orbitals,  $u(\mathbf{r}) = \sum_i n_i(2 - n_i)\chi_i^*(\mathbf{r})\chi_i(\mathbf{r})$ . The occupation number of natural orbital  $\chi_i$  satisfies  $0 \leq n_i \leq 2$ . For unrestricted determinants with  $n_i = 0, 1, 2$ , the trace of  $u$  counts singly occupied orbitals, and the  $u(\mathbf{r})$  density the sum of the densities provided by those singly occupied functions. The properties of  $u$  have been extensively studied,<sup>31</sup> and unveil how its interpretation in terms of unpaired electrons suffers from severe shortcomings in the case of multideterminant wavefunctions. For instance, its trace can grow twice as large as the total number of electrons,  $0 \leq \text{Tr}(u) \leq 2N$ , and when partitioned into fragments, the use of  $u$  may lead to a non-integer number of unpaired electrons for a fragment in the dissociation limit. In the supporting information (SI) we also show that a CAS[2,2] description of the first  $^1\Sigma_g^+$  excited state in  $\text{H}_2$ , which at dissociation describes the pure ionic resonance  $\text{H}^+ - \text{H}^- \longleftrightarrow \text{H}^- - \text{H}^+$ , leads to one effectively unpaired electron per H atom. This results from the one-particle density matrix (1RDM) being unable to tell the sign of the linear combination  $\lambda|\sigma_g\bar{\sigma}_g| \pm \mu|\sigma_u\bar{\sigma}_u|$ , with both  $\lambda, \mu \geq 0$ . In both cases we obtain two  $n_i = 1$  natural occupations at dissociation. The state described with a minus sign dissociates to two ground state H atoms, with one unpaired electron on each H. However, the state bearing the plus sign dissociates to the ionic resonance with no unpaired electrons whatsoever on any of the two H atoms.

Since the CD partition (Eq. 6) provides non-zero local spins in restricted single determinants, Ramos-Cordoba et al<sup>17</sup> (RC) proposed to use  $u$  as a simplification tool. To that end,

the 2RDM is expanded à la Fock-Dirac,

$$\begin{aligned}\rho_2(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}'_1, \mathbf{r}'_2) &= \rho(\mathbf{r}_1; \mathbf{r}'_1)\rho(\mathbf{r}_2; \mathbf{r}'_2) - \frac{1}{2}\rho(\mathbf{r}_1; \mathbf{r}'_2)\rho(\mathbf{r}_2; \mathbf{r}'_1) \\ &- \frac{1}{2}\rho^s(\mathbf{r}_1; \mathbf{r}'_2)\rho^s(\mathbf{r}_2; \mathbf{r}'_1) + \Gamma(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}'_1, \mathbf{r}'_2),\end{aligned}\quad (9)$$

where  $\rho^s(\mathbf{r}_1; \mathbf{r}'_2) = \rho^\alpha(\mathbf{r}_1; \mathbf{r}'_2) - \rho^\beta(\mathbf{r}_1; \mathbf{r}'_2)$  is the spin-density matrix, and  $\Gamma(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}'_1, \mathbf{r}'_2)$  is the spinless cumulant. Introducing Eq. 9 into Eq. 5 one can recognize the integral in Eq. 8, which is thus used to recover  $u$  and to obtain,

$$\begin{aligned}\langle \hat{S}^2 \rangle &= \frac{3}{8} \int u(\mathbf{r}) d\mathbf{r} - \frac{1}{4} \iint [\Gamma(\mathbf{r}_1, \mathbf{r}_2) + 2\Gamma(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}_2, \mathbf{r}_1) \\ &- \frac{1}{2}\rho^s(\mathbf{r}_1; \mathbf{r}_2)\rho^s(\mathbf{r}_2; \mathbf{r}_1) - \rho^s(\mathbf{r}_1)\rho^s(\mathbf{r}_2)] d\mathbf{r}_1 d\mathbf{r}_2,\end{aligned}\quad (10)$$

with  $\Gamma(\mathbf{r}_1, \mathbf{r}_2) \equiv \Gamma(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}_1, \mathbf{r}_2)$  and  $\rho^s(\mathbf{r}) \equiv \rho^s(\mathbf{r}; \mathbf{r})$ . This expression is now subjected to fragment projection, giving rise to one- and two-center contributions. Notice that all the terms in the second integrand vanish for a closed-shell single-determinant, so that no local spins appear in this case. This procedure satisfies Mayer's condition (i). Our point, again, is that the  $u$  substitution operation just is algebraically admissible but not physically sound, in the sense that it should be performed after projection (i.e. in Eq. 6), not before. The origin of the difference between the CD and the RC results is now crystal clear: a one-center  $A$  contribution obtained from the  $\int_A \int \rho(\mathbf{r}_1; \mathbf{r}_2)\rho(\mathbf{r}_2; \mathbf{r}_1) d\mathbf{r}_1 d\mathbf{r}_2$  term in Eq 8 sums up a set of two-fragment contributions in Eq. 6:  $\sum_B \int_A \int_B \rho(\mathbf{r}_1; \mathbf{r}_2)\rho(\mathbf{r}_2; \mathbf{r}_1) d\mathbf{r}_1 d\mathbf{r}_2$ . Since the latter are inter-fragment exchange-like terms, describing much of the covalent delocalization between centers  $A$  and  $B$ , the procedure destroys the local spins due to covalent delocalization. Explicitly, the part of  $\langle \hat{S}^2 \rangle$  that depends exclusively on  $u(\mathbf{r})$  lacks only apparently interfragment terms. They have been absorbed by an algebraically correct, yet physically unjustified procedure into intra-fragment contributions.

On trying to satisfy the rest of the conditions imposed on local spins, a new twist was

envisaged by taking advantage of the expression (Eq. 10 in Ref. 15)

$$\int \left[ \Gamma(\mathbf{r}_1, \mathbf{r}_2) - \frac{1}{2} \rho^s(\mathbf{r}_1; \mathbf{r}_2) \rho^s(\mathbf{r}_2, \mathbf{r}_1) \right] d\mathbf{r}_2 = -\frac{1}{2} u(\mathbf{r}_1), \quad (11)$$

which is an independent condition on  $u$  that was used to propose a one-parameter family  $\text{RC}_a$  of expressions for  $\langle \hat{S}^2 \rangle$ :

$$\begin{aligned} \langle \hat{S}^2 \rangle_{\text{RC}_a} &= a \int u(\mathbf{r}_1) d\mathbf{r}_1 + (2a - 1) \iint \Lambda(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 \\ &\quad - \frac{1}{2} \iint \Lambda(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}_2, \mathbf{r}_1) d\mathbf{r}_1 d\mathbf{r}_2. \end{aligned} \quad (12)$$

where  $\Lambda(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}'_1, \mathbf{r}'_2) = \Gamma(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}'_1, \mathbf{r}'_2) - \frac{1}{2} \rho^s(\mathbf{r}_1; \mathbf{r}'_2) \rho^s(\mathbf{r}_2, \mathbf{r}'_1)$ , and  $a$  is a free parameter that modulates the weight of one- and two-electron terms, which are fragment-partitioned afterwards. The value  $a = 3/8$  corresponds to Eq. 8 of Ref. 17, and  $a = 1/2$  to the expression derived by Alcoba et al in Ref. 15. All fulfil Mayer's conditions (ii) (correct behavior at the dissociation limit) and (iii) (correlated results should reduce to uncorrelated ones in the case of single-determinant wave functions). All suffer from the same collapse of two-center terms into one-center contributions already described.

At this point, RC advocate for using  $a = 3/4$  in order to satisfy condition (iv). This is the only  $a$  that provides a correct  $\langle \hat{S}^2 \rangle = 3/4$  for a single electron system, and also the only value of the parameter  $a$  that guarantees the non-negativity of  $\langle \hat{S}_A^2 \rangle$  along the full dissociation curve of  $\text{H}_2$  in a minimal basis full-CI calculation.

The winding road taken by the scientific community in search of a chemically meaningful definition of local spins has been guided by trying to satisfy a set of more and more stringent constraints while maintaining some non-negotiable properties. This has led to the extremely clever  $a = 3/4$  RC proposal, which has provided much insight in the last years. We claim that simplicity is better, for one can never sure that the set of imposed constraints is complete. For instance, as shown in the SI, the  $\text{RC}_{3/4}$  recipe provides a local spin for the excited  ${}^1\Sigma_g^+$  state of  $\text{H}_2$  equal to  $\langle \hat{S}_A^2 \rangle = 3/4$  at dissociation. This is a completely wrong assignment from

our point of view, which will become clearer in the following.

We will now show how an open quantum systems perspective clarifies the meaning of the local spin as proposed by Clark and Davidson, opening whole new avenues to understand the role of electron localization and delocalization on magnetism and spin-related chemical reactivity.

### 3 Quantum fragments as open quantum (sub)systems

Whatever observable we may decide to partition into chemically relevant components, be it the electron count that leads to population analyses, the energy of the system and the plethora of energy decomposition techniques, or the electronic spin and the local spin machinery that we are analyzing, we face the extraction of an observable for a subsystem that is quantum mechanically coupled to an environment. This leads to the theory of open quantum systems (OQSs), an expanding discipline crucial to quantum control or quantum computing.<sup>33,34</sup> We have already shown how OQSs can be used to understand chemical bonding issues in Ref. 35, where a more detailed account of what follows can be found.

Very succinctly, if a quantum system  $U$  is described by a general mixed density operator  $\hat{\rho} = \sum_i |\Psi_i\rangle p_i \langle\Psi_i|$  and we are interested in a subsystem  $A$  ( $A \cup \bar{A} = U$ ,  $B \equiv \bar{A}$ ), then the subsystem expectation value of an operator  $\hat{O}$  can be obtained as  $\langle O_A \rangle = \text{Tr}(\hat{O}\hat{\rho}^A)$ , where  $\hat{\rho}^A$  is the  $A$  subsystem reduced density operator, obtained by tracing out all the degrees of freedom of  $\bar{A}$  from the full density operator,  $\hat{\rho}^A = \text{Tr}_{\bar{A}}\hat{\rho}$ . Even when the full system  $U$  is described by a pure state  $|\Psi\rangle$  the  $A$  subsystem reduced density operator is that of a mixed state (which is usually called a pseudo-mixed state). This means that its expectation values will be statistical mixtures of those of pseudo-pure states. For instance, as already explained, a subsystem has not a definite number of electrons, and the expectation value of the number operator,  $\langle \hat{N}_A \rangle = N_A$  has to be understood in terms of the probabilities  $p^A(n_i)$  that  $A$  displays an integer electron count  $n_i$ ,  $N_A = \sum_i p^A(n_i) \times n_i$ . In more general terms,

once a partition of real space into (say)  $m$  fragments has been chosen, the probability of finding an exact integer number of electrons  $n_1, n_2, \dots, n_m$  in regions 1, 2,  $\dots$ ,  $m$ , can be obtained.<sup>24,36–39</sup> This is the key to rationalize the meaning of the CD local spin formulation.

The subsystem reduced density operators of pure systems with  $\hat{\rho} \equiv \Psi^*(\mathbf{x}')\Psi(\mathbf{x})$ , where  $\mathbf{x} = \mathbf{x}_1 \dots \mathbf{x}_N$ , can be obtained easily by constructing multielectron fragment projection operators, starting from the  $\hat{P}^A$  objects of Section 2. Since we prefer orbital invariant real space fragments, we will use their real space analogs,<sup>35</sup> but all of our arguments are general. Our  $n$ -electron projector will thus be  $\mathbf{1}_n^A = \prod_{i=1}^n \omega_A(\mathbf{x}_i)$ . By noting that  $1 = \omega_A(\mathbf{x}) + \omega_B(\mathbf{x})$  for each electron, an  $N$ -electron unit operator  $\mathbf{1}^N = \prod_{i=1}^N [\omega_A(\mathbf{x}_i) + \omega_B(\mathbf{x}_i)]$  is immediately defined. Applying it to the  $\hat{\rho}$  operator,  $2^{2N}$  terms in which primed and unprimed coordinates are separated into  $A$  and  $B$  regions appear. The trace over  $B$  is obtained by integrating all coordinates over the  $B$  region, leaving only  $2^N$  surviving terms.<sup>35</sup> Each contains a given number of alpha and beta electrons in  $A$ , a so-called spin sector, which can be grouped by the total number of electrons, a sector:

$$\hat{\rho}^A = \bigoplus_{n=0}^N \hat{\rho}_n^A, \quad (13)$$

with  $\hat{\rho}_0^A = \int_B \Psi^*(\mathbf{x}_1 \dots \mathbf{x}_N)\Psi(\mathbf{x}_1 \dots \mathbf{x}_N)d\mathbf{x}_1 \dots d\mathbf{x}_N$  and, for  $n \geq 1$

$$\hat{\rho}_n^A(\mathbf{x}_{i \leq n}; \mathbf{x}'_{i \leq n}) = \mathbf{1}'_n \mathbf{1}_n^A \times \binom{N}{n} \int_B \Psi^*(\mathbf{x}'_{i \leq n}, \mathbf{x}_{i > n})\Psi(\mathbf{x}_{i \leq n}, \mathbf{x}_{i > n})d\mathbf{x}_{i > n}, \quad (14)$$

where  $\mathbf{x}_{i \leq n} = \mathbf{x}_1 \dots \mathbf{x}_n$  and  $\mathbf{x}_{i > n} = \mathbf{x}_{n+1} \dots \mathbf{x}_N$ . To simplify the notation, we will assume that, before doing any integration, the  $\mathbf{x}'_i \rightarrow \mathbf{x}_i$  identification has been performed for all the integrated variables, for instance,  $\mathbf{x}'_{i > n} \rightarrow \mathbf{x}_{i > n}$  in eq 14.

Subsystem  $A$  is thus described by a mixed density operator with  $N + 1$  possible sector densities  $\rho_n^A$  ( $n = 0, \dots, N$ ), each integrating to  $p^A(n)$ , the probability that  $n$  and only  $n$  electrons reside in domain  $A$  and the remaining  $N - n$  electrons in the domain  $B$ , i.e.  $\text{Tr}\rho_n^A = \int_A \rho_n^A(\mathbf{x}_{i \leq n}; \mathbf{x}'_{i \leq n})d\mathbf{x}_{i \leq n} = p^A(n)$ . Normalized sector densities can be defined as

$\tilde{\rho}_n^A = \rho_n^A/p^A(n)$ , so that  $\text{Tr}\tilde{\rho}_n^A = 1$  and  $\hat{\rho}^A = \bigoplus_n p^A(n)\tilde{\rho}_n^A$ . Then, each  $\tilde{\rho}_n^A$  can be dealt with as a pseudo-pure system operator.

Besides the subsystem reduced density operator, we can define standard reduced density matrices for each electron sector. The reduced density matrix of order  $m \leq n$  ( $m$ RDM) of sector  $n$  is

$$\rho_n^{A,m}(\mathbf{x}_{i \leq m}; \mathbf{x}'_{i \leq m}) = \frac{n!}{(n-m)!} \int \rho_n^A(\mathbf{x}_{i \leq n}; \mathbf{x}'_{i \leq n}) d\mathbf{x}_{i > m}, \quad (15)$$

with the spinless  $m$ th order RDM given by  $\rho_n^{A,m}(\mathbf{r}_{i \leq m}; \mathbf{r}'_{i \leq m}) = \int \rho_n^{A,m}(\mathbf{x}_{i \leq m}; \mathbf{x}'_{i \leq m})|_{\sigma'_i \rightarrow \sigma_i} d\sigma_{i \leq m}$ .

Using eq 14,  $\rho_n^{A,m}$  can also be put in the form

$$\rho_n^{A,m}(\mathbf{x}_{i \leq m}; \mathbf{x}'_{i \leq m}) = \mathbf{1}'_m \mathbf{1}_m^A \Lambda_{N,n}^m \int_{\mathcal{D}} \rho(\mathbf{x}; \mathbf{x}') d\mathbf{x}_{i > m}, \quad (16)$$

where  $\Lambda_{N,n}^m = N!/[(N-n)!(n-m)!]$ ,  $\mathcal{D}$  is a domain such that electrons  $m+1$  to  $n$  are integrated over  $A$ , and electrons  $n+1$  to  $N$  over  $B$ . Adding  $\Lambda_{N,n}^m \int_{\mathcal{D}} \rho(\mathbf{x}; \mathbf{x}') \mathbf{x}_{i > m}$  for values of  $n$  between 0 and  $N$  one obtains  $\rho^m(\mathbf{x}_{i \leq m}; \mathbf{x}'_{i \leq m})$ , the  $m$ RDM of the full  $A+B$  system. As a consequence, the sum of the  $m$ RDMs of all sectors  $n$  of domain  $A$  is given by  $\rho^{A,m} = \sum_n \rho_n^{A,m} = \mathbf{1}'_m \mathbf{1}_m^A \rho^m$ . Sectors behave as pseudo-pure systems. For instance, the trace of the normalized  $m$ RDM of sector  $n$  is  $n!/(n-m)!$ , so that 1RDMs integrate to the number of electrons of the sector, 2RDMs to the number of (ordered) pairs of electrons, and so on. Expressions for the first and second order sector RDMs for single- and multideterminant wavefunctions can be derived, and are found in the SI.

Each of the sector  $n$ RDMs can be independently diagonalized to obtain a set of sector natural orbitals, geminals and, in general,  $n$ -electron natural bases which allow to compact the description as much as possible. In the case of single-determinant wavefunctions (SDWs), it can be shown that all the natural bases are built from the same set of one-electron natural functions  $\phi_i$ , which are related to Ponc's domain natural orbitals (DNO)  $\varphi_i$ <sup>35,40,41</sup> by  $\phi_i = s_i^{-1/2} \varphi_i$ , where  $s_i = \int_A |\varphi_i(\mathbf{r})|^2 d\mathbf{r}$  denotes the fragment overlap integral of orbital  $\varphi_i$  (see the SI for more details). In this sense, if the SDW is written in the  $\phi$  basis as  $|\Psi\rangle =$

$(N!)^{-1/2} \det |\phi_1(\mathbf{x}_1) \dots \phi_N(\mathbf{x}_n)|$ , and  $\mathbf{k} = \{k_1, \dots, k_n\}$  is a set of  $n$  ordered integers  $k_1 < \dots < k_n$ ,  $n \leq N$ , then

$$\rho_n^A(\mathbf{x}_{i \leq n}; \mathbf{x}'_{i \leq n}) = \mathbf{1}'_n \mathbf{1}_n^A \times \sum_{\mathbf{k}} |\phi_{\mathbf{k}}\rangle p_n^{\mathbf{k}} \langle \phi_{\mathbf{k}}|, \quad \text{where} \quad (17)$$

$$|\phi_{\mathbf{k}}\rangle = \frac{1}{\sqrt{n!}} |\phi_{k_1}(\mathbf{x}_1) \dots \phi_{k_n}(\mathbf{x}_n)\rangle. \quad (18)$$

This expression shows that for a SDW, the  $n$ -sector is described as a mixture of all the  $n$ -electron subdeterminants that can be drawn from the original SDW, with weights  $p_n^{\mathbf{k}}$  that add to the total sector weight,  $\sum_{\mathbf{k}} p_n^{\mathbf{k}} = p^A(n)$ . As shown,<sup>35</sup>  $p_n^{\mathbf{k}} = \prod_i^N p_i$ , where  $p_i = s_i$  if  $i \in \mathbf{k}$  and  $p_i = (1 - s_i)$  otherwise. Normalized sector densities  $\tilde{\rho}_n^A$  can also be used if coupled to normalized weights,  $\tilde{p}_n^{\mathbf{k}} = p_n^{\mathbf{k}}/p^A(n)$ . The multi-determinant case is more complex, but follows the same agenda (see the SI). The  $n$ -sector is a mixture of pseudo-pure  $n$ -electron determinant states, now built from all the configuration state functions populating the wavefunction expansion.

## 4 Local spin from an OQS perspective

The previous account allows us to cope easily with the squared spin operator  $\hat{S}^2$ . The flow of ideas is simple. The CD local spin expectation value for a fragment  $A$ ,  $\langle \hat{S}_A^2 \rangle$ , is obviously equivalent to that obtained from an OQS viewpoint:  $\langle \hat{S}_A^2 \rangle = \text{Tr} \left( \hat{S}^2 \hat{\rho}^A \right)$ . By partitioning  $\hat{\rho}^A$  into its  $N+1$  sectors,  $\langle \hat{S}_A^2 \rangle = \sum_n p^A(n) \langle \hat{S}_{A,n}^2 \rangle$ , where we use normalized sectors. As with other OQS observables, the snapshot analogy is revealing. If we imagine a multitude of snapshots of the electron system, then the local spin of a fragment is a statistical average of the spins of each electron configuration of the fragment with weights equal to the probabilities of finding those configurations. This is a fully rigorous result. If a fragment displays a probability greater than zero of hosting one and only one electron, its local spin will not be zero (since this contribution will provide 3/4 to the local spin). This solves the problem of non-zero

local spins for closed-shells.

Using the previous machinery,

$$\langle \hat{S}_{A,n}^2 \rangle = \frac{3}{4} \int \tilde{\rho}_n^{A,1}(\mathbf{r}) d\mathbf{r} - \frac{1}{4} \iint [\tilde{\rho}_n^{A,2}(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}_1, \mathbf{r}_2) + 2\tilde{\rho}_n^{A,2}(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}_2, \mathbf{r}_1)] d\mathbf{r}_1 d\mathbf{r}_2. \quad (19)$$

In the SDW case with restricted orbitals, as shown in the SI,

$$\langle \hat{S}_{A,n}^2 \rangle = \sum_{\mathbf{k}} \tilde{p}_n^{\mathbf{k}} [M_{\mathbf{k}}^2 + n_d/2] = \sum_{\mathbf{k}} \tilde{p}_n^{\mathbf{k}} \langle \hat{S}_{A,n,\mathbf{k}}^2 \rangle, \quad (20)$$

where  $M_{\mathbf{k}} = (n^\alpha - n^\beta)/2$  is the eigenvalue of  $\hat{S}_z$  for the each  $\mathbf{k}$  determinant, and  $n_d$  is the number of not-matched orbitals from either spin, i.e. the total number of orbitals which have not an opposite spin couple in the determinant.<sup>12</sup> For instance, if  $\mathbf{k} = \{\phi_1, \phi_2, \phi_3, \phi_4, \phi_5, \bar{\phi}_4, \bar{\phi}_5, \phi_6, \phi_7\}$ ,  $n_d = 5$ . As shown by Clark and Davidson,  $M_{\mathbf{k}}^2 + n_d/2$  is the expectation value of  $\hat{S}^2$  for a standard Slater determinant. More general expressions are found in the SI, which also covers MDW cases. It is also clear that  $n_d$  is the trace of the density of effectively unpaired electrons  $u(\mathbf{r})$ . Then, a high spin determinant in which every  $\beta$  orbital is equal to a single  $\alpha$  one orbital and orthogonal to all the other  $\alpha$  orbitals has  $n_d = 2 \times |M_{\mathbf{k}}|$ , and its contribution to the local spin is  $n_d/2(n_d/2 + 1)$ , which corresponds naively to the expected spin from  $n_d$  unpaired electrons.

Notice that spin symmetry guarantees that appropriate linear combinations of subdeterminants  $\mathbf{k}$  which are spin eigenfunctions can always be found, so that the local spin can be written as  $\sum_i p_i S_i(S_i + 1)$ , a weighted sum of proper  $S(S + 1)$  squared spins. We will show how to do this in examples below, and a general framework will be published elsewhere. This remark answers the criticism regarding the difficulty to interpret the CD local spin as  $S_A(S_A + 1)$ .

Finally, we will point out that the  $\mathbf{k}$  sets in Eq. 20 can be grouped into as many subsets as the number of ways of choosing  $n^\alpha$  and  $n^\beta$  such that  $n^\alpha + n^\beta = n$ , i.e.  $\langle \hat{S}_{A,n}^2 \rangle = \sum'_{n^\alpha, n^\beta} \sum_{\mathbf{k}} \tilde{p}_n^{\mathbf{k}} [M_{\mathbf{k}}^2 + n_d/2]$ , where the prime (') in the first sum means than only terms with



$n_\alpha^A + n_\beta^A = n$  are included, and in the second that only  $\mathbf{k}$ 's associated to these  $n^\alpha$  and  $n^\beta$  have to be considered. This allows to consider spin-resolved sectors.

## 5 Gaining insight through models

We will devote this Section to examine the behavior of local spins in the light of our OQS viewpoint. We will examine several models to gain intuition on what we may expect from CD local spins.

### 5.1 Local spin and bond order

It was already Clark and Davidson who noticed the intimate link between Wiberg-Mayer bond orders<sup>42,43</sup> and the  $\langle \hat{\mathbf{S}}_A \cdot \hat{\mathbf{S}}_B \rangle$  values. It is useful to show the origin of this relation in density matrix language. For a closed-shell restricted determinant (RHF) the  $\Gamma$  cumulant in Eq. 9 vanishes, as well as the spin-density matrix  $\rho_s$ . Substituting Eq. 9 into Eq. 6 results in

$$\langle \hat{\mathbf{S}}_A \cdot \hat{\mathbf{S}}_B \rangle = \frac{3}{4} \delta_{AB} \int_A \rho(\mathbf{r}) d\mathbf{r} - \frac{3}{8} \int_A \int_B \rho(\mathbf{r}_1; \mathbf{r}_2) \rho(\mathbf{r}_2; \mathbf{r}_1) d\mathbf{r}_1 d\mathbf{r}_2. \quad (21)$$

We immediately recognize  $\rho(\mathbf{r}_1; \mathbf{r}_2) \rho(\mathbf{r}_2; \mathbf{r}_1)$  as  $2\rho_{xc}(\mathbf{r}_1; \mathbf{r}_2)$  for a RHF function, with  $\rho_{xc}$  being the exchange-correlation density,<sup>25</sup> so that

$$\begin{aligned} \langle \hat{\mathbf{S}}_A \cdot \hat{\mathbf{S}}_B \rangle &= -\frac{3}{8} \delta^{AB} \quad B \neq A, \\ \langle \hat{\mathbf{S}}_A \cdot \hat{\mathbf{S}}_A \rangle = \langle \hat{S}_A^2 \rangle &= \frac{3}{4} (N_A - \lambda^A). \end{aligned} \quad (22)$$

Here,  $\delta^{AB}$  is the so-called delocalization index between the fragments (the Wiberg-Mayer bond-order in Fock projections), and  $\lambda^A$  is the localization index of fragment  $A$ . The former measures the number of delocalized electron (pairs) between regions, the latter the number of localized electrons in a fragment. These are simply the covariance and variance, respectively,

of the electron populations in our OQS description,

$$\begin{aligned}\delta^{AB} &= -2 \times \text{cov}(n_A, n_B) = \sum_{n_A, n_B} p(n_A, n_B) \times (n_A - \bar{n}_A)(n_B - \bar{n}_B), \\ \lambda^A &= \text{var}(n_A) = \sum_{n_A} p(n_A) \times (n_A - \bar{n}_A)^2.\end{aligned}\quad (23)$$

$p(n_A, n_B)$  is the joint probability of finding  $n_A$  electrons in  $A$  and  $n_B$  electrons in  $B$ , and  $p(n_A) = p^A(n_A)$ .<sup>24</sup> Using the symbol  $\text{cov}(n_A, n_A)$  as a proxy for the variance, then  $\langle \hat{\mathbf{S}}_A \cdot \hat{\mathbf{S}}_B \rangle = 3/4 \times \text{cov}(n_A, n_B)$ .

At the RHF level, the local spin and the spin couplings simply measure how localized (or delocalized) the electrons are. This leads to large atomic local spins which are deemed as unphysical by many, as we have explained. From our point of view, on the contrary, this is particularly illuminating. To show it, we could use Eq. 20 to gain insight, but the combinatorial number of  $\mathbf{k}$  possibilities makes this choice not appropriate for models.

## 5.2 Localized and itinerant spin models: Aufbau rules

For a simple  $N$  electron SDW with real orbitals  $u_i$ , and using Slater rules for the 2RDM, it is not difficult to find that

$$\langle \hat{\mathbf{S}}_A \cdot \hat{\mathbf{S}}_B \rangle = \frac{3}{4} N_A \delta_{AB} - \frac{1}{4} \sum_{ij}^N \{ S_{ii}^A S_{jj}^B (1 - 2\delta_{\sigma_i \sigma_j}) + S_{ij}^A S_{ij}^B (2 - \delta_{\sigma_i \sigma_j}) \}, \quad (24)$$

valid for both  $A = B$  and  $A \neq B$ . In the above equation, which expresses in a less compact way Eq. 20, we sum over spinorbitals,  $\sigma_i$  is the spin variable of the spatial orbital  $u_i$  and  $S_{ij}^A = \langle u_i | u_j \rangle_A$  is the (spatial only) overlap between orbitals, projected onto fragment  $A$  (the atomic or fragment overlap if in real space). Notice that the  $i = j$  terms cancel out, since the Coulomb-like terms are equal to the exchange-like contributions. Eq. 24 can be applied both when the determinant is expressed with canonical or localized orbitals, including Ponec's ones. Localized descriptions lead to a smaller number of non-cancelling terms, and are thus

easier to use for back of the envelope calculations. As we are showing, much insight can be obtained from manipulating Eq. 24 in simple cases.

Let us then consider two interacting atoms,  $A$  and  $B$ , described by a (non-necessarily closed-shell) SDW. To ease manual calculations, we consider the two atoms at large distances, so that an  $S_{ij}^A$  overlap will vanish for two localized orbitals centered on different atoms. Residual overlaps at general geometries will alter the results quantitatively, but not the rules that will emerge.

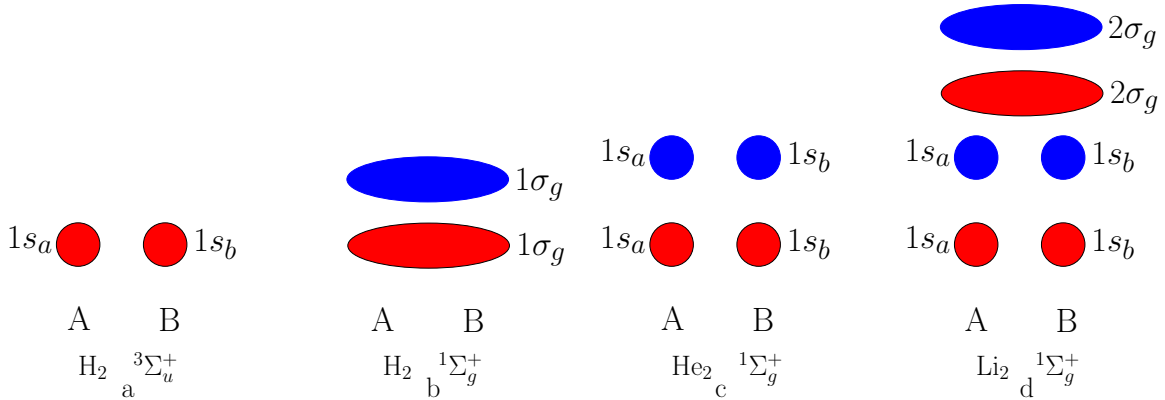


Figure 1: Structure of the localized SDW spinorbitals for the first singlet and triplet states of  $H_2$ , and for the ground states of  $He_2$  and  $Li_2$ , all at large internuclear distance. Red and blue identify the  $\alpha$  and  $\beta$  spin projection, for instance.

Fig. 1 shows the structure of the localized orbitals in the first triplet (a) and singlet (b) states of dihydrogen, and in the ground state of  $He_2$  (c) and  $Li_2$  (d). The  $|\sigma_g\sigma_u|$  determinant describing the  ${}^3\Sigma_u^+$  state of  $H_2$  can be subjected to a unitary rotation that leaves two strictly localized  $1s$  functions at each center. This cannot be done in the singlet, since the two electrons belong to different spin symmetry. Similarly, in  $He_2$  one can rotate the  $\alpha$  and  $\beta$  sets and come to a completely localized description, while in dilithium the  $2\sigma_g$  orbitals remain delocalized.

Application of Eq. 24 to case (a) shows that the sum vanishes if  $A = B$ , and that it leaves only one term otherwise, in which  $i = 1s_a$  and  $j = 1s_b$ , with  $S_{ii}^A = S_{ii}^B = 1$ ,  $S_{ij}^{A,B} = 0$ . Thus,  $\langle \hat{S}_A^2 \rangle = 3/4 + 0 = 3/4$ ,  $\langle \hat{\mathbf{S}}_A \cdot \hat{\mathbf{S}}_B \rangle = 1/4$ . In case (b), since  $1\sigma_g \approx (1s_a + 1s_b)/\sqrt{2}$ , all the overlap integrals are equal to  $1/2$ ,  $\langle \hat{S}_A^2 \rangle = 3/4 - 3/8 = 3/8$ , and  $\langle \hat{\mathbf{S}}_A \cdot \hat{\mathbf{S}}_B \rangle = -3/8$ .

When shifting to  $\text{He}_2$ , with full localization of the  $1s$  block, it is interesting to examine the contributions to the local spin for each atom ( $A = B$ ). Only contributions from  $\phi_i$  and  $\phi_j$  localized in  $A$  will contribute in Eq. 24:  $i = 1s_a, j = \bar{1}s_a$  and viceversa. Each pair will add  $-1/4(1 + 2) = -3/4$ , cancelling the 1RDM contributions of each electrons. The local spin vanishes. It is easy to grasp how this also occurs when different subshells become filled. In  $\text{Be}_2$ , for instance, the block coming from the  $2s$  orbitals get also localized, and all  $i, j$  pairs mixing  $1s$  and  $2s$  orbitals do not contribute due to  $1s, 2s$  orthogonality. Different subshells are then isolated from each other, and behave as independent electron blocks. This ceases to be so if residual overlaps are allowed, so that in actual calculations at actual geometries, this picture will be slightly altered. Moving to  $\text{Li}_2$ , the  $2\sigma_g$  orbital cannot be localized. However, the mixed atomic overlaps  $\langle 2\sigma_g | 1s_{a,b} \rangle_A$  still vanish due to  $1s, 2s$  orthogonality, so that, again, the  $2s$  block is isolated from the  $1s$  set of functions.  $\text{Li}_2$  behaves as  $\text{H}_2$ .

This draws a very simple picture that also rationalizes the link between local spin couplings and bond orders. Again, it is the delocalization of electrons that causes non-zero local spins in closed-shells. Each ideal, symmetric electron-pair covalent bond includes two opposite spin *delocalizable* electrons. Each of these pairs provide a  $3/8$  local spin and a  $-3/8$   $AB$  coupling. Localized pairs do not contribute at all. An interesting exercise is that of describing the local spin of  $\text{O}_2$  in its triplet ground state. A model SDW may be written as  $\Psi = |KK2\sigma_g^2 2\sigma_u^2 3\sigma_g^2 1\pi_{ux}^2 1\pi_{uy}^2 1\pi_{gx} 1\pi_{gy}|$ . Following our Aufbau rules, the  $1\sigma$  and  $2\sigma$  subshells are closed, can be localized, and do not participate. Similarly, the  $\alpha$   $1\pi$  subshell is full. This leads the  $3\sigma_g$  electrons as well as two independent (orthogonal)  $1\pi_{x,y}$  electrons as delocalized entities. With the help of Eq. 24 one can easily find that two orthogonal same-spin electrons coupled to a triplet SDW provide  $\langle \hat{S}_A^2 \rangle = 3/4 + 1/8 = 7/8$ . Adding the independent  $\sigma$  and  $\pi$  contributions we get that  $\langle \hat{S}_O^2 \rangle = 3/8 + 7/8 = 10/8$ .

The above rules are illuminating when mean-field solutions are reasonable, describing our expectation in the case of itinerant electrons. SDWs however fail when electron correlation is necessary. We can yet propose simple models for strong static correlation, like that found

in the homolytic dissociation of an electron pair, or in situations where correlation-induced localization appears. The OQS approach makes this extremely easy. In this Section we will examine the prototype cases of local spin couplings for a symmetric two-center two-electron case. We notice that only global singlet and triplet squared-spin are allowed. To simplify, only the limiting cases of totally (spatially) localized and completely delocalized electrons will be considered.

If the pair of electrons is ideally delocalized, the two electrons act on average as if they were statistically independent objects. For symmetric fragments  $(A, B) \equiv (\text{left}, \text{right})$  this implies that the probability that any of them is found in each is  $p = 1/2$ .  $p(1, 0) = p(0, 1) = 1/2$  in the language of fragment populations. The joint probability distribution is the direct product of the above, so that  $p(2, 0) = p(0, 2) = 1/4$  and  $p(1, 1) = 1/2$ , the binomial distribution well known from the theory of electron distribution functions.<sup>24,38</sup> On the contrary, if the electrons are localized in the two fragments, then  $p(2, 0) = p(0, 2) = 0$ , and  $p(1, 1) = 1$ . If two opposite spins are considered, the delocalized setup can be matched with a single delocalized canonical orbital, for instance through a  $|\sigma\bar{\sigma}|$  determinant. For two same-spin electrons, we need two independent (i.e. orthogonal) functions, like in a  $|\pi_x\pi_y|$  state. Another symmetric delocalization possibility exists, in which  $p(2, 0) = p(0, 2) = 1/2$ , and  $p(1, 1) = 0$ . This corresponds to the ionic resonance that has been commented before for the excited  $^1\Sigma_g^+$  state of  $\text{H}_2$ . The two electrons behave as a bosonic entity, and are found together, either on one center or on the other. This situation cannot be modeled at the SDW level. We distinguish these states with the  $z$  label (zwitterionic).

With those probabilities at hand, we can now couple the two electrons either to a singlet or to a triplet, and apply Eq. 20, which is trivial since the sums have just one or at most two components. We have

$$\langle S_A^2 \rangle = p(1, 1) \langle \hat{S}_{A,(1,1)}^2 \rangle + p(2, 0) \langle \hat{S}_{A,(2,0)}^2 \rangle + p(0, 2) \langle \hat{S}_{A,(0,2)}^2 \rangle. \quad (25)$$

We only need to consider the following cases: (i) if no electron lies in  $A$ , no local spin exists; (ii) if one electron lies in  $A$ , then  $\langle \hat{S}^2 \rangle = 3/4$  necessarily; (iii) If the two electrons are in  $A$ , they have to be coupled as the full two-electron system, so  $\langle S^2 \rangle = 2$  in the triplet and zero in the singlet. Nothing else is needed, just appropriate snapshots of the spatial location of electrons.

Table 1: Local spin analysis of ideal localized and delocalized singlet and triplet states in a symmetric two-electron  $AB$  system. S is used for singlet, T for triplet,  $n - z$  labels a normal versus a zwitterionic resonance, and  $D, L$  a delocalized from a localized situation.  $\delta$  is the intercenter delocalization index.

	$\langle \hat{S}_A^2 \rangle$	$\langle \hat{\mathbf{S}}_A \cdot \hat{\mathbf{S}}_B \rangle$	$\delta^{AB}$
$S_D^z$	0	0	2
$S_D^n$	3/8	-3/8	1
$S_L^n$	3/4	-3/4	0
$T_L^n$	3/4	+1/4	0
$T_D^n$	7/8	+1/8	1
$T_D^z$	1	0	2

Plugging in these numbers we get the results shown in Table 1. There is a considerable amount of information summarized there. First, it is interesting to check that singlets display negative couplings while the contrary is true for triplets, whatever the case. This is a particularly appealing, physically consequent result. Second, all states can be distinguished nominally from comparing local spins and spin couplings. This is not the case if plain electron delocalization is used, which just separates three categories: localized, normal-delocalized, zwitterionic-delocalized. The use of  $u$  or of  $RC_{3/4}$  would fail to provide physically consistent results in some of these cases.

Even more interesting is the identification of chemical species from the Table. We have localized singlets, which are chemically *diradicals*, delocalized singlets or *covalent bonds*, *zwitterionic singlets* and *triplets*, and *itinerant triplets*. All categorized through simple descriptors. We find this extremely appealing, although actual results will be considerably more difficult to classify appropriately when the indicators of this Table evolve continuously. We hope to examine how well real systems fit this scheme in the near future.

### 5.3 Localized polyelectronic spin couplings

Once the role of localization and delocalization in the building of local spins has been clarified, we recognize that local spin applications in chemistry are to be expected mainly to recognize radicals or polyradicals, particularly in singlet states for which standard spin densities are useless. These states are expected to bear localized unpaired electrons, where the RC and CD results should not differ considerably, at least in ground states.

It is therefore relevant to examine the local spins and spin couplings of sets of  $N$  fully localized electrons in  $N$  different sites. The electronic label  $i$  is thus equivalent to the site index  $A$ . This problem is equivalent to that of computing the expectation value of the  $\langle \hat{\mathbf{S}}_i \cdot \hat{\mathbf{S}}_j \rangle$  operators over  $N$ -electron eigenfunctions of  $\mathbf{S}^2$ . These can be constructed easily, or taken from monographs like that of Pauncz.<sup>44</sup> We have examined couplings from  $N = 3$  to  $N = 6$ , non-exhaustively, and also the limiting infinite spin chain. Notice that since electrons are fully localized,  $\langle \hat{S}_A^2 \rangle$  is fixed to  $3/4$ , and only the  $ij$  couplings contain information. It is known<sup>44</sup> that there are  $(2S + 1)N! / (N/2 + S + 1)! / (N/2 - S)!$  independent eigenstates of spin  $S$  for an  $N$  electron system, each composed of  $2S + 1$   $M_S$  projections. Thus we have one quartet and two independent doublets for  $N = 3$ , two singlets, three triplets and one quintuplet for  $N = 4$ , and so on. The functions examined are summarized on Table 2. Expectation values of the  $\hat{\mathbf{S}}_i \cdot \hat{\mathbf{S}}_j$  operators are easily found with the help of the standard ladder formalism.

The maximum  $S = N/2$  single-component  $(\alpha \dots \alpha)$  functions are easily shown to have  $\langle \hat{\mathbf{S}}_i \cdot \hat{\mathbf{S}}_j \rangle$  couplings equal to  $1/4$  between all electron pairs. Recall that our results are independent on the spin projection. Localized polyradicals in their maximum  $S$  states would thus be easy to identify. The situation becomes more interesting as  $S$  decreases. For instance, the local spin analysis of the two  $N = 3$  doublets reflects the genealogy of the states examined very clearly. It is customary<sup>44</sup> to build spin eigenfunctions sequentially, such that the  $(n + 1)$ -electron state is constructed through Clebsch-Gordan coupling a well-defined  $n$ -electron eigenfunction with spin  $S$  to a new electron to form the two possible  $S \pm 1/2$  final states,

Table 2: Spin eigenfunctions examined in this work. The maximum  $M_S = S$  multiplicity state is shown in the standard genealogical notation in which the total spin of each newly added electron is depicted. The final number is the total spin of the state.  $|1/2, 1, 3/2\rangle$  is thus read as one electron that couples to a second as a triplet and to the third as a quartet.

State	$ \psi\rangle$
$ 1/2, 1, 3/2\rangle$	$\alpha\alpha\alpha$
$ 1/2, 1, 1/2\rangle$	$\sqrt{\frac{2}{3}}\alpha\alpha\beta - \sqrt{\frac{1}{6}}\alpha\beta\alpha - \sqrt{\frac{1}{6}}\beta\alpha\alpha$
$ 1/2, 0, 1/2\rangle$	$\sqrt{\frac{1}{2}}\alpha\beta\alpha - \sqrt{\frac{1}{2}}\beta\alpha\alpha$
$ 1/2, 1, 3/2, 2\rangle$	$\alpha\alpha\alpha\alpha$
$ 1/2, 1, 3/2, 1\rangle$	$\sqrt{\frac{3}{4}}\alpha\alpha\alpha\beta - \sqrt{\frac{1}{12}}\alpha\alpha\beta\alpha - \sqrt{\frac{1}{12}}\alpha\beta\alpha\alpha - \sqrt{\frac{1}{12}}\beta\alpha\alpha\alpha$
$ 1/2, 1, 1/2, 1\rangle$	$\sqrt{\frac{2}{3}}\alpha\alpha\beta\alpha - \sqrt{\frac{1}{6}}\alpha\beta\alpha\alpha - \sqrt{\frac{1}{6}}\beta\alpha\alpha\alpha$
$ 1/2, 0, 1/2, 1\rangle$	$\sqrt{\frac{1}{2}}\alpha\beta\alpha\alpha - \sqrt{\frac{1}{2}}\beta\alpha\alpha\alpha$
$ 1/2, 1, 1/2, 0\rangle$	$\sqrt{\frac{1}{3}}\alpha\alpha\beta\beta - \sqrt{\frac{1}{12}}\alpha\beta\alpha\beta - \sqrt{\frac{1}{12}}\alpha\beta\beta\alpha - \sqrt{\frac{1}{12}}\beta\alpha\alpha\beta - \sqrt{\frac{1}{12}}\beta\alpha\beta\alpha + \sqrt{\frac{1}{3}}\beta\beta\alpha\alpha$
$ 1/2, 0, 1/2, 0\rangle$	$\sqrt{\frac{1}{4}}\alpha\beta\alpha\beta - \sqrt{\frac{1}{4}}\alpha\beta\beta\alpha - \sqrt{\frac{1}{4}}\beta\alpha\alpha\beta + \sqrt{\frac{1}{4}}\beta\alpha\beta\alpha$

that we will call the plus-coupled and the minus-coupled states, if  $S \neq 0$ , or the final doublet if  $S = 0$ . This is how the states in Table 2 are labeled.

For a triradical, there are two non-trivial doublets beyond the maximal  $S$  quartet. In the first, two electrons are coupled to a triplet that then couple to a final doublet, while in the second, the first coupling gives rise to a singlet. Fig. 2 provides a pictorial sketch. We use  $Q$  for quartets, etc, and order the states by decreasing value of the total  $S$  that couples to the final electron in the genealogical notation.  $D_1$  is the first doublet, corresponding to  $|1/2, 1, 1/2\rangle$ , and  $D_2$  the second. The pictures show very clearly the genealogy. In  $D_1$ , we see two spins with a positive coupling linked negatively to the third. One can very easily group the spins into sets by adding the local spin and interspin couplings. In  $D_1$ , for instance, the first two spins on the base of the triangle give rise to a triplet:  $\langle\hat{S}^2\rangle = 3/4 + 3/4 + 2 \times (1/4) = 2$ , which now minus-couples to the remaining doublet, so that  $\langle\hat{S}^2\rangle = 2 + 3/4 + 2 \times (-1/2 - 1/2) = 3/4$ . In  $D_2$ , the analysis shows that a singlet has zero couplings to the rest of the spin system, a result that is general.

Analysis of the  $N = 4$  case allows to isolate rather general patterns. For instance,  $T_1$  is made of an  $N = 3$   $Q_1$  spin group that minus-couples with an isolated electron spin. All



the negative couplings are symmetric, and warrant the final triplet state. Similarly,  $T_2$  is a  $D_1$  plus-coupling to the final spin, and  $T_3$  is two-electron triplet coupling to a two-electron singlet. Whenever one group of electrons coupled to a singlet interacts with a second group, like in the  $D_2, T_3$ , and  $S_2$  cases, we think that we should better consider these two groups as two independent sets of lower-rank polyradicals better than a full  $N$ -electron radical species.

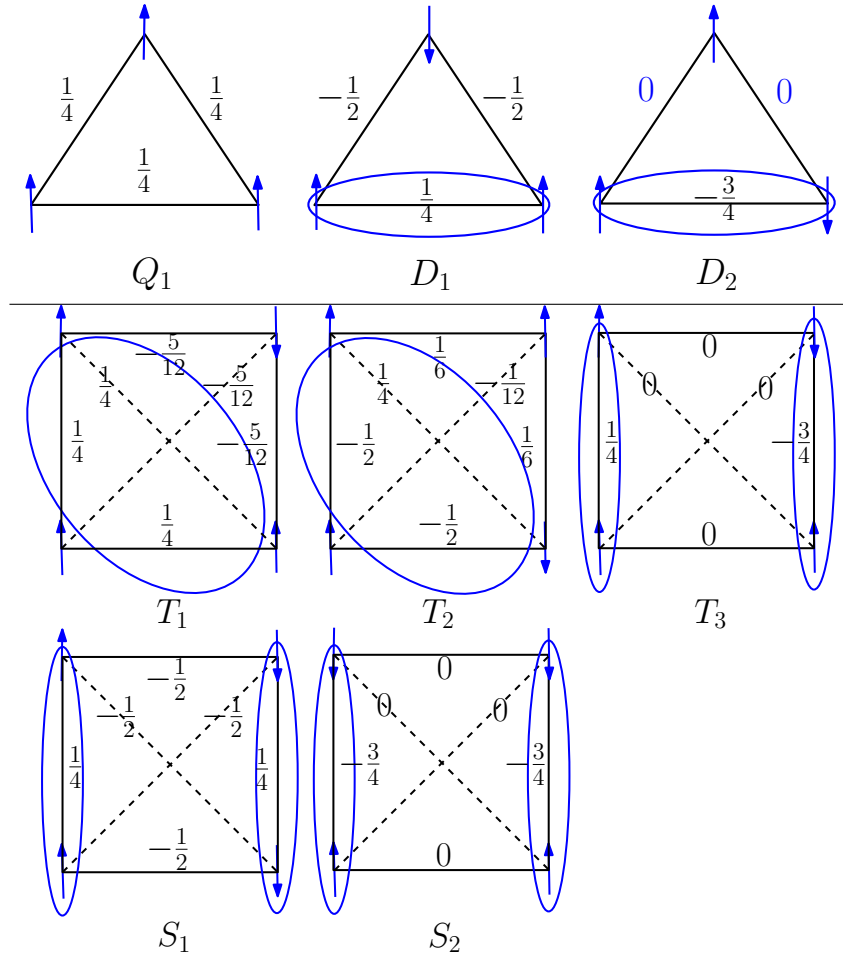


Figure 2: Spin couplings  $\langle \hat{\mathbf{S}}_i \cdot \hat{\mathbf{S}}_j \rangle$  between all pairs of localized spins for the cases  $N = 3$  and  $N = 4$ . The state is identified as explained in the main text. Intermediate spin couplings are sketched pictorially. The quintet in the  $N = 4$  case is not shown, since it is equivalent to the quartet for the  $N = 3$  situation.

Nothing precludes us from extending this analysis further. Adding a certain character of itinerancy for all or some of the electrons is also possible by considering OQS models, as done in the previous Section, but we will not pursue this further in this introductory paper.

We end up the Section by mentioning that for even  $N$ , the maximally entangled singlet (the first in our labeling), can be understood as coming from the annihilation of two  $S = N/2$  subsystems found in their maximum spin states. For instance, in the  $N = 4$ , the  $S_1$  state comes from two triplets that couple to a singlet. General analytical formulas for this state exist:<sup>44</sup> for an even number of electrons  $N$ , if  $|M\rangle_1$  is the  $|S, M\rangle$  state with  $S = N/2$  for the first of these subsystems and  $|M\rangle_2$  its equivalent for the second, the coupled singlet is written as  $\sum_{M=-S}^{M=+S} (-1)^{S-M} |M\rangle_1 | -M\rangle_2$ . We can thus star the alternating nodes of an even number of node chain and consider the antiferromagnetic coupling of two opposite spin ferromagnetic  $N/2$  subchains to form a maximally entangled singlet. Each of the subsystems is in its maximal  $S$  state, so that the spin couplings between all the possible pairs of its nodes (electrons) is equal to  $+1/4$ . Since the two subsystems couple to a singlet and all the pairs in which one electron belongs to the first and the other to the second are equivalent, a simple calculation shows that the inter-subsystem spin couplings have to be equal to  $-1/4 - 1/N$ .

## 5.4 Evolution of local spins with electron correlation: the Hubbard model

Electron correlation may impact both the magnitude and the couplings of local spins in several ways. Since we are here interested in gaining insight through simple models, the Hubbard Hamiltonian,<sup>45</sup> offers an appealing possibility to change from a mean-field situation to a strongly correlated regime continuously.<sup>45</sup> In its simplest formulation, the Hubbard Hamiltonian models a one-dimensional chain of identical single energy level sites with only nearest neighbor interactions. In the half-filled case, each site bears one electron on average, can hold up to two electrons with opposite spin, and we talk of an  $N$ -sites  $N$ -electron ( $N/2 \alpha$  electrons and  $N/2 \beta$  electrons) problem. Periodic boundary conditions can be imposed, and in this case,  $N$  is usually made to tend to infinity. When two electrons lie at the same site they are subjected to an interaction energy  $U$  (usually repulsive), which is called the on-site Coulomb repulsion. Electrons can delocalize to neighboring sites via a hopping parameter  $t$ ,

which acts as a kind of site overlap. In second quantized form,

$$\hat{H} = -t \sum_{\langle i,j \rangle, \sigma} (\hat{c}_{i\sigma}^+ \hat{c}_{j\sigma} + \hat{c}_{j\sigma}^+ \hat{c}_{i\sigma}) + U \sum_i \hat{n}_{i\uparrow} \hat{n}_{i\downarrow}, \quad (26)$$

where  $\hat{c}_{i\sigma}^+$  ( $\hat{c}_{i\sigma}$ ) is the standard fermionic creation (annihilation) operator at site  $i$  and spin projection  $\sigma$ , and  $\hat{n}_{i\sigma} = \hat{c}_{i\sigma}^+ \hat{c}_{i\sigma}$  counts the number of electrons with spin projection  $\sigma$  at site  $i$ . The  $\langle i, j \rangle$  sum runs over first neighbors, with each term describing the hopping of an electron from site  $j$  to site  $i$ . The second sum includes the Coulombic repulsion energy (a positive energy  $U$ ), added to each doubly occupied site.  $t$  and  $U$  play drive the system in opposite ways, and there is only one effective  $U/t$  adimensional correlating parameter. Small  $U/t$  values favor hopping, thus delocalized solutions. In the infinite  $U/t$  limit, the chain fully localizes, with one electron per site and no hopping at all. At  $U/t = 0$ , the Hubbard model converges to the tight-binding mean-field single-determinant solution.

We have previously shown how the usual real space delocalization indices are nothing but the order parameters used to detect phase transitions in strongly correlated systems.<sup>46</sup> Given the relation between the expectation value of spin couplings and DIs for restricted SDWs, the general behavior of these parameters both for open and closed finite and infinite chains (that approximate the  $\pi$  system of alternating hydrocarbons) is thus known. For instance,<sup>47</sup> in a linear chain with sites  $i$  starting at position  $i = 1$ ,

$$\begin{aligned} \langle \hat{\mathbf{S}}_i \cdot \hat{\mathbf{S}}_j \rangle &= -\frac{6}{\pi^2} \frac{j^2}{(i^2 - j^2)^2}, \quad (i + j) \text{ odd} \\ \langle \hat{\mathbf{S}}_i \cdot \hat{\mathbf{S}}_j \rangle &= 0, \quad (i + j) \text{ even.} \end{aligned} \quad (27)$$

which shows a squared-distance algebraic decay of spin correlations in the case of these metallic-like systems. Spin correlation shows the same type of mesomeric oscillation as bond orders in conjugated systems. If periodic boundary conditions are imposed, the first relation in the above expression becomes simply  $-3/(2\pi^2)$ , and bond equalization leads to a uniform

distribution of spin coupling over the chain.

Increasing the  $r = U/(4t)$  correlating parameter allows to follow the transition from the fully delocalized tight-binding solution to the fully localized state. Lieb<sup>48</sup> showed that there is no phase transition in the 1D Hubbard chain, and that the ground state is an isolating antiferromagnet at any  $r$  value. In  $N = 4n + 2$  Hückel-aromatic cyclic Hubbard lattices, for instance, it was found<sup>46</sup> that at about  $r = 1$  a clear change from the oscillatory decay of the delocalization indices  $\delta^{1j}$  (see Eq. 27) changed to its long-range exponential decay. Mesomeric or resonance effects disappear as correlation increases.

Table 3: Evolution of  $\langle \hat{\mathbf{S}}_1 \cdot \hat{\mathbf{S}}_j \rangle$  couplings for Hubbard benzene as  $r = U/(4t)$  increases.

$r$	$j = 1$	$j = 2$	$j = 3$	$j = 4$
0.000	0.417	-0.167	0.000	-0.042
0.250	0.426	-0.200	0.016	-0.058
1.000	0.583	-0.327	0.106	-0.147
2.500	0.711	-0.435	0.186	-0.213
12.50	0.748	-0.466	0.207	-0.231

Table 3 shows the evolution of  $\langle \hat{\mathbf{S}}_i \cdot \hat{\mathbf{S}}_j \rangle$  in the Hubbard analog of the benzene  $\pi$  system, an  $N = 6$  cyclic chain. The calculations have been performed after reconstructing the Hubbard 2RDMs with the pySCF suite.<sup>49</sup> It is apparent how each site’s local spin moves from its SDW value, equal to  $5/12$ , to its fully localized  $3/4$  counterpart. Similar changes are found for the *meta* couplings, which vanish only at  $U/t = 0$ , and the *para* one, which starts at  $-1/24$  for the mean-field solution. We stress that the closed-shell tight-binding SDW cannot show positive spin couplings, but that as soon as this restriction is liberated, the meta couplings become positive and grow with  $r$ , leading to a clear antiferromagnetic spin alternation. We notice that the mean-field coupling for the *ortho* pair in a full SDW of benzene can be well approximated by adding the tight-binding result  $-0.17$  to the standard coupling of a normal  $\sigma$  bond, which is close to  $-0.4$ . This gives a coupling of about  $-0.57$ , in close agreement with that initially published by Clark and Davidson.<sup>6</sup>

We think that this simple Hubbard example sheds light on how electron correlation can grow polyradicals by localizing electrons at specific sites. A full account of these and other

results will be presented elsewhere. We now leave models and turn to actual calculations.

## 6 Examples

We have selected in this Section a small number of simple, yet representative examples of results that show the insights that can be obtained from the OQS viewpoint described in this work.

### 6.1 The H<sub>2</sub> molecule

Although the dihydrogen molecule is always used as the basic model in the theory of chemical bonding, it is still today a continuous source of inspiration. We gather here results in the the  $^1\Sigma_g^+$  ground and first excited states of the H<sub>2</sub> molecule, as well as in the first excited  $^3\Sigma_u^+$  triplet. The first two are described at the simplest correlated level, i.e. with CAS[2,2] wavefunctions given by  $\Psi = c_1|\sigma_g\bar{\sigma}_g| + c_2|\sigma_u\bar{\sigma}_u|$ , with  $c_1$  and  $c_2$  having opposite and equal signs for the ground and excited states, respectively. For comparison purposes, we also add a full configuration interaction calculation (FCI) of the ground state. The basis set used is 6-311G(p) in all the cases.

The value of  $\langle\hat{S}_H^2\rangle$  for both singlet states as a function of the internuclear distance  $R_{\text{H-H}}$  is plotted in Fig. 3. Since H<sub>2</sub> dissociates homolytically, each hydrogen atom in the ground state at large internuclear distances must be a doublet, so that  $\lim_{R_{\text{H-H}}\rightarrow\infty}\langle\hat{S}_H^2\rangle = \frac{3}{4}$ . As  $R_{\text{H-H}}$  decreases,  $\langle\hat{S}_H^2\rangle$  changes in tune with  $p^H(1)$ , the probability that each hydrogen atom harbors a single electron. At the equilibrium distance,  $p^H(1) \simeq 0.5833$  and  $p^H(1) \times \frac{3}{4} \simeq 0.4375$ . The sectors (or real space resonance structures) that assign zero or two electrons to the same H, with a probability  $0.5833/2 \simeq 0.292$  each, do not contribute to  $\langle\hat{S}_H^2\rangle$ . The  $^1\Sigma_g^+$  excited state dissociates to a half-and-half mixture of the ionic configurations  $1s_A(1)1s_A(2)$  and  $1s_B(1)1s_B(2)$ , which implies  $p^H(1) = 0$ ,  $p^H(2) = \frac{1}{2}$ , and  $p^H(0) = \frac{1}{2}$ , so that  $\lim_{R_{\text{H-H}}\rightarrow\infty}\langle\hat{S}_H^2\rangle = 0$ , in agreement with what should be expected from a resonant singlet electron pair. Moreover,

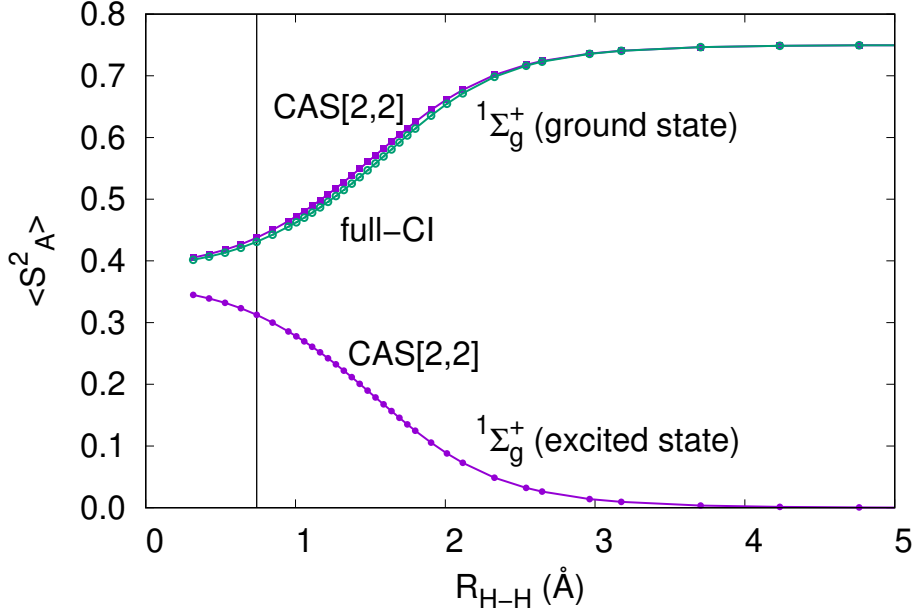


Figure 3: Value of  $\langle \hat{S}_H^2 \rangle$  for the  $\text{H}_2$  molecule at the CAS[2,2] level in the  $^1\Sigma_g^+$  ground (GS) and excited (ES) electronic states, as well as full-CI value of  $\langle \hat{S}_H^2 \rangle$  in the  $^1\Sigma_g^+$  GS. The vertical line signals the GS equilibrium distance. The CAS[2,2] curves coincide exactly with  $p^H(1) \times \frac{3}{4}$ .

as in the  $^1\Sigma_g^+$  ground state,  $\langle \hat{S}_H^2 \rangle$  at any  $R_{\text{H-H}}$  is also given by  $p^H(1) \times \frac{3}{4}$ . Actually, for any atom or fragment (say  $A$ ) of any molecule described at any level of theory, the equation  $\langle \hat{S}_{A,n=1}^2 \rangle = p^A(1) \times \frac{3}{4}$  holds. This means that the contribution to the local spin of  $A$  of the sector  $n = 1$  is always  $\frac{3}{4}$  times the probability that  $A$  contains a single electron.

The behavior observed in Fig. 3 can be fully understood in an analytical way. Calling  $A$  and  $B$  the left and right hydrogen atoms of  $\text{H}_2$ , respectively,  $\langle \hat{S}_A^2 \rangle$ , in terms of  $c_1$ ,  $c_2$ , and the atomic overlap integral  $s = \langle g|u \rangle_A$ , is given by  $\langle \hat{S}_A^2 \rangle = 3/8 - 3c_1c_2s^2$ . In any closed-shell molecule divided in two fragments  $A$  and  $B$ ,  $\langle \hat{\mathbf{S}}_A \cdot \hat{\mathbf{S}}_B \rangle = -\langle \hat{S}_A^2 \rangle$ , so that  $\langle \hat{\mathbf{S}}_A \cdot \hat{\mathbf{S}}_B \rangle = -3/8 + 3c_1c_2s^2$ . On the other hand, the bond-order between  $A$  and  $B$ , measured through the delocalization index, defined as  $\delta = 2 \int_A \int_B [\rho(\mathbf{r}_1)\rho(\mathbf{r}_2) - \rho_2(\mathbf{r}_1, \mathbf{r}_2)] d\mathbf{r}_1 d\mathbf{r}_2$ , takes in this case the form  $\delta = 1 + 8c_1c_2s^2$ . This gives  $\langle \hat{\mathbf{S}}_A \cdot \hat{\mathbf{S}}_B \rangle = 3/8(\delta - 2)$ . Using covariances,  $\delta = 2[1 - p^H(1)]$ . In the  $^1\Sigma_g^+$  ground state,  $c_1 = -c_2 = 1/\sqrt{2}$  and  $p^H(1) = 1$  in the  $R_{\text{H-H}} \rightarrow \infty$  limit. This leads to  $\langle \hat{\mathbf{S}}_A \cdot \hat{\mathbf{S}}_B \rangle = -\langle \hat{S}_A^2 \rangle = -\frac{3}{4}$  and  $\delta = 0$  at large internuclear distances. However,

in the  ${}^1\Sigma_g^+$  excited state,  $c_1 = c_2 = 1/\sqrt{2}$  and  $p^H(1) = 0$  in the  $R_{\text{H-H}} \rightarrow \infty$  limit, giving  $\langle \hat{\mathbf{S}}_A \cdot \hat{\mathbf{S}}_B \rangle = -\langle \hat{S}_A^2 \rangle = 0$ , as well as  $\delta = 2$ . All this is in perfect agreement with our previous insights.

A FCI calculation in the  ${}^1\Sigma_g^+$  electronic ground state of the  $\text{H}_2$  molecule gives  $\langle \hat{S}_H^2 \rangle$  values marginally lower than those in the CAS[2,2] calculation (Fig. 3). The small differences are due to the slightly different value of  $p^H(1)$  in the CAS[2,2] and full-CI calculations, and show that good qualitative evolutions can be predicted from wavefunctions as soon as the limitations of the SDW are liberated.

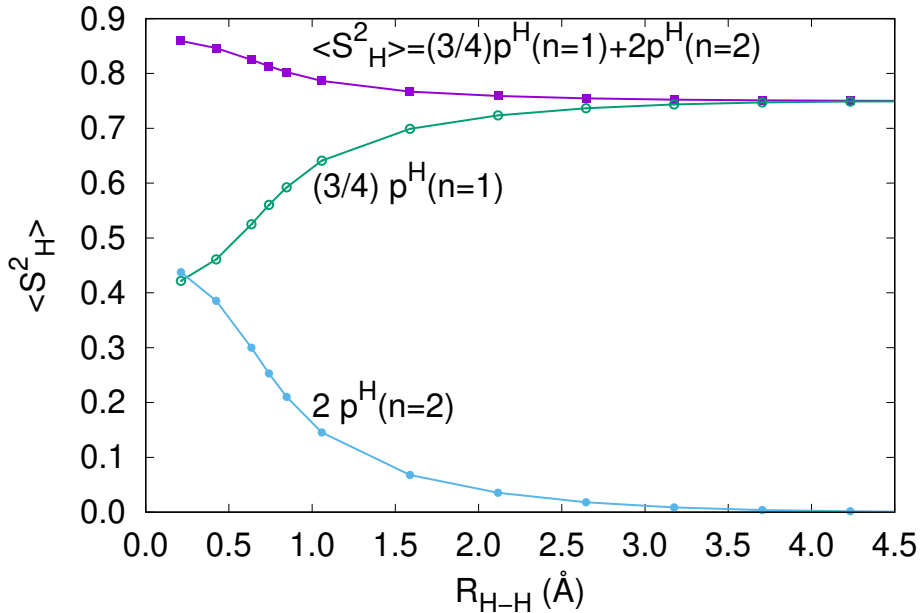


Figure 4: Value of  $\langle \hat{S}_H^2 \rangle$  for the  $\text{H}_2$  molecule in the first  ${}^3\Sigma_u^+$  excited electronic state. This is the direct sum of the  $n = 1$  and  $n = 2$  contributions, equal to  $S(S + 1)p^H(n = 1)$  and  $S(S + 1)p^H(n = 2)$ , with  $S = 1/2$  and  $S = 1$ , respectively.

The local spin for the  ${}^3\Sigma_u^+$  state of the  $\text{H}_2$  molecule is very well described at the ROHF level, and is plotted as a function  $R_{\text{H-H}}$  in Fig. 4. At variance with the ground state, both electrons are coupled to a triplet, so that the contribution coming from sector  $n = 2$  to  $\langle \hat{S}_H^2 \rangle$  is not zero but is given by  $S(S + 1) \times p^H(2)$  with  $S = 1$ . The sector  $n = 1$  has an analogous expression, i.e.  $S(S + 1) \times p^H(1)$  with  $S = 1/2$ . However, the  $p^H(n)$  probabilities are now different. In the triplet state, the antisymmetry (Pauli) requirement keeps the equal-spin

electrons further apart than in the singlet state. Actually, for a one-state site Hamiltonian, the probability to occupy the same site would be exactly zero. This results in a  $p^H(1)$  probability that is greater for the triplet than for the singlet at any internuclear distance, although it correctly approaches the value 1.0 at long distances in both cases. Consequently, as in the ground state,  $\lim_{R \rightarrow \infty} \langle \hat{S}_H^2 \rangle = \frac{3}{4}$ . The progressive decrease of  $p^H(2)$  with  $R$  causes the sector  $n = 2$  to be less and less important as compared to the sector  $n = 1$  as the internuclear distance increases. However, at the shortest computed distance both sectors are equally important. Finally, it is worth noticing that the above behaviors of  $p^H(1)$  and  $p^H(2)$  are responsible for the local spin being a continuously decreasing function of  $R$  in the  ${}^3\Sigma_u^+$  excited state of  $\text{H}_2$ . It is interesting that a partial statistical argument was already put forward to understand the local spin of this triplet state by Ramos-Cordoba, Salvador and Reiher et al.<sup>50</sup> Here we put it on firm grounds.

## 6.2 The $\text{H}_3^-$ molecule

This anion allows us to show the emergence of new phenomena without leaving simplicity. We have performed a RHF//6-311G(p) calculation of the linear  $\text{H}_3^-$  anion in its ground singlet state and analyzed the local spin components. The SDW can be written as  $|\sigma_g \bar{\sigma}_g \sigma_u \bar{\sigma}_u|$ , and we have 5 sectors and 9 spin-sectors. If we use a minimal basis set model with zero differential overlap, this is the Pimentel-Rundle three-center four-electron bond,<sup>51,52</sup> where  $\sigma_g = 1/2(1s_b + \sqrt{2}1s_a + 1s_c)$  and  $\sigma_u = 1/\sqrt{2}(1s_b - 1s_c)$ , with the central H atom labeled as  $a$ . As soon as overlap is allowed, the atomic overlap integral  $\langle \sigma_g | \sigma_u \rangle_A$  ceases to be negligible, with interesting outcomes. We have collected in Table 4 the local spin components of the two non-equivalent H atoms in  $\text{H}_3^-$ :  $A \equiv \text{H}_a$  and  $A \equiv \text{H}_b$ .

Let us first comment on the probabilities of the different sectors. It is a straightforward, yet interesting exercise to build the atomic charges of the central and terminal H atoms from the sector probabilities ( $N_A = \sum_n p^A(n) \times n$ ).  $\text{H}_a$  is positively charged, and the extra anionic electron is accumulated in the terminal  $\text{H}_b$  and  $\text{H}_c$  atoms, with  $Q(\text{H}_b) = Q(\text{H}_c) = -0.633$



au. It is easy to check that the squared spin is fixed in all the possible distributions of electrons in the five sectors, except in one, when  $n^\alpha = n^\beta = 1$ . For instance, if there are no electrons, the contribution of this sector to the local spin is  $\langle \hat{S}^2 \rangle = 0$ . Similarly, if there is one, be it described by an  $\alpha$  or  $\beta$  subdeterminant, its squared spin contribution will be  $3/4$ ,  $2$  if we have two same spin electrons. However, when we consider a spin sector with two opposite spin electrons, these can be coupled either as a singlet or as a triplet, and the local spin contribution ceases to be symmetry fixed. A much more detailed view is possible, since a look at the weighted contributions (LS in the Table) shows that the  $(0, 2)$ ,  $(1, 1)$  and  $(2, 0)$  contributions are equal (although different in  $H_a$  and  $H_b$ ). This is due to the fact that one can only build triplets in this system from  $\sigma_g\sigma_u$  subdeterminants, since the use of two  $\sigma_g$  functions must lead to a singlet. Spin-adapted sectors are thus also possible, a general formulation of which will be developed in the near future.

We can thus state that the central/terminal H atoms have a probability  $0.412/0.041$  of being found with no electrons, a probability  $0.449/0.315$  of being found with one electron in a  $S = 1/2$  state, with its two  $M_S = \pm 1/2$  constituents, a probability  $0.017/0.012$  of being found in a two-electron triplet and  $0.117/0.602$  in a singlet,  $0.006/0.030$  in a three-electron doublet, and an almost negligible value of a four-electron singlet. Interatomic couplings can be analyzed in an equivalent way. We stress that all this complexity is lost in RC analyses which mix inter- with intra-fragment couplings. For instance, the preference for singlet coupling of the  $n = 2$  sector is considerably larger in the terminal atoms, which are behaving as a singlet hydride. In the end, as evidenced in the last column of Table 4, the local spin of each H atom is clearly dominated by the  $n = 1$  sector. Being  $p^A(1)$  larger in the central hydrogen, its local spin is consequently larger.

We have previously shown<sup>24</sup> that the above-mentioned zero differential overlap model for this system leads to a neutral central atom and two  $Q = -0.5$  terminal ones. The model distribution functions for the full system,  $p(n_c, n_a, n_b)$ , are  $p(2, 0, 2) = 1/4$ ,  $p(2, 2, 0) = p(0, 2, 2) = 1/16$ ,  $p(2, 1, 1) = p(1, 1, 2) = 1/4$ , and  $p(2, 1, 1) = 1/8$  with zero probability of

triplet coupled electrons at the same atom due to Pauli exclusion, so that two ones in the above trios, like in (1, 1, 2) implies opposite spins for them. It is immediate to show that this model leads to  $\langle \hat{S}_{H_a}^2 \rangle = 1/2 \times 3/4 = 0.375$ , and to  $\langle \hat{S}_{H_b}^2 \rangle = 3/8 \times 3/4 = 0.281$ , which are rather close to the results in Table 4. As it is starting to become clear, it is electron localization and delocalization patterns which govern local spins.

Table 4: Local spin components of a single H atom of the  $H_3^-$  molecule at the restricted Hartree-Fock (RHF) level.  $n^\alpha$  and  $n^\beta$  are the number of  $\alpha$  and  $\beta$  electrons in H, respectively,  $n = n^\alpha + n^\beta$ , and  $LS(n^\alpha, n^\beta) = p^H(n^\alpha, n^\beta) \times \langle \hat{S}_{A, n^\alpha, n^\beta}^2 \rangle$ . Data for the central and terminal H atoms are found in the upper and lower parts of the Table, respectively.

$n^\alpha$	$n^\beta$	$p^H(n^\alpha, n^\beta)$	$\langle \hat{S}_{A, n^\alpha, n^\beta}^2 \rangle$	$LS(n^\alpha, n^\beta)$	n	$\langle \hat{S}_{H, n}^2 \rangle$
0	0	0.4119	0	0.0000	0	0.0000
0	1	0.2243	3/4	0.1683	1	0.3365
0	2	0.0056	2	0.0111	2	0.0333
1	0	0.2243	3/4	0.1683	3	0.0045
1	1	0.1222	0.0910	0.0111	4	0.0000
1	2	0.0030	3/4	0.0023	Total	0.3744
2	0	0.0056	2	0.0111		
2	1	0.0030	3/4	0.0023		
2	2	0.0001	0	0.0000		
$n^\alpha$	$n^\beta$	$p^H(n^\alpha, n^\beta)$	$\langle \hat{S}_{A, n^\alpha, n^\beta}^2 \rangle$	$LS(n^\alpha, n^\beta)$	n	$\langle \hat{S}_{H, n}^2 \rangle$
0	0	0.0410	0	0.0000	0	0.0000
0	1	0.1576	3/4	0.1182	1	0.2364
0	2	0.0039	2	0.0077	2	0.0231
1	0	0.1576	3/4	0.1182	3	0.0222
1	1	0.6061	0.0127	0.0077	4	0.0000
1	2	0.0148	3/4	0.0111	Total	0.2818
2	0	0.0039	2	0.0077		
2	1	0.0148	3/4	0.0111		
2	2	0.0004	0	0.0000		

### 6.3 The NaF and Ne<sub>2</sub> molecules

Small, or even negligible local spins can be found in closed-shell molecules even though the CD and not Mayer's or RC's approaches are used. From what we have said up to now, this will be clearly the case when the fragments are spin paired and there is little covalent delocalization among them. This is the situation expected in largely ionic or van der Waals

molecules. Since the local spins of this type of systems will not be impacted much by electron correlation, we show here RHF data on the NaF and Ne<sub>2</sub> molecules. Only spinless sectors with non-negligible probabilities are shown in Table 5.

Table 5: Local spin components of the Na atom in the NaF molecule (left), and of the Ne atom in Ne<sub>2</sub> at the RHF level. Only results for sectors  $n = 8 - 12$  of NaF and  $n = 9 - 11$  of Ne<sub>2</sub> are shown.

n	$p^{\text{Na}}(n)$	$\langle \hat{S}_{\text{Na},n}^2 \rangle$	n	$p^{\text{Ne}}(n)$	$\langle \hat{S}_{\text{Ne},n}^2 \rangle$
8	0.0001	0.0001	9	0.0005	0.0004
9	0.0186	0.0140	10	0.9990	0.0000
10	0.9113	0.0021	11	0.0005	0.0004
11	0.0681	0.0511		Total	0.0008
12	0.0018	0.0017			
	Total	0.0690			

In NaF, the Na atom has only three contributing sectors, with 9, 10 and 11 electrons. The electron distribution is vastly dominated by the Na<sup>+</sup> cation, which is clearly almost fully closed-shell paired, since the sector with  $n = 10$  provides a very small squared-spin. There is a 7% probability to find the neutral Na atom distribution, and about 2% to find the Na<sup>2+</sup> cation. In both cases,  $3/4 \times p$  provides a very good match with the spin contributions found in the Table, which demonstrates that the  $n - 1$  remaining electrons (ten or eight, respectively) are coupled to a singlet, leaving a double behind. The situation in dineon is taken to the limit. The ten electrons of each atom form a singlet. We think that these two simple cases demonstrate that there are strong theoretical reasons supporting the use of non-zero local spins in closed-shell systems.

## 6.4 Subdeterminant partition in LiH

We consider here an even thinner partition of the local spin in the LiH molecule. At the RHF//6-311G(d,p) level the local spin of each atom is small, 0.073, showing the largely ionic character of the system. The SDW takes the form  $|1\sigma 1\bar{\sigma} 2\sigma 2\bar{\sigma}|$ , with rather localized  $1\sigma$  and  $2\sigma$  functions on the Li and H atoms, respectively. There are several subdeterminants

comprising each spin sector. For instance, if we deal with one  $\beta$  electron, we have two subdeterminants (in this case one electron functions):  $1\bar{\sigma}, 2\bar{\sigma}$ . Their contributions, in the notation already commented, are found in entries 2 and 3 of the left panel of Table 6. The first of these two determinants contributes negligibly to the H local spin. The second,  $2\bar{\sigma}$ , together with its one-electron  $\alpha$  counterpart ( $k = 6$ ), make 90% of it. In orbital parlance, single electrons described by a  $2\sigma$ -like function, which are part of the neutral LiH resonant structure, build the local spin of the sytem.

Table 6: Local spin components of the H atom of the LiH molecule,  $\langle \hat{S}_H^2 \rangle$ , at the restricted Hartree-Fock (RHF) level.  $\Psi_{\mathbf{k}}$  is the subdeterminant,  $n^\alpha$  and  $n^\beta$  are the number of  $\alpha$  and  $\beta$  electrons in H, respectively,  $n = n^\alpha + n^\beta$ ,  $M_{\mathbf{k}} = \frac{1}{2}(n^\alpha - n^\beta)$ ,  $n_d$  has been defined in the text, and  $\text{sum} = n_d/2 + M_{\mathbf{k}}^2 \equiv \langle \hat{S}_{H,n,\mathbf{k}}^2 \rangle$ .  $\langle \hat{S}_H^2 \rangle = \sum_{n=0}^4 \langle \hat{S}_{H,n}^2 \rangle = 0.072979$ .

$k$	$\Psi_{\mathbf{k}}$	$n/2$	$M_{\mathbf{k}}^2$	$n_d/2$	sum	$p_n^k$	$p_n^k \times \text{sum}$	$n^\alpha$	$n^\beta$	$\langle \hat{S}_{A,n^\alpha,n^\beta}^2 \rangle$	n	$\langle \hat{S}_{A,n}^2 \rangle$
1	$  $	0	0	0	0	0.002205	0.000000	0	0	0.000000	0	0.000000
2	$ 1\sigma $	1/2	1/4	1/2	3/4	0.000008	0.000006	0	1	0.033439	1	0.066878
3	$ 1\bar{\sigma} $	1/2	1/4	1/2	3/4	0.000008	0.000006	1	0	0.033439	2	0.001008
4	$ 2\sigma $	1/2	1/4	1/2	3/4	0.044577	0.033433	1	1	0.000336	3	0.005094
5	$ 2\bar{\sigma} $	1/2	1/4	1/2	3/4	0.044577	0.033433	0	2	0.000336	4	0.000000
6	$ 1\sigma 2\sigma $	1	1	1	2	0.000168	0.000336	2	0	0.000336		
7	$ 1\sigma 2\bar{\sigma} $	1	0	1	1	0.000168	0.000168	1	2	0.002547		
8	$ 1\sigma 1\bar{\sigma} $	1	0	0	0	0.000000	0.000000	2	1	0.002547		
9	$ 2\sigma 2\bar{\sigma} $	1	0	0	0	0.901148	0.000000	2	2	0.000000		
10	$ 1\bar{\sigma} 2\sigma $	1	0	1	1	0.000168	0.000168					
11	$ 1\bar{\sigma} 2\bar{\sigma} $	1	1	1	2	0.000168	0.000336					
12	$ 1\sigma 1\bar{\sigma} 2\sigma $	3/2	1/4	1/2	3/4	0.003395	0.002546					
13	$ 1\sigma 1\bar{\sigma} 2\bar{\sigma} $	3/2	1/4	1/2	3/4	0.000001	0.000000					
14	$ 1\sigma 1\bar{\sigma} 2\sigma $	3/2	1/4	1/2	3/4	0.003395	0.002546					
15	$ 1\bar{\sigma} 2\sigma 2\bar{\sigma} $	3/2	1/4	1/2	3/4	0.000001	0.000000					
16	$ 1\sigma 1\bar{\sigma} 2\bar{\sigma} 2\bar{\sigma} $	2	0	0	0	0.000013	0.000000					

The rest of the table can be interpreted easily. For instance, there is only one subdeterminant with either two  $\alpha$  or two  $\beta$  electrons,  $|1\sigma 2\sigma|$  and  $|1\bar{\sigma} 2\bar{\sigma}|$ , respectively. Being its probability negligible, it does not contribute to the local spin. The two subdeterminants  $|1\sigma 1\bar{\sigma}|$ , and  $|2\sigma 2\bar{\sigma}|$  contribute zero to  $\langle S_H^2 \rangle$  ( $k = 8, 9$ , respectively). Interestingly, the second one, in which the two electrons are singlet-coupled in the  $2\sigma$  function, accounts for about 90% of all the possible electron distributions. Finally, it is also relevant to consider entries

7 and 10, each contributing 1 to the local spin. This value is not a valid  $S(S + 1)$  squared spin. The first of these two subdeterminants is  $|1\sigma\bar{2}\sigma|$ , while the second becomes  $|2\sigma\bar{1}\sigma|$ , and we face here the same situation already commented. Spin adapted sector would lead to triplet/singlet plus/minus linear combinations of the above, respectively. The first would contribute 2 and the second 0 to the local spin.

Although we leave a detailed account of the following for future works, an electron-hole analogy is apparent at this point. Each *electron* subdeterminant for the H atom in Table 6 can be associated to a *hole* counterpart in the Li atom that completes the global wavefunction. We have organized them such that  $k_e + k_h = 17$  in the table. The first and the last entries, or entries 4 and 13. An electron in determinant as  $k = 4$  contributes with its probability  $p_n^k \approx 0.04$  and spin  $3/4$  to  $\langle S_H^2 \rangle$ . These numbers correspond to the probability of finding a  $2\sigma$  electron in H contributing with its single-electron squared spin. Its *hole* companion determinant  $k = 13$  would also contribute with the same probability and spin to  $\langle S_{Li}^2 \rangle$ , since it now describes the three remaining electrons in the other region, an event which has of course the same probability and carries the same squared spin.

In other words, Table 6 for the Li atom is obtained by changing the determinants in the  $\Psi_k$  column by those of the  $\Psi_{17-k}$  one. This is another demonstration that the local spins of the two atoms of diatomic singlets are equal. Another interesting look focuses in the interatomic spin couplings. The  $n = 1$  spin doublet formed by the  $k = 2, 5$  subdeterminants in H couples to a singlet with its hole equivalent doublet in Li, formed by the  $k = 14, 11$  subdeterminants. Similarly, the  $n = 2$  H triplet formed by entries  $k = 4, 13$  and the plus linear combination of 7 and 9 couples also to a singlet with its equivalent hole entries in Li. More complex rules needing from simple Clebsch-Gordan algebra can be found in more general cases. Going to the middle panel of Table 6, we also recognize that the  $A \equiv H (n^\alpha, n^\beta)$  local spin contributions will be equal to the  $(N/2 - n^\alpha, N/2 - n^\beta)$  ones in Li, or that in the rightmost panel the local spin of each  $n$ -electron sector in the H atom is equal to that of the partner  $(N - n)$ -electron sector in Li. We find this symmetry particularly appealing.

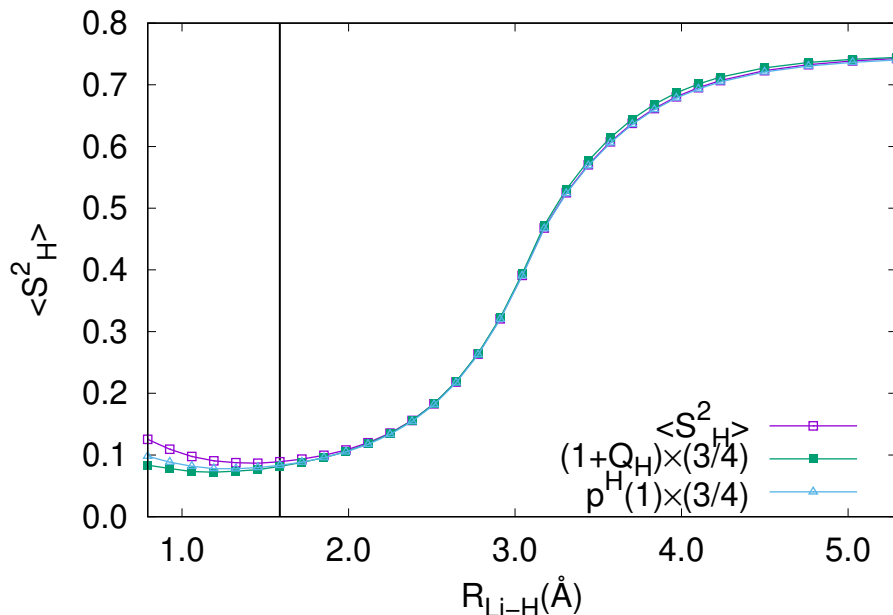


Figure 5: CAS[2,2] values of  $\langle \hat{S}_H^2 \rangle$ ,  $(1 + Q^H) \times \frac{3}{4}$ , and  $p^H(1) \times \frac{3}{4}$  for the H atom of the LiH molecule in the ground electronic state as a function of the Li–H distance,  $R_{\text{Li-H}}$ .

We also analyze here the evolution of the local spins in LiH at the simple CAS[2,2] level, which allows for a correct molecular dissociation, maintaining the basis set. We have already shown,<sup>53</sup> that the LiH dissociation can be well understood by a one-parameter ionization. An electron from the Li atom is transferred as the interatomic distance decreases to the H moiety. In the process, only the  $p(n^{\text{Li}} = 3, n^{\text{H}} = 1)$  and  $p(n^{\text{Li}} = 2, n^{\text{H}} = 2)$  probabilities become affected. The second grows at the expense of the first, and the sum of the two remains very close to 1. With this,  $\langle \hat{S}_H^2 \rangle$  should be just measuring how large  $p(3, 1)$  (or  $p^H(1)$ ) is. Fig. 5 shows how well this assumption works.

We end the subsection by showing the impact of static correlation on the spin sectors. Table 7 contains a CAS[4,12]//6-311G(d,p) calculation in LiH at the RHF geometry. It is known that in highly ionic compounds the introduction of electron correlation increases covalency. This increases the  $p^H(1)$  probability, and thus the H local spin slightly.

Table 7: Sector-resolved local spin components of the H atom in LiH,  $\langle \hat{S}_H^2 \rangle$ . CAS[4,12]//6-311G(d,p) calculation at the RHF geometry. The total value of  $\langle \hat{S}_H^2 \rangle$  for the RHF and CAS calculation is 0.072979 and 0.081586, respectively.

$n$	$\langle \hat{S}_{A,n}^2 \rangle$
0	0.000000
1	0.075411
2	0.001245
3	0.004930
4	0.000000

## 6.5 Second period diatomics

We close the presentation of representative examples by examining the global local spins of the first and second period homonuclear diatomics. We have performed high level heat-bath configuration interaction (HCI)<sup>54</sup> calculations in their ground states with the aug-cc-pVTZ basis set, using the pySCF suite.<sup>49</sup> He<sub>2</sub> and Ne<sub>2</sub> have been excluded since their local spins are close to zero and do not offer any additional insight. RHF (or ROHF) calculations have also been performed for comparison purposes. Results are contained in Table 8

Table 8: Local spin  $\langle \hat{S}_A^2 \rangle$  in the ground state HCI//aug-cc-pVTZ wavefunctions of the first and second period homonuclear diatomics. R(O)HF values are also included for comparison.

Molecule	R(O)HF	HCI
H <sub>2</sub>	0.375	0.431
Li <sub>2</sub>	0.367	0.427
Be <sub>2</sub>	0.279	0.395
B <sub>2</sub>	1.288	1.626
C <sub>2</sub>	1.205	2.016
N <sub>2</sub>	1.140	1.382
O <sub>2</sub>	1.354	1.410
F <sub>2</sub>	0.466	0.603

Several considerations are due. First, the  $\langle \hat{\mathbf{S}}_A \cdot \hat{\mathbf{S}}_B \rangle$  spin couplings are just the negatives of  $\langle \hat{S}_A^2 \rangle$  except in the two triplets, B<sub>2</sub> and O<sub>2</sub>, where  $\langle \hat{\mathbf{S}}_A \cdot \hat{\mathbf{S}}_B \rangle = -\langle \hat{S}_A^2 \rangle + 1$ . Notice that standard single bonds provide correlated local spins close to 0.43 as in H<sub>2</sub> and Li<sub>2</sub>. This shows how correlation induces localization of the bonding Lewis electron pair in the atomic

regions: Increasing the atomic localized character of the electron pair changes the local spin from  $3/8$  in an ideally delocalized situation to  $3/4$  in a perfect diradical.

Let us consider now  $\text{Be}_2$ , where correlation is important. At the HF level, the local spin is significantly smaller than  $3/8$ . We must recall that the dissociation limit provides two closed-shell singlet atoms, and that the RHF solution provides a local spin directly related to bond order. A small bond order leads to a small local spin. Correlation is important, as expected, to account for bonding in  $\text{Be}_2$ . It is known that the bond order of this molecule increases considerably if a correlated description is used.

The mean-field description of diboron is known<sup>55</sup> to lead to two delocalized triplet coupled electrons in the  $1\pi_u$  block and a  $2\sigma$  bonding pair from strong  $sp$  hybridization that leaves a delocalization index close to 2.0. This is basically our delocalized triplet+delocalized singlet model with local spin equal to 1.25. The introduction of electron correlation seems to localize these pairs in their atomic regions, increasing the local spin considerably. RHF dinitrogen is close to a pure triple bond with local spin equal to  $3 \times 3/8 = 9/8 \approx 1.125$ . Correlation induces a large decrease of its bond order from about 3.0 at the RHF level to about 2 at the correlated one. Here we also see a localization that increases its local spin to 1.38. Dioxygen seems to be well described by our simple singlet+triplet model at the ROHF level, with a local spin not far from 1.25, that again increases through correlation induced localization. Similarly,  $\text{F}_2$  is shown to be closer to a proto-covalent bond, and not to a fluctuating charge-shift link.<sup>56</sup> If we imagine a dissociating electron pair similar to that in  $\text{H}_2$ , we can take Fig. 3 to check that its local spin, about 0.6, corresponds to that of  $\text{H}_2$  at around  $1.5 \text{ \AA}$ , more than twice the dihydrogen internuclear equilibrium distance. If the electron pair fluctuations that are assumed to exist in charge-shift bonds would be relevant, their spin singlet nature would decrease, not increase its local spin.

Last, but not least, the singlet ground-state dicarbon deserves a final comment. Notice that this is the system with a largest HF/HCI difference by large. At the mean-field level,<sup>55</sup> the bond order rises to about 3.2, and a local spin of 1.2. The bond order decreases to



about 1.8 on including correlation. Even in the most naïve case in which the eight valence electrons were engaged in ideal covalent bonds leading to a bond order of 4, this would lead to a top covalent local spin of 1.5. The large C local spin can only be explained by a prominent localized singlet diradical component. If the extra valence electron pair would be considered as a localized singlet diradical, this would add 0.75 to the local spin. This, together with correlation enhanced local spins of the covalent terms, would justify a 2.0 local spin. Notice that the localization of this singlet diradical would contribute neither to the interatomic delocalization nor to a substantial increase of the binding energy of the system. These results are in consonance with those obtained from RC local spins.<sup>22</sup> Further work is still needed to pinpoint chemical bonding in this system.

## 7 Conclusions

We have presented in this work an open quantum systems comprehensive account of local spins. These were introduced by Clark and Davidson<sup>6</sup> as descriptors of the local distribution of the electronic spins and their couplings in molecules. These authors used projection operators to define Hermitian fragment spin operators that fulfil all quantum mechanical requirements for well-behaved angular momenta. Fragment spins solve the inability of traditional measures to offer any insight on spin coupling in global singlets, where the spin density is everywhere exactly zero. Several authorized voices have since then argued against CD local spins, for they provide considerable values for closed-shell singlets. Over the years, a set of *ad hoc* requisites for local spins to be considered physically meaningful were introduced, which have led to an evolution in their definition which culminates with Ramos-Cordoba et al proposal.<sup>17</sup>

We take here the inverse road, and show that the original path that transforms CD local spins into RC ones is based on physically unjustified transformations when a decomposition of two-electron operators into fragments is performed. By understanding atoms or fragments

in-molecules as open quantum mechanical subsystems (OQSs), we rigorously show that the CD operators are in fact offering a crystal clear picture of the distribution of spin in a fragment-in-the-molecule. An OQS is in a general mixed state, being composed of sectors characterized by a given number of electrons with characteristic probabilities. For each of these  $n$ -electron sectors well-defined  $n$ -electron spin operators can be used to obtain spins which are then weighted by the sector probability to build the CD local spin. Non-zero fragment spins for a closed-shell singlet arise from electron delocalization. When electrons are allowed to delocalize between fragments (a signature of covalent bonding among them), non-zero probabilities of finding an odd number of them, for instance, appear, giving rise to sizeable local spins. The relation of CD spins to bond orders in closed-shell molecules discovered by Clark and Davidson thus acquires a clear meaning after these insights.

The OQS viewpoint allows for a fruitful use of models. One can propose back-of-the-envelope sets of sector probabilities for covalent, ionic, and zwitterionic situations, and tune their degree of localization. This leads to an easy road to classification. In fact, the two-center, two-electron cases are fully mapped. We algebraically show that RC local spins fail, for instance, in assigning physically meaningful spins in the dissociative limit of the zwitterionic excited state of dihydrogen. Classification in multielectron cases is also sketched by examining general spin eigenfunctions. We show that the local spin couplings can be used to reflect the genealogy of the couplings, a property that we expect to use further.

The general effect of static correlation is also analyzed through the use of the Hubbard Hamiltonian, which allows to tune the amount of correlation. We show how correlation induced localization in a H-chain model changes completely the spin coupling pattern, which evolves from all-negative, algebraically decaying spin couplings between all site pairs toward an alternation of positive and negative couplings characteristic of an antiferromagnet.

Finally, a set of simple systems that exemplify our findings is examined. We think that they demonstrate how electron localization and delocalization modulate local spins, and open many windows into future work. In particular, we show that CD local spins in closed-

shell molecules can actually be close to zero when delocalization is small, as in ionic or van der Waals systems, and that high level calculations in the dicarbon molecule display anomalously large local spins, which can probably not be understood without invoking a considerable singlet diradical character, in agreement with results obtained with RC local spins.<sup>50</sup> The latter should provide results considerably similar to those of CD whenever spins are localized. This means that RC local spins, which mix a number of ingredients in a very clever way, maintain their usefulness, at least in ground states where zwitterionic or even weirder resonances do not dominate.

Besides helping to clarify the many approaches and misconceptions that surround the local spin concepts, the OQS approach will surely provide much light on issues that range from understanding the atomic promotion concept to providing a firm ground to spin model Hamiltonians in extended systems.

## Acknowledgements

We thank the Spanish MICINN, grant PGC2018-095953-B-I00, the FICYT, grant FC-GRUPIN-IDI/2018/000177, and the European Union FEDER for funding.

## References

- (1) Jammer, M. *The philosophy of quantum mechanics; the interpretations of quantum mechanics in historical perspective*; Wiley: New York, 1974.
- (2) Jaeger, G. *Quantum entanglement, information, and the foundations of quantum mechanics*; Springer: Berlin, 2009.
- (3) von Hopffgarten, M.; Frenking, G. Energy decomposition analysis. *WIREs Computational Molecular Science* **2011**, *2*, 43–62.

- (4) Young, D. C. *Computational Chemistry: A practical Guide for Applying Techniques to Real World Problems*; John Wiley & Sons, Inc., pp 99–106.
- (5) Chen, L.-Q.; Chen, L.-D.; Kalinin, S. V.; Klimeck, G.; Kumar, S. K.; Neugebauer, J.; Terasaki, I. Design and discovery of materials guided by theory and computation. *npj Computational Materials* **2015**, *1*.
- (6) Clark, A. E.; Davidson, E. R. Local spin. *The Journal of Chemical Physics* **2001**, *115*, 7382–7392.
- (7) Davidson, E. R.; Clark, A. E. Local spin II. *Molecular Physics* **2002**, *100*, 373–383.
- (8) Clark, A. E.; Davidson, E. R. Local Spin III: Wave Function Analysis along a Reaction Coordinate, H Atom Abstraction, and Addition Processes of Benzyne. *The Journal of Physical Chemistry A* **2002**, *106*, 6890–6896.
- (9) Herrmann, C.; Reiher, M.; Hess, B. A. Comparative analysis of local spin definitions. *The Journal of Chemical Physics* **2005**, *122*, 034102.
- (10) Reiher, M. On the definition of local spin in relativistic and nonrelativistic quantum chemistry. *Faraday Discussions* **2007**, *135*, 97–124.
- (11) Mayer, I. Local spins: An alternative treatment for single determinant wave functions. *Chemical Physics Letters* **2007**, *440*, 357–359.
- (12) Davidson, E. R.; Clark, A. E. Analysis of wave functions for open-shell molecules. *Physical Chemistry Chemical Physics* **2007**, *9*, 1881.
- (13) Mayer, I. Local spins: An improved treatment for correlated wave functions. *Chemical Physics Letters* **2009**, *478*, 323–326.
- (14) Mayer, I.; Matito, E. Calculation of local spins for correlated wave functions. *Physical Chemistry Chemical Physics* **2010**, *12*, 11308.

- (15) Alcoba, D. R.; Torre, A.; Lain, L.; Bochicchio, R. C. Determination of Local Spins by Means of a Spin-Free Treatment. *Journal of Chemical Theory and Computation* **2011**, *7*, 3560–3566.
- (16) Mayer, I. Local spins: Improving the treatment for single determinant wave functions. *Chemical Physics Letters* **2012**, *539-540*, 172–174.
- (17) Ramos-Cordoba, E.; Matito, E.; Mayer, I.; Salvador, P. Toward a Unique Definition of the Local Spin. *Journal of Chemical Theory and Computation* **2012**, *8*, 1270–1279.
- (18) Ramos-Cordoba, E.; Matito, E.; Salvador, P.; Mayer, I. Local spins: improved Hilbert-space analysis. *Physical Chemistry Chemical Physics* **2012**, *14*, 15291.
- (19) The magnetic landscape. *Nature Materials* **2019**, *18*, 651–651.
- (20) Zheng, B.-X.; Chan, G. K.-L. Ground-state phase diagram of the square lattice Hubbard model from density matrix embedding theory. *Physical Review B* **2016**, *93*, 035126.
- (21) Alcoba, D. R.; Lain, L.; Torre, A.; Bochicchio, R. C. Local spin: A treatment beyond single determinant wave functions. *Chemical Physics Letters* **2009**, *470*, 136–139.
- (22) Ramos-Cordoba, E.; Salvador, P. Diradical character from the local spin analysis. *Physical Chemistry Chemical Physics* **2014**, *16*, 9565.
- (23) Ramos-Cordoba, E.; Salvador, P. Characterization and Quantification of Polyradical Character. *Journal of Chemical Theory and Computation* **2014**, *10*, 634–641.
- (24) Martín Pendás, Á.; Francisco, E. Chemical Bonding from the Statistics of the Electron Distribution. *ChemPhysChem* **2019**, *20*, 2722–2741.
- (25) Bader, R. F. W. *Atoms in Molecules*; Oxford University Press: Oxford, 1990.

- (26) Quantum mechanics of many-electron systems. *Proceedings of the Royal Society of London. Series A, Containing Papers of a Mathematical and Physical Character* **1929**, *123*, 714–733.
- (27) Podewitz, M.; Herrmann, C.; Malassa, A.; Westerhausen, M.; Reiher, M. Spin–Spin interactions in polynuclear transition-metal complexes. *Chemical Physics Letters* **2008**, *451*, 301–308.
- (28) Löwdin, P.-O. Quantum Theory of Many-Particle Systems. I. Physical Interpretations by Means of Density Matrices, Natural Spin-Orbitals, and Convergence Problems in the Method of Configurational Interaction. *Physical Review* **1955**, *97*, 1474–1489.
- (29) Takatsuka, K.; Fueno, T.; Yamaguchi, K. Distribution of odd electrons in ground-state molecules. *Theoretica Chimica Acta* **1978**, *48*, 175–183.
- (30) Staroverov, V. N.; Davidson, E. R. Diradical Character of the Cope Rearrangement Transition State. *Journal of the American Chemical Society* **2000**, *122*, 186–187.
- (31) Staroverov, V. N.; Davidson, E. R. Distribution of effectively unpaired electrons. *Chemical Physics Letters* **2000**, *330*, 161–168.
- (32) Staroverov, V. N.; Davidson, E. R. Charge densities for singlet and triplet electron pairs. *International Journal of Quantum Chemistry* **2000**, *77*, 651–660.
- (33) Breuer, H.-P.; Petruccione, F. *The theory of open quantum systems*; Oxford University Press: Oxford New York, 2002.
- (34) Nielsen, M.; Chuang, I. L. *Quantum computation and quantum information*; Cambridge University Press: Cambridge New York, 2010.
- (35) Martín Pendás, A.; Francisco, E. Quantum Chemical Topology as a Theory of Open Quantum Systems. *Journal of Chemical Theory and Computation* **2018**, *15*, 1079–1088.

- (36) Francisco, E.; Martín Pendás, A.; Blanco, M. A. Electron number probability distributions for correlated wave functions. *The Journal of Chemical Physics* **2007**, *126*, 094102.
- (37) Martín Pendás, A.; Francisco, E.; Blanco, M. A. Spin resolved electron number distribution functions: How spins couple in real space. *The Journal of Chemical Physics* **2007**, *127*, 144103.
- (38) Martín Pendás, A.; Francisco, E.; Blanco, M. A. An electron number distribution view of chemical bonds in real space. *Phys. Chem. Chem. Phys.* **2007**, *9*, 1087–1092.
- (39) Francisco, E.; Martín Pendás, A. Electron number distribution functions from molecular wavefunctions. Version 2. *Computer Physics Communications* **2014**, *185*, 2663–2682.
- (40) Ponec, R. Electron pairing and chemical bonds. Chemical structure, valences and structural similarities from the analysis of the Fermi holes. *Journal of Mathematical Chemistry* **1997**, *21*, 323–333.
- (41) Ponec, R. Electron pairing and chemical bonds. Molecular structure from the analysis of pair densities and related quantities. *Journal of Mathematical Chemistry* **1998**, *23*, 85–103.
- (42) Wiberg, K. Application of the pople-santry-segal CNDO method to the cyclopropylcarbinyl and cyclobutyl cation and to bicyclobutane. *Tetrahedron* **1968**, *24*, 1083–1096.
- (43) Mayer, I. Bond order and valence indices: A personal account. *Journal of Computational Chemistry* **2006**, *28*, 204–221.
- (44) Pauncz, R. *Spin eigenfunctions: Construction and use*; Plenum Press: New York, 1979.
- (45) Electron correlations in narrow energy bands. *Proceedings of the Royal Society of London. Series A. Mathematical and Physical Sciences* **1963**, *276*, 238–257.

- (46) Gallo-Bueno, A.; Kohout, M.; Martín Pendás, A. Decay Rate of Correlated Real-Space Delocalization Measures: Insights into Chemical Bonding and Mott Transitions from Hydrogen Chains. *Journal of Chemical Theory and Computation* **2016**, *12*, 3053–3062.
- (47) Gallo-Bueno, A.; Francisco, E.; Martín Pendás, A. Decay rate of real space delocalization measures: a comparison between analytical and test systems. *Physical Chemistry Chemical Physics* **2016**, *18*, 11772–11780.
- (48) Lieb, E. H.; Wu, F. Y. Absence of Mott Transition in an Exact Solution of the Short-Range, One-Band Model in One Dimension. *Physical Review Letters* **1968**, *20*, 1445.
- (49) Sun, Q.; Berkelbach, T. C.; Blunt, N. S.; Booth, G. H.; Guo, S.; Li, Z.; Liu, J.; McClain, J. D.; Sayfutyarova, E. R.; Sharma, S.; Wouters, S.; Chan, G. K.-L. PySCF: the Python-based simulations of chemistry framework. *Wiley Interdisciplinary Reviews: Computational Molecular Science* **2018**, *8*, e1340.
- (50) Ramos-Cordoba, E.; Salvador, P.; Reiher, M. Local Spin Analysis and Chemical Bonding. *Chemistry - A European Journal* **2013**, *19*, 15267–15275.
- (51) Rundle, R. E. Electron Deficient Compounds. *Journal of the American Chemical Society* **1947**, *69*, 1327–1331.
- (52) Pimentel, G. C. The Bonding of Trihalide and Bifluoride Ions by the Molecular Orbital Method. *The Journal of Chemical Physics* **1951**, *19*, 446–448.
- (53) Martín Pendás, A.; Francisco, E.; Blanco, M. A. Charge transfer, chemical potentials, and the nature of functional groups: answers from quantum chemical topology. *Faraday Discuss.* **2007**, *135*, 423–438.
- (54) Holmes, A. A.; Tubman, N. M.; Umrigar, C. J. Heat-Bath Configuration Interaction: An Efficient Selected Configuration Interaction Algorithm Inspired by Heat-Bath Sampling. *Journal of Chemical Theory and Computation* **2016**, *12*, 3674–3680.



- (55) Menéndez, M.; Boto, R. Á.; Francisco, E.; Martín Pendás, Á. One-electron images in real space: Natural adaptive orbitals. *Journal of Computational Chemistry* **2015**, *36*, 833–843.
- (56) Shaik, S.; Danovich, D.; Wu, W.; Hiberty, P. C. Charge-shift bonding and its manifestations in chemistry. *Nature Chemistry* **2009**, *1*, 443–449.

# Supporting Information

## Local spin and open quantum systems: clarifying misconceptions, unifying approaches

Ángel Martín Pendás\* and Evelio Francisco\*

*Departamento de Química Física y Analítica. Universidad de Oviedo. Spain.*

E-mail: ampendas@uniovi.es

### 1 Effectively unpaired electrons and local spin

The scalar field

$$u(\mathbf{r}_1; \mathbf{r}'_1) = 2\rho(\mathbf{r}_1; \mathbf{r}'_1) - \int \rho(\mathbf{r}_1; \mathbf{r}_2)\rho(\mathbf{r}_2; \mathbf{r}'_1)d\mathbf{r}_2, \quad (1)$$

known as the effectively unpaired electrons density,<sup>1</sup> and several of its properties<sup>2</sup> have been thoroughly investigated. This name seems to be almost always justified since, in many cases, its integration to all the space in different systems results in what one expects for the number of electrons that are not paired with equivalent electrons of opposite spin. To cite just two very well-known examples: the integration of  $u(\mathbf{r})$  over  $R^3$  for a single-electron system correctly predicts a value of 1, as it should. In the limit  $R \rightarrow \infty$  of the properly dissociating  $\text{H}_2$  molecule in the  $^1\Sigma_g^+$  ground electronic state, the integration of  $u(\mathbf{r})$  gives 2, again the correct number. However, some properties of  $u(\mathbf{r})$  incite to think that the name of effectively unpaired electrons density may not be the most accurate. For instance, the trace of  $u$ , that in terms of the occupation numbers,  $n_i$ , of the natural orbitals of the system, is given by  $n_d = \sum_i n_i(2 - n_i)$  has an upper limit of  $2N$ ,<sup>2</sup> i.e. *the number of effectively unpaired electrons can be greater than the number of electron themselves*. An example

of this is a molecule with only spin up or spin down electrons described at the configuration interaction level. Another case in which  $n_d \geq N$ , also pointed out by Staroverov and Davidson, is the  ${}^1\Sigma_u^+$  excited electronic state of the  $\text{H}_2$  molecule at large internuclear distances. We will show in this subsection another counterintuitive behavior of  $u(\mathbf{r})$ .

Let us consider the two  ${}^1\Sigma_g^+$  states that can be formed for the  $\text{H}_2$  molecule from a linear combination of the Slater determinants  $|\sigma_g \bar{\sigma}_g|$  and  $|\sigma_u \bar{\sigma}_u|$ :  $\Psi = c_1 |\sigma_g \bar{\sigma}_g| + c_2 |\sigma_u \bar{\sigma}_u|$ . The state with  $c_1$  and  $c_2$  of the opposite sign corresponds to the ground state cited above, while  $c_1$  and  $c_2$  with the same sign indicates an excited state (ES). From  $|\sigma_g \bar{\sigma}_g| = \sigma_g(\mathbf{r}_1)\sigma_g(\mathbf{r}_2)\Theta$  and  $|\sigma_u \bar{\sigma}_u| = \sigma_u(\mathbf{r}_1)\sigma_u(\mathbf{r}_2)\Theta$ , where  $\Theta = 2^{-1/2}(\alpha\beta - \beta\alpha)$  is the spin function, the electron density of the above  $\Psi$  is given by  $\rho(\mathbf{r}; \mathbf{r}) \equiv \rho(\mathbf{r}) = n_g \sigma_g^2(\mathbf{r}) + n_u \sigma_u^2(\mathbf{r})$ , where  $n_g = 2c_1^2$  and  $n_u = 2c_2^2$ , so the natural orbitals are also  $\sigma_g$  and  $\sigma_u$ , and  $u(\mathbf{r})$  is given by  $u(\mathbf{r}) = n_g(2 - n_g)\sigma_g^2(\mathbf{r}) + n_u(2 - n_u)\sigma_u^2(\mathbf{r})$ . For both the ground and excited states,  $n_g \rightarrow 1$  and  $n_u \rightarrow 1$  in the limit  $R \rightarrow \infty$ . Hence,  $\lim_{R \rightarrow \infty} u(\mathbf{r}) = \sigma_g^2(\mathbf{r}) + \sigma_u^2(\mathbf{r})$  and  $\lim_{R \rightarrow \infty} \int u(\mathbf{r}) d\mathbf{r} = 2$ . On the other hand, given that  $\sigma_g = 2^{-1/2}(a + b)$ ,  $\sigma_u = 2^{-1/2}(a - b)$ ,  $c_1 = -c_2 = 2^{-1/2}$  (ground state) and  $c_1 = c_2 = 2^{-1/2}$  (excited state) in the  $R \rightarrow \infty$  limit (where  $a \equiv 1s_A$  and  $b \equiv 1s_B$ ), the spatial parts of  $\Psi$ (ground state) and  $\Psi$ (excited state) at large internuclear distances behave as

$$\lim_{R \rightarrow \infty} \Psi(\mathbf{r}_1, \mathbf{r}_2)(\text{ground state}) \sim 2^{-1/2}(ab + ba) \quad (2)$$

$$\lim_{R \rightarrow \infty} \Psi(\mathbf{r}_1, \mathbf{r}_2)(\text{excited state}) \sim 2^{-1/2}(aa + bb). \quad (3)$$

The second equation shows that the wave function for the  ${}^1\Sigma_g^+$  excited state becomes, at large values of  $R$ , into a half-and-half mixture of two ionic components ( $aa$  and  $bb$ ), with both electrons in each of them with opposite spin. In other words, both electrons have perfectly paired spins, so a scalar field purportedly giving the number of effectively unpaired electrons at  $R \rightarrow \infty$  should integrate to 0 and not to 2.

For the above wave function,  $\rho^2(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}_1, \mathbf{r}_2) = \rho^2(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}_2, \mathbf{r}_1)$  is given by

$$\begin{aligned} \rho^2(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}_1, \mathbf{r}_2) &= 2c_1^2 \sigma_g^2(\mathbf{r}_1) \sigma_g^2(\mathbf{r}_2) + 2c_2^2 \sigma_u^2(\mathbf{r}_1) \sigma_u^2(\mathbf{r}_2) \\ &+ 4c_1 c_2 \sigma_g(\mathbf{r}_1) \sigma_g(\mathbf{r}_2) \sigma_u(\mathbf{r}_1) \sigma_u(\mathbf{r}_2). \end{aligned} \quad (4)$$

Taking into account that  $\langle \sigma_g | \sigma_g \rangle_A = \langle \sigma_u | \sigma_u \rangle_A = \langle \sigma_g | \sigma_g \rangle_B = \langle \sigma_u | \sigma_u \rangle_B = \frac{1}{2}$  and calling  $S = \langle \sigma_g | \sigma_u \rangle_A = -\langle \sigma_g | \sigma_u \rangle_B$ , the direct application of Eq. 6 of the main text leads to  $\langle \hat{S}_A^2 \rangle = \langle \hat{S}_B^2 \rangle = \frac{3}{8} - 3c_1 c_2 S^2$ . In the limit  $R \rightarrow \infty$ ,  $S = \frac{1}{2}$ , so that  $\lim_{R \rightarrow \infty} \langle \hat{S}_A^2 \rangle = +3/4$  and 0 for the the ground and excited states, respectively. These numbers are the expected ones for the asymptotic limits given by eqs 2 and 3. In the ground state, each atomic basin harbors a single  $\alpha$  or  $\beta$  electron, and there is never an  $(\alpha, \beta)$  electron pair in any of the two atoms. Hence, the local spin of that basin is simply  $s(s+1)$  with  $s = \frac{1}{2}$ . On the contrary, in the excited state the  $(\alpha, \beta)$  electron pair is always in  $A$  or  $B$ , giving a null local spin in the  $R \rightarrow \infty$  limit.

## 2 Ramos-Cordoba et al. local spins

As shown in Eq. 12 in the main text, Ramos-Cordoba (RC) and coworkers proposed a one-parameter family one-parameter family  $RC_a$  of expressions for  $\langle \hat{S}^2 \rangle$ :

$$\begin{aligned} \langle \hat{S}^2 \rangle_{RC_a} &= a \int u(\mathbf{r}_1) d\mathbf{r}_1 + (2a-1) \iint \Lambda(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 \\ &- \frac{1}{2} \iint \Lambda(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}_2, \mathbf{r}_1) d\mathbf{r}_1 d\mathbf{r}_2. \end{aligned} \quad (5)$$

where  $\Lambda(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}'_1, \mathbf{r}'_2) = \Gamma(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}'_1, \mathbf{r}'_2) - \frac{1}{2} \rho^s(\mathbf{r}_1; \mathbf{r}'_2) \rho^s(\mathbf{r}_2, \mathbf{r}'_1)$ , and  $a$  is a free parameter. This expression satisfies Mayer's requisites and shows correct local spins for one electron systems when  $a = 3/4$ .

Let us examine now the excited  ${}^1\Sigma_g^+$  state of  $H_2$  of the previous Section in the dissociation

limit. The spin density vanishes for a singlet, so that  $\Lambda(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}'_1, \mathbf{r}'_2) = \Gamma(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}'_1, \mathbf{r}'_2)$ , with

$$\begin{aligned} \rho^2(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}'_1, \mathbf{r}'_2) &= \rho(\mathbf{r}_1; \mathbf{r}'_1)\rho(\mathbf{r}_2; \mathbf{r}'_2) - \frac{1}{2}\rho(\mathbf{r}_1; \mathbf{r}'_2)\rho(\mathbf{r}_2; \mathbf{r}'_1) \\ &- \frac{1}{2}\rho^s(\mathbf{r}_1; \mathbf{r}'_2)\rho^s(\mathbf{r}_2; \mathbf{r}'_1) + \Gamma(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}'_1, \mathbf{r}'_2) \end{aligned} \quad (6)$$

defining  $\Gamma$ . With the expressions derived in the previous section, it is easy to show that  $\rho(\mathbf{r}_1; \mathbf{r}'_1) = 2c_1^2\sigma_g(\mathbf{r}_1)\sigma_g(\mathbf{r}'_1) + 2c_2^2\sigma_u(\mathbf{r}_1)\sigma_u(\mathbf{r}'_1)$ , so using the atomic overlap integrals for the  $\sigma_g$  and  $\sigma_u$  orbitals, including  $\langle\sigma_g|\sigma_u\rangle_A = -1/2$  in the dissociation limit, we easily come to the following expressions valid for the dissociated excited singlet:  $\int_A u(\mathbf{r})d\mathbf{r} = 1$ ,  $\int_A \int_A \Gamma(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}_1, \mathbf{r}_2)d\mathbf{r}_1d\mathbf{r}_2 = \int_A \int_A \Gamma(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}_2, \mathbf{r}_1)d\mathbf{r}_1d\mathbf{r}_2 = 1/2$ . With them, Ramos-Cordoba et al local spin becomes

$$\langle\hat{S}_A^2\rangle = a - (1 - 2a) \times 1/2 - 1/4 = 2a - 3/4. \quad (7)$$

As show by RC in their Fig. 2, when  $a = 3/4$ , the above expression takes the value  $\langle\hat{S}_A^2\rangle = 3/4$ , and the local spin for the dissociating excited state becomes equal to that of the dissociating ground state, a notoriously wrong result. It is interesting to notice that if  $a = 3/8$ , which coincides with the expression proposed by Mayer and Matito,<sup>3</sup> the local spin tends correctly to zero at dissociation. Unfortunately, this limit is approached from below, and as RC showed, the local spin in the CAS[2,2] model becomes negative in all the  $\text{sgn}(c_1) = \text{sgn}(c_2)$  branch.

### 3 Reduced density matrices and local spin for open quantum systems

This is an slightly expanded version of the main text treatment. We start by adopting from the start a QCT viewpoint. Changing the indicator functions by center projections allows to read the following in Fock space equally. We thus divide the physical space  $R^3$  into a spatial domain  $A$  and its complementary region  $B = \bar{A}$ ,  $A \cup B = R^3$   $A \cap B = \emptyset$ . Since electrons can freely flow between

both domains,  $A$  and  $B$  can be considered as open quantum systems (OQS). In a pure state, the density operator of a  $N$ -electron system can be written as  $\hat{\rho}(\mathbf{x}; \mathbf{x}') = \Psi^*(\mathbf{x}')\Psi(\mathbf{x})$ , where  $\mathbf{x} = \mathbf{r}\boldsymbol{\sigma}$  denotes a spatial( $\mathbf{r}$ )-spin( $\boldsymbol{\sigma}$ ) coordinate and  $\mathbf{x}$  stands for  $\mathbf{x}_1 \cdots, \mathbf{x}_N$ . The reduced density operator of domain  $A$ ,  $\hat{\rho}^A$ , is obtained from  $\hat{\rho}$  by performing a spatial trace over the  $B$  region, with the usual  $\mathbf{x}'_i \rightarrow \mathbf{x}_i$  identification before integration. Defining the indicator function  $\mathbf{1}_n^A = \prod_{i=1}^n \omega_A(\mathbf{x}_i)$ , where  $\omega_A(\mathbf{x}_i)$  is a Heaviside-like domain weight function such that  $\omega_A(\mathbf{x}_i) = 0$  for  $\mathbf{x}_i \notin A$  and  $\omega_A(\mathbf{x}_i) = 1$  for  $\mathbf{x}_i \in A$ , with an equivalent definition for  $\omega_A(\mathbf{x}'_i)$ ,  $\hat{\rho}^A$  can be written in the form<sup>4</sup>,

$$\hat{\rho}^A = \sum_{n=0}^N \rho_n^A(\mathbf{x}_{i \leq n}; \mathbf{x}'_{i \leq n}), \quad (8)$$

where  $\rho_0^A = \int_B \Psi^*(\mathbf{x})\Psi(\mathbf{x})d\mathbf{x}$  and, for  $n \geq 1$

$$\rho_n^A(\mathbf{x}_{i \leq n}; \mathbf{x}'_{i \leq n}) = \mathbf{1}_n'^A \mathbf{1}_n^A \binom{N}{n} \int_B \hat{\rho}(\mathbf{x}; \mathbf{x}') d\mathbf{x}_{i > n}, \quad (9)$$

where  $d\mathbf{x}_{i > n} = d\mathbf{x}_{i+1} \times \cdots \times d\mathbf{x}_N$  and  $\mathbf{x}_{i \leq n} = \mathbf{x}_1 \times \cdots \times \mathbf{x}_n$ . To simplify the notation, we will assume that, before doing any integration, the  $\mathbf{x}'_i \rightarrow \mathbf{x}_i$  identification has been performed for all the integrated variables, for instance,  $\mathbf{x}'_{i > n} \rightarrow \mathbf{x}_{i > n}$  in eq 9. The subsystem  $A$  is thus described by a mixed density operator with  $N + 1$  possible sector densities  $\rho_n^A$  ( $n = 0, \dots, N$ ), each integrating to  $p^A(n)$ , which is the probability that  $n$  and only  $n$  electrons reside in domain  $A$  and the remaining  $N - n$  electrons in the domain  $B$ , i.e.  $\text{Tr}\rho_n^A = \int_A \rho_n^A d\mathbf{x}_{i \leq n} = p^A(n)$ . Normalized sector densities can be defined as  $\tilde{\rho}_n^A = \rho_n^A / p^A(n)$ , so that  $\text{Tr}\tilde{\rho}_n^A = 1$  and  $\hat{\rho}^A = \sum_n p^A(n)\tilde{\rho}_n^A$ . Then, each  $\tilde{\rho}_n^A$  can be dealt with as a pseudo pure system operator.

We define the reduced density matrix of order  $m \leq n$  ( $m$ RDM) of sector  $n$  as

$$\rho_n^{A,m}(\mathbf{x}_{i \leq m}; \mathbf{x}'_{i \leq m}) = \frac{n!}{(n-m)!} \int \rho_n^A(\mathbf{x}_{i \leq n}; \mathbf{x}'_{i \leq n}) d\mathbf{x}_{i > m}, \quad (10)$$

with the spinless  $m$ th order RDM given by  $\rho_n^{A,m}(\mathbf{r}_{i \leq m}; \mathbf{r}'_{i \leq m}) = \int \rho_n^{A,m}(\mathbf{x}_{i \leq m}; \mathbf{x}'_{i \leq m})|_{\sigma'_i \rightarrow \sigma_i} d\boldsymbol{\sigma}_{i \leq m}$ .

Using eq 9,  $\rho_n^{A,m}$  can also be put in the form

$$\rho_n^{A,m}(\mathbf{x}_{i \leq m}; \mathbf{x}'_{i \leq m}) = \mathbf{1}'_m \mathbf{1}_m^A \Lambda_{N,n}^m \int_D \rho(\mathbf{x}; \mathbf{x}') d\mathbf{x}_{i > m}, \quad (11)$$

where  $\Lambda_{N,n}^m = N! / [(N-n)!(n-m)!]$ ,  $D$  is a domain such that electrons  $m+1$  to  $n$  are integrated over  $A$ , and electrons  $n+1$  to  $N$  over  $B$ . Adding  $\Lambda_{N,n}^m \int_D \rho(\mathbf{x}; \mathbf{x}') d\mathbf{x}_{i > m}$  for values of  $n$  between 0 and  $N$  one obtains  $\rho^m(\mathbf{x}_{i \leq m}; \mathbf{x}'_{i \leq m})$ , the  $m$ RDM of the full  $A+B$  system. As a consequence, the sum of the  $m$ RDMs of all sectors  $n$  of domain  $A$  is given by  $\rho^{A,m} = \sum_n \rho_n^{A,m} = \mathbf{1}'_m \mathbf{1}_m^A \rho^m$ . If the  $\tilde{\rho}_n^A$ 's are used in the rhs integral of eq 10, one obtains  $\tilde{\rho}_n^{A,m}$  the normalized  $m$ RDMs of sector  $n$ . Then,  $\rho^{A,m} = \sum_n p^A(n) \tilde{\rho}_n^{A,m}$ . In the following two subsections we will consider separately the RDMs of OQSs for single-determinant (SDW) and multi-determinant (MDW) wave functions.

### 3.1 The single-determinant case

Let us consider a  $N$ -electron system described by a SDW  $|\Psi\rangle = (N!)^{-1/2} \det|u_1(\mathbf{x}_1) \cdots u_N(\mathbf{x}_N)|$ . To aid in the derivation of  $\rho_n^A$  and  $\rho_n^{A,m}$ , we will introduce some definitions. We call  $S^A$  and  $S^B$  the  $N \times N$  atomic overlap matrices (AOM) between the molecular spin-orbitals (MSO)  $|u_i\rangle$  in  $A$  and  $B$ , respectively, i.e.  $S_{ij}^A = \langle u_i | u_j \rangle_A$  and  $S_{ij}^B = \langle u_i | u_j \rangle_B$ ,  $\mathbf{k} = \{k_1, \dots, k_n\}$  and  $\mathbf{l} = \{l_1, \dots, l_n\}$  are two ordered sets ( $k_1 < \dots < k_n$  and  $l_1 < \dots < l_n$ ) of  $n \leq N$  numbers,  $\tilde{\mathbf{k}}$  and  $\tilde{\mathbf{l}}$  their complementary sets of  $N-n$  elements, and  $S^A(\mathbf{k}|\mathbf{l})$  and  $S^B(\mathbf{k}|\mathbf{l})$  the  $n \times n$  matrices obtained by selecting the rows indicated by  $\mathbf{k}$  and the columns indicated by  $\mathbf{l}$  from  $S^A$  and  $S^B$ , respectively. Similarly,  $S^A(\tilde{\mathbf{k}}|\tilde{\mathbf{l}})$  and  $S^B(\tilde{\mathbf{k}}|\tilde{\mathbf{l}})$  are the  $(N-n) \times (N-n)$  matrices obtained from  $S^A$  and  $S^B$  by selecting the rows  $\tilde{\mathbf{k}}$  and the columns  $\tilde{\mathbf{l}}$ . Each of the above arrays is square, so that their determinants can be determined. Each of these determinants is a number which, in turn, defines an element of another array. For instance,  $\det|S^A(\mathbf{k}|\mathbf{l})|$  is the  $\mathbf{k}\mathbf{l}$  element of an array  $S^A$ , and  $\det|S^B(\mathbf{k}|\mathbf{l})|$  is the  $\mathbf{k}\mathbf{l}$  element of an array  $S^B$ . Notice that  $S^A$  and  $S^B$  are  $m \times m$  matrices, where  $N! / [n!(N-n)!]$  is the full number of  $\mathbf{k}$  and  $\mathbf{l}$  ordered sets. The  $m \times m$  arrays  $\tilde{S}_{\mathbf{k}\mathbf{l}}^A$  and  $\tilde{S}_{\mathbf{k}\mathbf{l}}^B$  are defined from  $S^A(\tilde{\mathbf{k}}|\tilde{\mathbf{l}})$  and  $S^B(\tilde{\mathbf{k}}|\tilde{\mathbf{l}})$  in a

similar way. Using the above definitions, the sector density of domain  $A$ ,  $\rho_n^A$ , can be written as

$$\rho_n^A(\mathbf{x}_{i \leq n}; \mathbf{x}'_{i \leq n}) = \mathbf{1}_n^A \mathbf{1}_n^A \times \sum_{\mathbf{k}, \mathbf{l}} |U_{\mathbf{k}}\rangle \langle U_{\mathbf{l}}| \tilde{S}_{\mathbf{k}\mathbf{l}}^B, \quad (12)$$

with  $|U_{\mathbf{k}}\rangle = (n!)^{-1/2} |u_{k_1}(\mathbf{x}_1) \cdots u_{k_n}(\mathbf{x}_n)\rangle$  and  $\langle U_{\mathbf{l}}| = (n!)^{-1/2} |u_{l_1}(\mathbf{x}'_1) \cdots u_{l_n}(\mathbf{x}'_n)\rangle$ .

Important simplifications arise when a one-electron basis  $|u_i^p\rangle$ , orthonormal in  $R^3$  and orthogonal in  $A$  and  $B$ , is used to construct  $|\Psi\rangle$ . This can be achieved by diagonalizing  $S^A$ ,  $U^\dagger S^A U = \text{diag}(s_i) = s$ . Then, the basis  $|u^p\rangle = |u\rangle U$  is obviously orthonormal in  $R^3$ , so that  $|\Psi\rangle$  does not change, and orthogonal in  $A$  ( $\langle u_i^p | u_j^p \rangle_A = \delta_{ij} s_i$ ), and  $B$  ( $\langle u_i^p | u_j^p \rangle_B = \delta_{ij} (1 - s_i)$ ). Moreover, an orthonormal one-electron basis in  $A$ ,  $|\phi\rangle$ , can also be obtained as  $|\phi\rangle = |u^p\rangle s^{-1/2}$ .<sup>1</sup> The  $|u^p\rangle$  basis is exactly that proposed by Ponec for SDW's, and Ponec's orbitals  $|u_i^p\rangle$ , or domain natural orbitals (DNOs), have been successfully used to extract chemical information, and have been also interpreted in statistical terms. It can be shown that, in the DNO basis,  $\rho_n^A$  is given by

$$\rho_n^A(\mathbf{x}_{i \leq n}; \mathbf{x}'_{i \leq n}) = \mathbf{1}_n^A \mathbf{1}_n^A \times \sum_{\mathbf{k}} |\phi_{\mathbf{k}}\rangle p_n^{\mathbf{k}} \langle \phi_{\mathbf{k}}|, \quad \text{where} \quad (13)$$

$$|\phi_{\mathbf{k}}\rangle = \frac{1}{\sqrt{n!}} |\phi_{k_1}(\mathbf{x}_1) \cdots \phi_{k_n}(\mathbf{x}_n)\rangle, \quad (14)$$

and  $p_n^{\mathbf{k}} = \prod_i^N p_i$ , with  $p_i = s_i$  if  $i \in \mathbf{k}$  and  $p_i = 1 - s_i$  if  $i \in \tilde{\mathbf{k}}$ . Hence,  $p_n^{\mathbf{k}}$  provides the contribution of  $|\phi_{\mathbf{k}}\rangle$  to  $p^A(n)$ , which is finally obtained by adding all the possible arrangements of the  $n$  electrons in the the  $|\phi\rangle$  basis:  $\sum_{\mathbf{k}} p_n^{\mathbf{k}} = p^A(n)$ . The normalized sector density  $\tilde{\rho}_n^A$  is also given by eq 13 substituting  $p_n^{\mathbf{k}}$  by  $\tilde{p}_n^{\mathbf{k}} = p_n^{\mathbf{k}} / p^A(n) = p_n^{\mathbf{k}} / \sum_{\mathbf{k}} p_n^{\mathbf{k}}$ .

Being  $|\phi\rangle$  an orthonormal basis within the domain  $A$ , the 1 and 2RDMs  $\rho_n^{A,1}$  and  $\rho_n^{A,2}$  for each determinant  $|\phi_{\mathbf{k}}\rangle$  are easily obtained from Eqs. 10, 13 and 14 by simple application of the Slater

<sup>1</sup>Since  $S^A$  is blocked by spin ( $S^A = S^{A,\alpha} \oplus S^{A,\beta}$ ), in case of a closed-shell SDW,  $S^{A,\alpha} = S^{A,\beta}$ , and the  $N/2$  orbitals derived from diagonalizing  $S^{A,\alpha}$  and  $S^{A,\beta}$  are the same, which means that, leaving aside the spin part of MSO's, each  $\alpha$  orbital is equal to an equivalent  $\beta$  orbital, and is orthogonal to all the other  $\beta$  orbitals. However, in open-shell SDW's  $S^{A,\alpha} \neq S^{A,\beta}$  and the  $\alpha$  and  $\beta$  orbitals are not, in general, orthogonal to each other. The  $\alpha - \beta$  orthogonality is due in this case to the spin parts of MSO's.



rules:

$$\rho_n^{A,1}(\mathbf{x}_1; \mathbf{x}'_1) = \mathbf{1}_1^A \mathbf{1}_1^A \sum_{\mathbf{k}} p_n^{\mathbf{k}} \rho_{n,\mathbf{k}}^{A,1}(\mathbf{x}_1; \mathbf{x}'_1) \quad (15)$$

$$\rho_n^{A,2}(\mathbf{x}_1, \mathbf{x}_2; \mathbf{x}'_1, \mathbf{x}'_2) = \mathbf{1}_2^A \mathbf{1}_2^A \sum_{\mathbf{k}} p_n^{\mathbf{k}} \rho_{n,\mathbf{k}}^{A,2}(\mathbf{x}_1, \mathbf{x}_2; \mathbf{x}'_1, \mathbf{x}'_2), \quad \text{where} \quad (16)$$

$$\rho_{n,\mathbf{k}}^{A,1}(\mathbf{x}_1; \mathbf{x}'_1) = \sum_{i=1}^n \phi_{k_i}(\mathbf{x}_1) \phi_{k_i}^*(\mathbf{x}'_1) \quad \text{and} \quad (17)$$

$$\rho_{n,\mathbf{k}}^{A,2}(\mathbf{x}_1, \mathbf{x}_2; \mathbf{x}'_1, \mathbf{x}'_2) = \sum_{i,j=1}^n \phi_{k_i}(\mathbf{x}_1) \phi_{k_j}(\mathbf{x}_2) [1 - \hat{p}_{ij}] \phi_{k_i}^*(\mathbf{x}'_1) \phi_{k_j}^*(\mathbf{x}'_2). \quad (18)$$

Since  $\text{Tr}(\rho_{n,\mathbf{k}}^{A,1}) = n$  and  $\text{Tr}(\rho_{n,\mathbf{k}}^{A,2}) = n(n-1)$  for any  $\mathbf{k}$ , we have  $\text{Tr}(\rho_n^{A,1}) = n \times p^A(n)$  and  $\text{Tr}(\rho_n^{A,2}) = n(n-1) \times p^A(n)$ , that represent the contributions of sector  $n$  to the total number of electrons and pairs of electrons of domain  $A$ , respectively.

### 3.2 The multi-determinant case

We will assume now that  $|\Psi\rangle$  is a  $N$ -electron MDW expressed in terms of a set of  $2f$  orthonormal MSO's  $|u\rangle = \{|u_1\rangle \cdots |u_{2f}\rangle\}$  as  $|\Psi\rangle = \sum_{r=1}^M C_r \psi_r(1, N)$ , where  $\psi_r(1, N) = (N!)^{-1/2} \det|u_{r_1} \cdots u_{r_N}|$ , and  $u_{r_i}$  ( $i = 1 \cdots N$ ) is the subset of  $N$  MSO's that define  $\psi_r(1, N)$ . We will collectively label this subset as  $\mathbf{r} = (r_1, \cdots, r_N)$ . As in the above section, let us consider now the transformed set  $|u^p\rangle = |u\rangle U$ , where  $U$  is the eigenvector matrix of  $S^A = \langle u|u\rangle_A$ , i.e.  $U^\dagger S^A U = \text{diag}(s_i) = s$ . Here, it is also possible to compute  $|\phi\rangle = |u^p\rangle s^{-1/2}$ , the orthonormal one-electron basis in  $A$ . In the  $|u^p\rangle$  basis,  $|\Psi\rangle$  can be written as (see Supplementary Information of Ref. 4)

$$\Psi(1, N) = \sum_{\mathbf{j}} D_{\mathbf{j}} \chi_{\mathbf{j}}(1, N), \quad (19)$$

where  $\mathbf{j} \equiv \{j_1 \cdots j_N\}$ ,  $D_{\mathbf{j}} = \sum_{r=1}^M C_r \det[U_{r\mathbf{j}}]$ ,  $\chi_{\mathbf{j}} = (N!)^{-1/2} \det|u_{j_1}^p \cdots u_{j_N}^p|$ , and  $U_{r\mathbf{j}}$  is the  $(N \times N)$  matrix obtained from  $U$  by selecting the rows and columns denoted by  $\mathbf{r}$  and  $\mathbf{j}$ , respectively. The summation over  $\mathbf{j}$  in eq 19 runs, in principle, over all possible ordered subsets of  $N$  elements obtained from the first  $2f$  natural numbers. However, given that all  $\chi_{\mathbf{j}}$ 's are built with the same

number of  $\alpha$  and  $\beta$  MSO's (say,  $N_\alpha$  and  $N_\beta$ ),  $j_1, \dots, j_{N_\alpha}$  and  $j_{N_\alpha+1}, \dots, j_N$  must be necessarily in the ranges  $[1, f]$  and  $[f + 1, 2f]$ , respectively, reducing considerably the number of terms in eq 19. Matrix  $U$  is unitary but, in general,  $U_{rj}$  is not. However, for a closed-shell SDW  $f = N/2$ ,  $j$  and  $r$  can only be  $j = r = (1, 2, \dots, N)$ , and  $U_{rj} = U$ . This is the well-known invariance of a Slater determinant under an unitary transformation of all of its MSO's.

As in the SDW case, we only need the 1RDM ( $\rho_n^{A,1}$ ) and 2RDM ( $\rho_n^{A,2}$ ) of sector  $n$ . Using eq 19 in eq 11, we obtain

$$\rho_n^{A,m}(\mathbf{x}_{i \leq m}; \mathbf{x}'_{i \leq m}) = \mathbf{1}_m^A \mathbf{1}_m^A \sum_{j,k} D_j D_k^* I_{jk}^m(\mathbf{x}_{i \leq m}; \mathbf{x}'_{i \leq m}), \quad \text{where} \quad (20)$$

$$I_{jk}^m(\mathbf{x}_{i \leq m}; \mathbf{x}'_{i \leq m}) = \Lambda_{N,n}^m \int_D \chi_j(\mathbf{x}) \chi_k^*(\mathbf{x}') d\mathbf{x}_{i > m}. \quad (21)$$

The orthogonality in  $A$  and  $B$  of the  $|u^p\rangle$  basis greatly simplifies the computation of the  $I_{jk}^m$  integrals. After a lengthy manipulation, that we omit here for brevity, we have

$$I_{jj}^1(\mathbf{x}_1; \mathbf{x}'_1) = \sum_{i=1}^N \phi_{j_i}(\mathbf{x}_1) \phi_{j_i}^*(\mathbf{x}'_1) \times n_{j_i j_i}^{A,1}. \quad (22)$$

If  $\chi_j$  and  $\chi_k$  differ in a single MSO, say  $u_{j_i}^p \neq u_{k_i}^p$  we have

$$I_{jk}^1(\mathbf{x}_1; \mathbf{x}'_1) = \phi_{j_i}(\mathbf{x}_1) \phi_{k_i}^*(\mathbf{x}'_1) \times n_{j_i k_i}^{A,1} \quad (u_{j_i}^p \neq u_{k_i}^p), \quad (23)$$

and finally,  $I_{jk}^1 = 0$  if  $\chi_j$  and  $\chi_k$  differ in two or more MSO's. In Eqs. 22 and 23,  $n_{j_i k_i}^{A,1} = (s_{j_i} s_{k_i})^{1/2} \times p^{j_i}(n-1)$  and  $p^{j_i}(n-1)$  represents the probability that  $n-1$  electrons lie in  $A$  and  $N-n$  electrons lie in  $B$  for a hypothetical  $(N-1)$ -electron determinant built with all MSO's of  $\chi_j$  except  $u_{j_i}^p$ .

The computation of  $I_{jk}^2$  runs parallel to that of  $I_{jk}^1$ . We obtain

$$I_{jj}^2(\mathbf{x}_1, \mathbf{x}_2; \mathbf{x}'_1, \mathbf{x}'_2) = \frac{1}{2} \hat{A}_{12} \hat{A}'_{12} \sum_{i,l} \phi_{j_i}(\mathbf{x}_1) \phi_{j_l}(\mathbf{x}_2) \phi_{j_i}^*(\mathbf{x}'_1) \phi_{j_l}^*(\mathbf{x}'_2) n_{j_i j_l j_i j_l}^{A,2} \quad (24)$$

where  $n_{j_i j_l j_i j_l}^{A,2} = (s_{j_i} s_{j_l} s_{k_i} s_{k_l})^{1/2} \times p^{j_i j_l}(n-2)$ ,  $\hat{A}_{12} = 1 - \hat{p}_{12}$  is an operator that antisymmetrizes

with respect to variables in the unstarred MSO's,  $\hat{A}'_{12}$  acts likewise in the starred MSO's, and  $p^{j_i j_l}(n-2)$  represents the probability that  $n-2$  electrons lie in  $A$  and  $N-n$  electrons lie in  $B$  for a hypothetical  $(N-2)$ -electron SDW built with all MSO's of  $\chi_j$  except  $u_{j_i}^p$  and  $u_{j_l}^p$ . If  $\chi_j$  and  $\chi_k$  differ in a single MSO  $u_{j_i}^p \neq u_{k_i}^p$  (or  $\phi_{j_i} \neq \phi_{k_i}$ ) one has

$$I_{jk}^2(\mathbf{x}_1, \mathbf{x}_2; \mathbf{x}'_1, \mathbf{x}'_2) = \hat{A}_{12} \sum_{l \neq i} \phi_{j_i}(\mathbf{x}_1) \phi_{j_l}(\mathbf{x}_2) \phi_{k_i}^*(\mathbf{x}'_1) \phi_{j_l}^*(\mathbf{x}'_2) n_{j_i j_l k_i j_l}^{A,2} \quad (25)$$

If  $\chi_j$  and  $\chi_k$  differ in two MSO's  $u_{j_i}^p \neq u_{k_i}^p$  (or  $\phi_{j_i} \neq \phi_{k_i}$ ) and  $u_{j_l}^p \neq u_{k_l}^p$  (or  $\phi_{j_l} \neq \phi_{k_l}$ ), we obtain

$$I_{jk}^2(\mathbf{x}_1, \mathbf{x}_2; \mathbf{x}'_1, \mathbf{x}'_2) = \hat{A}_{12} \phi_{j_i}(\mathbf{x}_1) \phi_{j_l}(\mathbf{x}_2) \phi_{k_i}^*(\mathbf{x}'_1) \phi_{k_l}^*(\mathbf{x}'_2) n_{j_i j_l k_i k_l}^{A,2}. \quad (26)$$

Finally,  $I_{jk}^2 = 0$  if  $\chi_j$  and  $\chi_k$  differ in three or more MSO's.

Equations 22-26 can be expressed in the  $|u^p\rangle$  one-electron basis instead of the  $|\phi\rangle$  basis simply removing the  $(s_{j_i} s_{k_i})^{1/2}$  and  $(s_{j_i} s_{j_l} s_{k_i} s_{k_l})^{1/2}$  factors from the definition of  $n_{j_i k_i}^{A,1}$  and  $n_{j_i j_l k_i k_l}^{A,1}$ .

Based on all the above expressions, three steps are necessary to compute the 1RDM and 2RDM of each sector  $n$ : (1) Diagonalize  $S^A$ , obtaining the matrix  $U$ , the eigenvectors  $s_i$ , and the transformed MSO's  $|u^p\rangle$  and  $|\phi\rangle$ ; (2) Transform  $\Psi(1, N)$  to the form given by eq 19; (3) For each sector  $n$  and determinant  $\chi_j$ , compute the probabilities  $p^{j_i}(n-1)$  and  $p^{j_i j_l}(n-2)$ . Clearly, we can obviate the sector  $n=0$ , since the 1RDM and 2RDM are zero in this case,  $\rho_0^{A,1} = \rho_0^{A,2} = 0$ . Similarly, only  $p^{j_i}(n-1)$  is needed for  $n=1$ , since  $\rho_1^{A,2} = 0$ . Once these calculations have been performed,  $\rho_n^{A,1}$  and  $\rho_n^{A,2}$  in the  $|\phi\rangle$  basis can be written as

$$\rho_n^{A,1}(\mathbf{x}_1; \mathbf{x}'_1) = \mathbf{1}_1^A \mathbf{1}_1^A \sum_{i,k} \gamma_{ik}^n \phi_i(\mathbf{x}_1) \phi_k(\mathbf{x}'_1), \quad (n \geq 1), \quad (27)$$

$$\rho_n^{A,2}(\mathbf{x}_1, \mathbf{x}_2; \mathbf{x}'_1, \mathbf{x}'_2) = \mathbf{1}_2^A \mathbf{1}_2^A \sum_{i,j,k,l} \Gamma_{ijkl}^n \phi_i(\mathbf{x}_1) \phi_j(\mathbf{x}_2) \phi_k^*(\mathbf{x}'_1) \phi_l^*(\mathbf{x}'_2) \quad (n \geq 2). \quad (28)$$

Their spinless analogues are obtained after integrating the spin variables. To avoid an overexcess of definitions, we will continue to maintain, however, the names of  $\gamma_{ik}^n$  and  $\Gamma_{ijkl}^n$  for the coefficient that multiplies  $\phi_i(\mathbf{r}_1) \phi_k(\mathbf{r}'_1)$  and  $\phi_i(\mathbf{r}_1) \phi_j(\mathbf{r}_2) \phi_k^*(\mathbf{r}_1) \phi_l^*(\mathbf{r}_2)$ , respectively, after this integration of

the spin is carried out. Similarly, we will continue to maintain the  $\gamma_{ik}^n$  and  $\Gamma_{ijkl}^n$  names when the  $|u^p\rangle$  basis is employed instead of the  $|\phi\rangle$  basis.

The sum  $\sum_{n=1}^N p^{j_i}(n-1)$  is equal to 1 since it gives the probability that the domain  $A$  contains between 0 and  $N-1$  electrons for a hypothetical  $(N-1)$ -electron SDW. Similarly,  $\sum_{n=2}^N p^{j_i j_l}(n-2) = 1$ , since this is the probability that  $A$  holds between 0 and  $N-2$  electrons for a  $(N-2)$ -electron SDW. As a consequence,  $\sum_{n=1}^N \gamma_{ik}^n = \gamma_{ik}$  and  $\sum_{n=2}^N \gamma_{ijkl}^n = \Gamma_{ijkl}$ , where  $\gamma_{ik}$  and  $\Gamma_{ijkl}$  are the expansion coefficients of the 1RDM and 2RDM of the full system in the  $|\phi\rangle$  basis. The expressions for the  $m$ RDMs ( $m = 1, 2, \dots$ ) of any sector  $n$  are thus formally equal to those of the full system, and the expansion coefficients of the latter in the  $|u^p\rangle$  or  $|\phi\rangle$  basis are the sum of the coefficients of all its sectors. Actually, Eqs. 22-26, without the  $n^{A,1}$  and  $n^{A,2}$  factors, are the well known Slater rules Quantum Chemistry.

The  $\gamma_{ik}^n$ 's and  $\Gamma_{ijkl}^n$ 's of equations 27 and 28 adopt simpler forms for a SDW. Taking into account that, in that case, only the diagonal term  $j = k = \{1, \dots, N\}$  appears in eq 20, and Eqs. 21 and 22, we obtain  $\gamma_{ik}^n = \delta_{ik} s_i p^i(n-1)$  and  $\Gamma_{ijkl}^n = (\delta_{ik} \delta_{jl} - \delta_{il} \delta_{jk}) s_i s_l p^{il}(n-2)$  for a SDW.

### 3.3 Local spin from an OQS perspective

Within the OQS formalism the local spin of an open region  $A$  is given by  $\langle \hat{S}_A^2 \rangle = \text{Tr}(\hat{S}^2 \hat{\rho}^A)$ , and expressing  $\hat{\rho}^A$  in terms of its  $N+1$  sectors,  $\langle \hat{S}_A^2 \rangle = \sum_n \langle \hat{S}_{A,n}^2 \rangle$ . The sector  $n=0$  trivially does not contribute to  $\langle \hat{S}_A^2 \rangle$ , and the sector  $n=N$  neither does if  $|\Psi\rangle$  is a closed-shell wave function. On the other hand,  $\hat{S}^2$  for the sector  $n$  is given by

$$\hat{S}^2 = \sum_{i,j}^n \hat{s}(i) \hat{s}(j) = \sum_{i=1}^n \hat{s}^2(i) + \sum_{i \neq j}^n \hat{s}(i) \hat{s}(j) = \hat{S}_1^2 + \hat{S}_2^2, \quad \text{so that} \quad (29)$$

$$\langle \hat{S}_A^2 \rangle = \langle \hat{S}_{1,A}^2 \rangle + \langle \hat{S}_{2,A}^2 \rangle, \quad \text{with} \quad (30)$$

$$\langle \hat{S}_{1,A}^2 \rangle = \sum_n \langle \hat{S}_{1,A,n}^2 \rangle = \sum_n \text{Tr} \left( \hat{S}_1^2 \rho_n^{A,1}(\mathbf{x}; \mathbf{x}') \right), \quad (31)$$

$$\langle \hat{S}_{2,A}^2 \rangle = \sum_n \langle \hat{S}_{2,A,n}^2 \rangle = \sum_n \text{Tr} \left( \hat{S}_2^2 \rho_n^{A,2}(\mathbf{x}_1, \mathbf{x}_2; \mathbf{x}'_1, \mathbf{x}'_2) \right). \quad (32)$$

In the SDW case, from Eqs. 15-18, Eqs. 31-32, and the property  $\langle \phi_i | \phi_j \rangle_A = \delta_{ij}$ , we find (See Appendix 1)

$$\langle \hat{S}^2 \rangle_{A,n} = \sum_{\mathbf{k}} p_n^{\mathbf{k}} [n/2 + M_{\mathbf{k}}^2 - S_{\mathbf{k}}] = \sum_{\mathbf{k}} p_n^{\mathbf{k}} \langle \hat{S}^2 \rangle_{A,n,\mathbf{k}} \quad (33)$$

In eq 33,  $M_{\mathbf{k}} = (n^\alpha - n^\beta)/2$  is the eigenvalue of  $\hat{S}_z$  for the determinant  $|\phi_{\mathbf{k}}\rangle$ , with  $n^\alpha + n^\beta = n$ , and  $S_{\mathbf{k}} = \sum_{k_i \in \alpha} \sum_{k_j \in \beta} |\langle k_i^\alpha | k_j^\beta \rangle_A|^2$ , where  $k_i^\alpha$  and  $k_j^\beta$  are the real parts of MSO's  $k_i$  and  $k_j$ , respectively.<sup>2</sup> We should note that the  $\alpha$  (or  $\beta$ ) subset of MSO's is orthonormal in the domain  $A$ , but both subsets, in general, are not orthogonal to each other, i.e.  $|\phi_{\mathbf{k}}\rangle$  in the general case is a spin-unrestricted Slater determinant. Particular cases of eq 33 deserve to be commented. (i) A single  $\alpha$  or  $\beta$  electron in  $A$  has  $n/2 = \frac{1}{2}$ ,  $M_{\mathbf{k}}^2 = \frac{1}{4}$  and  $S_{\mathbf{k}} = 0$ , so that  $\langle \hat{S}^2 \rangle_{A,n,\mathbf{k}} = \frac{3}{4}$ . (ii) An arbitrary  $|\phi_{\mathbf{k}}\rangle$  with  $n^\alpha = n^\beta$  has  $M_{\mathbf{k}} = 0$ , so that  $\langle \hat{S}^2 \rangle_{A,n,\mathbf{k}} = n/2 - S_{\mathbf{k}}$ . (iii) A restricted Slater determinant made of  $n^\alpha$  and  $n^\beta < n^\alpha$  spin-restricted MSO's, where every  $\beta$  orbital is equal to a single  $\alpha$  orbital and orthogonal to all the other  $\alpha$  orbitals has  $S_{\mathbf{k}} = n^\beta$  and  $n/2 - S_{\mathbf{k}} = M_{\mathbf{k}} = |M_{\mathbf{k}}|$ . If the situation is the opposite, i.e.  $n^\beta > n^\alpha$  and every  $\alpha$  orbital is equal to a single  $\beta$  orbital and orthogonal to the remaining  $\beta$  orbitals, one has  $S_{\mathbf{k}} = n^\alpha$  and  $n/2 - S_{\mathbf{k}} = -M_{\mathbf{k}} = |M_{\mathbf{k}}|$ . Since  $M_{\mathbf{k}}^2 = |M_{\mathbf{k}}|^2$ , we obtain in both cases  $\langle \hat{S}^2_{A,n,\mathbf{k}} \rangle = |M_{\mathbf{k}}|(1 + |M_{\mathbf{k}}|)$ . If, in addition,  $n^\alpha = n^\beta$ ,  $\langle \hat{S}^2_{A,n,\mathbf{k}} \rangle = 0$ , that corresponds to a restricted closed-shell Slater determinant. (iv) Finally, for a Slater determinant formed from spin-restricted orbitals where  $n_c$   $\alpha$  and  $\beta$  orbitals are equal (with  $n_c \leq n_\alpha$  and  $n_c \leq n_\beta$ ),  $S_{\mathbf{k}} = n_c$ , and  $\langle \hat{S}^2_{A,n,\mathbf{k}} \rangle = M_{\mathbf{k}}^2 + n_d/2$ , where  $n_d = n_\alpha + n_\beta - 2n_c$  is the number of not-matched orbitals from either spin.<sup>5</sup> For instance, if  $\mathbf{k} = \{\phi_1, \phi_2, \phi_3, \phi_4, \phi_5, \bar{\phi}_4, \bar{\phi}_5, \phi_6, \phi_7\}$ , we have  $n_c = 2$  and  $n_d = 5$ . This is the most general case when  $\alpha$  and  $\beta$   $\phi_i$ 's are obtained in the same diagonalization which, in turn, happens when  $\Psi$  is a closed-shell SDW. As pointed out by Davidson and Clark<sup>5</sup>,  $n_d$  is the trace of the effectively unpaired density  $u(\mathbf{r})$ . When  $n_c = n_\alpha$  or  $n_c = n_\beta$  this case reduces to case (iii).

In case that  $\tilde{\rho}_n^{A,1}$  and  $\tilde{\rho}_n^{A,2}$  had been used instead of  $\rho_n^{A,1}$  and  $\rho_n^{A,2}$ , eq 33 would be the same

<sup>2</sup>The meaning of  $S_{\mathbf{k}}$  is the following. The set of spin-orbitals in  $\mathbf{k}$  is divided into the  $\alpha$  and  $\beta$  subsets, with  $n^\alpha$  and  $n^\beta$  MSO's, respectively. Then, the  $n^\alpha n^\beta$  overlaps between the  $\alpha$  and  $\beta$  MSO's (leaving aside their spin parts) are computed and added to give  $S_{\mathbf{k}}$ .

except that  $\tilde{p}_n^k$  must replace  $p_n^k$ . As it is evident from this equation, the expected value of  $\hat{S}^2$  for sector  $n$  of domain  $A$  is a weighted sum of the expected values of this operator for the  $N!/[(N-n)!]$  choices of  $\mathbf{k}$ . Given that  $p_n^k = \prod_i^N p_i$  with  $p_i = s_i$  if  $i \in \mathbf{k}$  and  $p_i = 1 - s_i$  if  $i \notin \mathbf{k}$ , it is clear that only  $\mathbf{k}$ 's with all of its MSO's partially localized in  $A$  will contribute significantly to  $\langle \hat{S}_{A,n}^2 \rangle$ .

The  $\mathbf{k}$  sets in eq 33 can be grouped into as many subsets as the number of ways of choosing  $n^\alpha$  and  $n^\beta$  such that  $n^\alpha + n^\beta = n$ , i.e.  $\langle \hat{S}_{A,n}^2 \rangle = \sum'_{n^\alpha, n^\beta} \sum'_{\mathbf{k}} p_n^k [n/2 + M_{\mathbf{k}}^2 - S_{\mathbf{k}}]$ , where the prime (') in the first sum means than only terms with  $n_\alpha^A + n_\beta^A = n$  are included, and the ' in the second that only  $\mathbf{k}$ 's associated to these  $n^\alpha$  and  $n^\beta$  have to be considered. All these restricted  $\mathbf{k}$ 's have  $n/2 = (n^\alpha + n^\beta)/2$  and  $M_{\mathbf{k}} = (n^\alpha - n^\beta)/2$ , so that

$$\langle \hat{S}_{A,n}^2 \rangle = \sum'_{n^\alpha, n^\beta} \left[ n/2 + (n_\alpha^A - n_\beta^A)^2/4 - S_{\mathbf{k}}^n \right] p^A(n^\alpha, n^\beta). \quad (34)$$

where  $p^A(n^\alpha, n^\beta) = \sum'_{\mathbf{k}} p_n^k$  is probability of having  $n^\alpha$   $\alpha$  and  $n^\beta$   $\beta$  electrons in the domain  $A$ , and we have defined  $S_{\mathbf{k}}^n = p^A(n^\alpha, n^\beta)^{-1} \sum'_{\mathbf{k}} p_n^k S_{\mathbf{k}}$ . The quantity  $[n/2 + (n_\alpha - n_\beta)^2/4 - S_{\mathbf{k}}^n]$  can be understood as  $\langle \hat{S}_{A, n_\alpha, n_\beta}^2 \rangle$ , the local spin of domain  $A$  for a spin-resolved sector. The local spin of sector  $n$  is thus the sum of all of its spin-resolved contributions, each weighted with the factor  $p^A(n^\alpha, n^\beta)$ .

In the MDW case, we use Eqs. 31-32 of Appendix 1 with  $\rho_n^{A,1}$  and  $\rho_n^{A,2}$  given by Eqs. 27 and 28, obtaining

$$\langle \hat{S}^2 \rangle_{A,n} = \frac{3}{4} \sum_i \gamma_{ii}^n - \frac{1}{4} \sum_{i,j} (\Gamma_{ijij}^n + 2\Gamma_{ijji}^n). \quad (35)$$

In some way, the expression of  $\langle \hat{S}^2 \rangle_{A,n}$  is formally simpler for MDW's than for SDW's. Of course, the complexity in the first case lies in the calculation of the  $\gamma_{ij}^n$  and  $\Gamma_{ijkl}^n$  coefficients. In addition, since we have not derived the 1RDM and 2RDM of spin-splitted sectors of MDW's (i.e. for given values of  $n^\alpha$  and  $n^\beta$ ), an expression for  $\langle \hat{S}_{A, n_\alpha^A, n_\beta^A}^2 \rangle$  is not available yet.

## 4 Appendix 1

In this appendix, we will prove eq 33. For an arbitrary  $N$ -electron wave function  $\Psi$  with 1RDM and 2RDM  $\rho^1(1;1')$  and  $\rho^2(1,2;1',2')$ , the expectation value of  $\hat{S}^2$  is given by

$$\langle \hat{S}^2 \rangle = \frac{3}{4} \int \rho(\mathbf{r}) d\mathbf{r} - \frac{1}{4} \iint [\rho^2(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}_1, \mathbf{r}_2) + 2\rho^2(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}_2, \mathbf{r}_2)] d\mathbf{r}_1 d\mathbf{r}_2. \quad (36)$$

This equation can be applied as well using  $\rho_{n,\mathbf{k}}^{A,1}$  instead of  $\rho$  and  $\rho_{n,\mathbf{k}}^{A,2}$  instead of  $\rho^2$ . Then, from Eqs. 15, 17 and 31 we have  $\langle \hat{S}_1^2 \rangle_{A,n} = \frac{3}{4} \sum_{\mathbf{k}} n p_n^{\mathbf{k}}$ . To obtain the second and third integrals, we will eliminate for clarity the subscripts  $n$  and  $\mathbf{k}$  and the superscript  $A$  from  $\rho_{n,\mathbf{k}}^{A,2}$ . Since  $\rho_{n,\mathbf{k}}^{A,2}$  corresponds to a SDW, we can write it as

$$\rho^2(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}_1, \mathbf{r}_2) = \rho(\mathbf{r}_1)\rho(\mathbf{r}_2) - \frac{1}{2}\rho(\mathbf{r}_1; \mathbf{r}_2)\rho(\mathbf{r}_2; \mathbf{r}_1) - \frac{1}{2}\rho^s(\mathbf{r}_1; \mathbf{r}_2)\rho^s(\mathbf{r}_2; \mathbf{r}_1), \quad (37)$$

$$\rho^2(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}_2, \mathbf{r}_1) = \rho(\mathbf{r}_1; \mathbf{r}_2)\rho(\mathbf{r}_2; \mathbf{r}_1) - \frac{1}{2}\rho(\mathbf{r}_1)\rho(\mathbf{r}_2) - \frac{1}{2}\rho^s(\mathbf{r}_1; \mathbf{r}_1)\rho^s(\mathbf{r}_2; \mathbf{r}_2), \quad (38)$$

where  $\rho(\mathbf{r}_1) \equiv \rho(\mathbf{r}_1; \mathbf{r}_1)$ ,  $\rho(\mathbf{r}_2) \equiv \rho(\mathbf{r}_2; \mathbf{r}_2)$ ,  $\rho(\mathbf{r}; \mathbf{r}') = \rho^\alpha(\mathbf{r}; \mathbf{r}') + \rho^\beta(\mathbf{r}; \mathbf{r}')$ , and  $\rho^s(\mathbf{r}; \mathbf{r}') = \rho^\alpha(\mathbf{r}; \mathbf{r}') - \rho^\beta(\mathbf{r}; \mathbf{r}')$ , with  $\rho^\sigma(\mathbf{r}; \mathbf{r}') = \sum_{k_i \in \sigma} \phi_{k_i}^*(\mathbf{r})\phi_{k_i}(\mathbf{r}')$  ( $\sigma = \alpha, \beta$ ), and  $n^\alpha + n^\beta = n$ . Since the  $\phi_i$  spin-orbitals are orthonormal in  $A$ , the integration of  $\rho^2(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}_1, \mathbf{r}_2)$  is analogous to that of a standard  $n$ -electron 2RDM in  $R^3$ , i.e.

$$\int_A \int_A \rho^2(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 = n(n-1). \quad (39)$$

The integration of  $\rho^2(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}_2, \mathbf{r}_1)$  is as follows. First,  $\int_A \int_A \rho(\mathbf{r}_1; \mathbf{r}_2)\rho(\mathbf{r}_2; \mathbf{r}_1) d\mathbf{r}_1 d\mathbf{r}_2 = \alpha\alpha + \beta\beta + \alpha\beta + \beta\alpha$ , where  $\sigma\sigma' = \int_A \int_A \rho^\sigma(\mathbf{r}_1; \mathbf{r}_2)\rho^{\sigma'}(\mathbf{r}_2; \mathbf{r}_1) d\mathbf{r}_1 d\mathbf{r}_2$ . The contribution  $\alpha\alpha$  can be written as  $\sum_{k_i \in \alpha} \sum_{k_j \in \alpha} |\langle \phi_{k_i} | \phi_{k_j} \rangle_A|^2$ . Since  $\phi_{k_i}$  and  $\phi_{k_j}$  are  $\alpha$  MOs, they come from the same diagonalization and are orthogonal if  $k_i \neq k_j$ . Then,  $\alpha\alpha = n^\alpha$ . Similarly,  $\beta\beta = n^\beta$ . The  $\alpha\beta$  contribution is given by  $\alpha\beta = \sum_{k_i \in \alpha} \sum_{k_j \in \beta} |\langle k_i^\alpha | k_j^\beta \rangle_A|^2 = |S_{ij}^{\alpha\beta}|^2 = S_k$ , where we have used an abbreviated notation for the overlap integrals. In a closed-shell molecule, the  $\alpha$  and  $\beta$   $\phi_i$ 's are

equal and each  $S_{ij}^{\alpha\beta}$  is simply 0 ( $k_i^\alpha \neq k_k^\beta$ ) or 1 ( $k_i^\alpha = k_k^\beta$ ), and  $S_{\mathbf{k}} = n_{\mathbf{k}}^k$ , where  $n_{\mathbf{k}}^k$  is the number  $\phi_i$ 's in  $\mathbf{k}$  that appear simultaneously in the  $\alpha$  and  $\beta$  sets. For instance, for the five-components  $\mathbf{k}$  vector with  $n^\alpha = 3$  and  $n^\beta = 2$  formed with the  $\alpha$  MOs  $\phi_1, \phi_3$ , and  $\phi_4$ , and the  $\beta$  MOs  $\phi_1$  and  $\phi_4$ , we will have  $n_{\mathbf{k}}^k = 2$ . The above situation also happens in an open-shell molecule if we decide to obtain the full set of  $\alpha + \beta$  MOs from the same diagonalization. However, in the most general case,  $S_{ij}^{\alpha\beta} \neq 0$ . The  $\beta\alpha$  contribution is also given by  $\beta\alpha = S_{\mathbf{k}}$ . In summary, we have  $\int_A \int_A \rho(\mathbf{r}_1; \mathbf{r}_2) \rho(\mathbf{r}_2; \mathbf{r}_1) d\mathbf{r}_1 d\mathbf{r}_2 = n + 2S_{\mathbf{k}}$ . From  $\int_A \rho(\mathbf{r}) d\mathbf{r} = n$ , we trivially obtain  $-\frac{1}{2} \int_A \int_A \rho(\mathbf{r}_1) \rho(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 = -\frac{1}{2} n^2$ . Finally, from  $\rho^s(\mathbf{r}; \mathbf{r}') = \rho^\alpha(\mathbf{r}; \mathbf{r}') - \rho^\beta(\mathbf{r}; \mathbf{r}')$  we have  $-\frac{1}{2} \int_A \int_A \rho^s(\mathbf{r}_1; \mathbf{r}_1) \rho^s(\mathbf{r}_2; \mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 = -\frac{1}{2} (n^\alpha - n^\beta)^2 = -2M_{\mathbf{k}}^2$ . Adding these three contributions

$$\int_A \int_A \rho_{n,\mathbf{k}}^{A,2}(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}_2, \mathbf{r}_1) d\mathbf{r}_1 d\mathbf{r}_2 = -\frac{1}{2} n(n-2) + 2 S_{\mathbf{k}} - 2M_{\mathbf{k}}^2. \quad (40)$$

Finally, adding the  $\langle \hat{S}_1^2 \rangle_{A,n}$  value,  $-\frac{1}{4}$  of eq 39, and  $-\frac{1}{2}$  of eq 40 we obtain eq 33.

## References

- (1) Takatsuka, K.; Fueno, T.; Yamaguchi, K. Distribution of odd electrons in ground-state molecules. *Theoretica Chimica Acta* **1978**, *48*, 175–183.
- (2) Staroverov, V. N.; Davidson, E. R. Distribution of effectively unpaired electrons. *Chemical Physics Letters* **2000**, *330*, 161–168.
- (3) Mayer, I.; Matito, E. Calculation of local spins for correlated wave functions. *Physical Chemistry Chemical Physics* **2010**, *12*, 11308.
- (4) Pendás, A. M.; Francisco, E. Quantum Chemical Topology as a Theory of Open Quantum Systems. *Journal of Chemical Theory and Computation* **2018**, *15*, 1079–1088.
- (5) Davidson, E. R.; Clark, A. E. Analysis of wave functions for open-shell molecules. *Physical Chemistry Chemical Physics* **2007**, *9*, 1881.