# Supporting Information

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

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## 1 Effectively unpaired electrons and local spin

The scalar field

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

known as the effectively unpaired electrons density,[1] and several of its properties[2] 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-know 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 $R \to \infty$ of the properly dissociating $H_2$ 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 $2N$,[2] i.e. *the number of effectively unpaired electrons can be greater that 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 $H_2$ molecule at large internuclear distances. We will show in this subsection another counterintuitive behavior of $u(\boldsymbol{r})$.

Let us consider the two ${}^1\Sigma_g^+$ states that can be formed for the $H_2$ 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 $|\sigma_g\bar{\sigma}_g| = \sigma_g(\boldsymbol{r}_1)\sigma_g(\boldsymbol{r}_2)\Theta$ and $|\sigma_u\bar{\sigma}_u| = \sigma_u(\boldsymbol{r}_1)\sigma_u(\boldsymbol{r}_2)\Theta$, where $\Theta = 2^{-1/2}(\alpha\beta - \beta\alpha)$ is the spin function, the electron density of the above $\Psi$ is given by $\rho(\boldsymbol{r};\boldsymbol{r}) \equiv \rho(\boldsymbol{r}) = n_g\sigma_g^2(\boldsymbol{r}) + n_u\sigma_u^2(\boldsymbol{r})$, where $n_g = 2c_1^2$ and $n_u = 2c_2^2$, so the natural orbitals are also $\sigma_g$ and $\sigma_u$, and $u(\boldsymbol{r})$ is given by $u(\boldsymbol{r}) = n_g(2-n_g)\sigma_g^2(\boldsymbol{r}) + n_u(2-n_u)\sigma_u^2(\boldsymbol{r})$. For both the ground and excited states, $n_g \to 1$ and $n_u \to 1$ in the limit $R \to \infty$. Hence, $\lim_{R\to\infty} u(\boldsymbol{r}) = \sigma_g^2(\boldsymbol{r}) + \sigma_u^2(\boldsymbol{r})$ and $\lim_{R\to\infty} \int u(\boldsymbol{r})d\boldsymbol{r} = 2$. 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 $R \to \infty$ 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

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

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

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 $R \to \infty$ should integrate to 0 and not to 2.

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

$$\begin{aligned}\rho^2(\boldsymbol{r}_1,\boldsymbol{r}_2;\boldsymbol{r}_1,\boldsymbol{r}_2) &= 2c_1^2\sigma_g^2(\boldsymbol{r}_1)\sigma_g^2(\boldsymbol{r}_2)+2c_2^2\sigma_u^2(\boldsymbol{r}_1)\sigma_u^2(\boldsymbol{r}_2)\\ &+ 4c_1c_2\sigma_g(\boldsymbol{r}_1)\sigma_g(\boldsymbol{r}_2)\sigma_u(\boldsymbol{r}_1)\sigma_u(\boldsymbol{r}_2).\end{aligned}\tag{4}$$

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 $\langle\hat{S}_A^2\rangle=\langle\hat{S}_B^2\rangle=\frac{3}{8}-3c_1c_2S^2$. In the limit $R\to\infty$, $S=\frac{1}{2}$, so that $\lim_{R\to\infty}\langle\hat{S}_A^2\rangle=+3/4$ 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 $R\to\infty$ 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 $\langle\hat{S}^2\rangle$:

$$\begin{aligned}\langle\hat{S}^2\rangle_{\mathrm{RC}_a} &= a\int u(\boldsymbol{r}_1)\,d\boldsymbol{r}_1+(2a-1)\iint\Lambda(\boldsymbol{r}_1,\boldsymbol{r}_2;\boldsymbol{r}_1,\boldsymbol{r}_2)\,d\boldsymbol{r}_1d\boldsymbol{r}_2\\ &- \frac{1}{2}\iint\Lambda(\boldsymbol{r}_1,\boldsymbol{r}_2;\boldsymbol{r}_2,\boldsymbol{r}_1)\,d\boldsymbol{r}_1d\boldsymbol{r}_2.\end{aligned}\tag{5}$$

where $\Lambda(\boldsymbol{r}_1,\boldsymbol{r}_2;\boldsymbol{r}_1',\boldsymbol{r}_2')=\Gamma(\boldsymbol{r}_1,\boldsymbol{r}_2;\boldsymbol{r}_1',\boldsymbol{r}_2')-\frac{1}{2}\rho^s(\boldsymbol{r}_1;\boldsymbol{r}_2')\rho^s(\boldsymbol{r}_2,\boldsymbol{r}_1')$, 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 $\Lambda(\boldsymbol{r}_1,\boldsymbol{r}_2;\boldsymbol{r}_1',\boldsymbol{r}_2') = \Gamma(\boldsymbol{r}_1,\boldsymbol{r}_2;\boldsymbol{r}_1',\boldsymbol{r}_2')$, with

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

defining $\Gamma$. With the expressions derived in the previous section, it is easy to show that $\rho(\boldsymbol{r}_1;\boldsymbol{r}_1') = 2c_1^2\sigma_g(\boldsymbol{r}_1)\sigma_g(\boldsymbol{r}_1') + 2c_2^2\sigma_u(\boldsymbol{r}_1)\sigma_u(\boldsymbol{r}_1')$, 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: $\int_A u(\boldsymbol{r})d\boldsymbol{r} = 1$, $\int_A\int_A \Gamma(\boldsymbol{r}_1,\boldsymbol{r}_2;\boldsymbol{r}_1,\boldsymbol{r}_2)d\boldsymbol{r}_1 d\boldsymbol{r}_2 = \int_A\int_A \Gamma(\boldsymbol{r}_1,\boldsymbol{r}_2;\boldsymbol{r}_2,\boldsymbol{r}_1)d\boldsymbol{r}_1 d\boldsymbol{r}_2 = 1/2$. With them, Ramos-Cordoba et al local spin becomes

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

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,[3] 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 $\mathrm{sgn}(c_1) = \mathrm{sgn}(c_2)$ 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 $\hat{\rho}(\boldsymbol{x};\boldsymbol{x}') = \Psi^\star(\boldsymbol{x}')\Psi(\boldsymbol{x})$, where $\boldsymbol{x} = \boldsymbol{r}\boldsymbol{\sigma}$ denotes a spatial($\boldsymbol{r}$)-spin($\sigma$) coordinate and $\boldsymbol{x}$ stands for $\boldsymbol{x}_1 \cdots, \boldsymbol{x}_N$. The reduced density operador of domain $A$, $\hat{\rho}^A$, is obtained from $\hat{\rho}$ by performing a spatial trace over the $B$ region, with the usual $\boldsymbol{x}'_i \to \boldsymbol{x}_i$ identification before integration. Defining the indicator function $\mathbf{1}^A_n = \Pi^n_{i=1}\omega_A(\boldsymbol{x}_i)$, where $\omega_A(\boldsymbol{x}_i)$ is a Heaviside-like domain weight function such that $\omega_A(\boldsymbol{x}_i) = 0$ for $\boldsymbol{x}_i \notin A$ and $\omega_A(\boldsymbol{x}_i) = 1$ for $\boldsymbol{x}_i \in A$, with an equivalent definition for $\omega_A(\boldsymbol{x}'_i)$, $\hat{\rho}^A$ can be written in the form[4],

$$\hat{\rho}^A = \sum_{n=0}^{N} \rho^A_n(\boldsymbol{x}_{i\leq n};\boldsymbol{x}'_{i\leq n}), \tag{8}$$

where $\rho^A_0 = \int_B \Psi^\star(\boldsymbol{x})\Psi(\boldsymbol{x})d\boldsymbol{x}$ and, for $n \geq 1$

$$\rho^A_n(\boldsymbol{x}_{i\leq n};\boldsymbol{x}'_{i\leq n}) = \mathbf{1}'^A_n \mathbf{1}^A_n \binom{N}{n} \int_B \hat{\rho}(\boldsymbol{x};\boldsymbol{x}')d\boldsymbol{x}_{i>n}, \tag{9}$$

where $d\boldsymbol{x}_{i>n} = d\boldsymbol{x}_{i+1} \times \cdots \times d\boldsymbol{x}_N$ and $\boldsymbol{x}_{i\leq n} = \boldsymbol{x}_1 \times \cdots \times \boldsymbol{x}_n$. To simplify the notation, we will assume that, before doing any integration, the $\boldsymbol{x}'_i \to \boldsymbol{x}_i$ identification has been performed for all the integrated variables, for instance, $\boldsymbol{x}'_{i>n} \to \boldsymbol{x}_{i>n}$ in eq 9. The subsystem $A$ is thus described by a mixed density operator with $N+1$ possible sector densities $\rho^A_n$ ($n = 0, \cdots, N$), 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. $\mathrm{Tr}\rho^A_n = \int_A \rho^A_n d\boldsymbol{x}_{i\leq n} = p^A(n)$. Normalized sector densities can be defined as $\tilde{\rho}^A_n = \rho^A_n/p^A(n)$, so that $\mathrm{Tr}\tilde{\rho}^A_n = 1$ and $\hat{\rho}^A = \sum_n p^A(n)\tilde{\rho}^A_n$. Then, each $\tilde{\rho}^A_n$ 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

$$\rho^{A,m}_n(\boldsymbol{x}_{i\leq m};\boldsymbol{x}'_{i\leq m}) = \frac{n!}{(n-m)!}\int \rho^A_n(\boldsymbol{x}_{i\leq n};\boldsymbol{x}'_{i\leq n})d\boldsymbol{x}_{i>m}, \tag{10}$$

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

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

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

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 $\Lambda_{N,n}^m \int_D \rho(\boldsymbol{x};\boldsymbol{x}')\boldsymbol{x}_{i>m}$ for values of $n$ between 0 and $N$ one obtains $\rho^m(\boldsymbol{x}_{i\leq m};\boldsymbol{x}'_{i\leq m})$, 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 $\rho^{A,m} = \sum_n \rho_n^{A,m} = \mathbf{1}_m^{\prime A}\mathbf{1}_m^{A}\rho^m$. 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 $|\Psi\rangle = (N!)^{-1/2}\det|u_1(\boldsymbol{x}_1)\cdots u_N(\boldsymbol{x}_N)|$. 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 $S_{ij}^B = \langle u_i|u_j\rangle_B$, $\boldsymbol{k} = \{k_1,\cdots,k_n\}$ and $\boldsymbol{l} = \{l_1,\cdots,l_n\}$ are two ordered sets ($k_1 < \cdots < k_n$ and $l_1 < \cdots < l_n$) of $n \leq N$ numbers, $\tilde{\boldsymbol{k}}$ and $\tilde{\boldsymbol{l}}$ their complementary sets of $N-n$ elements, and $S^A(\boldsymbol{k}|\boldsymbol{l})$ and $S^B(\boldsymbol{k}|\boldsymbol{l})$ the $n\times n$ matrices obtained by selecting the rows indicated by $\boldsymbol{k}$ and the columns indicated by $\boldsymbol{l}$ from $S^A$ and $S^B$, respectively. Similarly, $S^A(\tilde{\boldsymbol{k}}|\tilde{\boldsymbol{l}})$ and $S^B(\tilde{\boldsymbol{k}}|\tilde{\boldsymbol{l}})$ are the $(N-n)\times(N-n)$ matrices obtained from $S^A$ and $S^B$ by selecting the rows $\tilde{\boldsymbol{k}}$ and the columns $\tilde{\boldsymbol{l}}$. 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, $\det|S^A(\boldsymbol{k}|\boldsymbol{l})|$ is the $\boldsymbol{kl}$ element of an array $\boldsymbol{S}^A$, and $\det|S^B(\boldsymbol{k}|\boldsymbol{l})|$ is the $\boldsymbol{kl}$ element of an array $\boldsymbol{S}^B$. Notice that $\boldsymbol{S}^A$ and $\boldsymbol{S}^B$ are $m\times m$ matrices, where $N!/[n!(N-n)!]$ is the full number of $\boldsymbol{k}$ and $\boldsymbol{l}$ ordered sets. The $m\times m$ arrays $\tilde{\boldsymbol{S}}_{\boldsymbol{kl}}^A$ and $\tilde{\boldsymbol{S}}_{\boldsymbol{kl}}^B$ are defined from $S^A(\tilde{\boldsymbol{k}}|\tilde{\boldsymbol{l}})$ and $S^B(\tilde{\boldsymbol{k}}|\tilde{\boldsymbol{l}})$ in a similar way. Using the above definitions, the sector density of domain $A$, $\rho_n^A$, can be written as

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

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

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 $S^A$, $U^\dagger S^A U = \mathrm{diag}(s_i) = s$. 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 $|\phi\rangle = |u^p\rangle s^{-1/2}$. [1] 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

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

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

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

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 $|\phi_{\boldsymbol{k}}\rangle$ are easily obtained from Eqs. 10, 13 and 14 by simple application of the Slater

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[1] 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:

$$
\begin{aligned}
\rho_n^{A,1}(\boldsymbol{x}_1;\boldsymbol{x}'_1) &= \mathbf{1}_1^{\prime A}\mathbf{1}_1^{A} \sum_{\boldsymbol{k}} p_n^{\boldsymbol{k}} \rho_{n,\boldsymbol{k}}^{A,1}(\boldsymbol{x}_1;\boldsymbol{x}'_1) \qquad\qquad\qquad\qquad \tag{15}\\
\rho_n^{A,2}(\boldsymbol{x}_1,\boldsymbol{x}_2;\boldsymbol{x}'_1,\boldsymbol{x}'_2) &= \mathbf{1}_2^{\prime A}\mathbf{1}_2^{A} \sum_{\boldsymbol{k}} p_n^{\boldsymbol{k}} \rho_{n,\boldsymbol{k}}^{A,2}(\boldsymbol{x}_1,\boldsymbol{x}_2;\boldsymbol{x}'_1,\boldsymbol{x}'_2), \qquad \text{where} \tag{16}\\
\rho_{n,\boldsymbol{k}}^{A,1}(\boldsymbol{x}_1;\boldsymbol{x}'_1) &= \sum_{i=1}^{n} \phi_{k_i}(\boldsymbol{x}_1)\phi_{k_i}^{\star}(\boldsymbol{x}'_1) \qquad \text{and} \tag{17}\\
\rho_{n,\boldsymbol{k}}^{A,2}(\boldsymbol{x}_1,\boldsymbol{x}_2;\boldsymbol{x}'_1,\boldsymbol{x}'_2) &= \sum_{i,j=1}^{n} \phi_{k_i}(\boldsymbol{x}_1)\phi_{k_j}(\boldsymbol{x}_2)\left[1-\hat{p}_{ij}\right]\phi_{k_i}^{\star}(\boldsymbol{x}'_1)\phi_{k_j}^{\star}(\boldsymbol{x}'_2). \tag{18}
\end{aligned}
$$

Since $\mathrm{Tr}(\rho_{n,\boldsymbol{k}}^{A,1}) = n$ and $\mathrm{Tr}(\rho_{n,\boldsymbol{k}}^{A,2}) = n(n-1)$ for any $\boldsymbol{k}$, we have $\mathrm{Tr}(\rho_n^{A,1}) = n \times p^A(n)$ and $\mathrm{Tr}(\rho_n^{A,2}) = n(n-1) \times p^A(n)$, 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 $\boldsymbol{r} = (r_1,\cdots,r_N)$. 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. $U^{\dagger}S^AU = \mathrm{diag}(s_i) = s$. 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)

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

where $\boldsymbol{j} \equiv \{j_1\cdots j_N\}$, $D_{\boldsymbol{j}} = \sum_{r=1}^{M} C_r \det[U_{\boldsymbol{rj}}]$, $\chi_{\boldsymbol{j}} = (N!)^{-1/2}\det|u_{j_1}^p\cdots u_{j_N}^p|$, and $U_{\boldsymbol{rj}}$ is the $(N\times N)$ matrix obtained from $U$ by selecting the rows and columns denoted by $\boldsymbol{r}$ and $\boldsymbol{j}$, respectively. The summation over $\boldsymbol{j}$ 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 $\chi_{\boldsymbol{j}}$'s are built with the same number of $\alpha$ and $\beta$ MSO's (say, $N_\alpha$ and $N_\beta$), $j_1, \cdots, j_{N_\alpha}$ and $j_{N_\alpha+1}, \cdots, j_N$ 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, $U_{\boldsymbol{rj}}$ is not. However, for a closed-shell SDW $f = N/2$, $\boldsymbol{j}$ and $\boldsymbol{r}$ can only be $\boldsymbol{j} = \boldsymbol{r} = (1, 2, \cdots, N)$, and $U_{\boldsymbol{rj}} = U$. 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

$$\rho_n^{A,m}(\boldsymbol{x}_{i\le m};\boldsymbol{x}'_{i\le m}) = \mathbf{1}'^{A}_{m}\mathbf{1}^{A}_{m}\sum_{\boldsymbol{j},\boldsymbol{k}} D_{\boldsymbol{j}} D^\star_{\boldsymbol{k}} I^m_{\boldsymbol{jk}}(\boldsymbol{x}_{i\le m};\boldsymbol{x}'_{i\le m}), \qquad \text{where} \tag{20}$$

$$I^m_{\boldsymbol{jk}}(\boldsymbol{x}_{i\le m};\boldsymbol{x}'_{i\le m}) = \Lambda^m_{N,n}\int_D \chi_{\boldsymbol{j}}(\boldsymbol{x})\chi^\star_{\boldsymbol{k}}(\boldsymbol{x}')\, d\boldsymbol{x}_{i>m}. \tag{21}$$

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

$$I^1_{\boldsymbol{jj}}(\boldsymbol{x}_1;\boldsymbol{x}'_1) = \sum_{i=1}^{N} \phi_{j_i}(\boldsymbol{x}_1)\phi^\star_{j_i}(\boldsymbol{x}'_1) \times n^{A,1}_{j_i j_i}. \tag{22}$$

If $\chi_{\boldsymbol{j}}$ and $\chi_{\boldsymbol{k}}$ differ in a single MSO, say $u^p_{j_i} \neq u^p_{k_i}$ we have

$$I^1_{\boldsymbol{jk}}(\boldsymbol{x}_1;\boldsymbol{x}'_1) = \phi_{j_i}(\boldsymbol{x}_1)\phi^\star_{k_i}(\boldsymbol{x}'_1) \times n^{A,1}_{j_i k_i} \qquad (u^p_{j_i} \neq u^p_{k_i}), \tag{23}$$

and finally, $I^1_{\boldsymbol{jk}} = 0$ if $\chi_{\boldsymbol{j}}$ and $\chi_{\boldsymbol{k}}$ differ in two or more MSO's. In Eqs. 22 and 23, $n^{A,1}_{j_i k_i} = (s_{j_i} s_{k_i})^{1/2} \times p^{j_i}(n-1)$ 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 $\chi_{\boldsymbol{j}}$ except $u^p_{j_i}$.

The computation of $I^2_{\boldsymbol{jk}}$ runs parallel to that of $I^1_{\boldsymbol{jk}}$. We obtain

$$I^2_{\boldsymbol{jj}}(\boldsymbol{x}_1,\boldsymbol{x}_2;\boldsymbol{x}'_1,\boldsymbol{x}'_2) = \frac{1}{2}\hat{A}_{12}\hat{A}'_{12}\sum_{i,l}\phi_{j_i}(\boldsymbol{x}_1)\phi_{j_l}(\boldsymbol{x}_2)\phi^\star_{j_i}(\boldsymbol{x}'_1)\phi^\star_{j_l}(\boldsymbol{x}'_2)\, n^{A,2}_{j_i j_l j_i j_l} \tag{24}$$

where $n^{A,2}_{j_i j_l k_i k_l} = (s_{j_i} s_{j_l} s_{k_i} s_{k_l})^{1/2} \times p^{j_i j_l}(n-2)$, $\hat{A}_{12} = 1 - \hat{p}_{12}$ 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 $\chi_{\boldsymbol{j}}$ except $u^p_{j_i}$ and $u^p_{j_l}$. If $\chi_{\boldsymbol{j}}$ and $\chi_{\boldsymbol{k}}$ differ in a single MSO $u^p_{j_i} \neq u^p_{k_i}$ (or $\phi_{j_i} \neq \phi_{k_i}$) one has

$$I^2_{\boldsymbol{jk}}(\boldsymbol{x}_1,\boldsymbol{x}_2;\boldsymbol{x}'_1,\boldsymbol{x}'_2) \;=\; \hat{A}_{12}\sum_{l\neq i}\phi_{j_i}(\boldsymbol{x}_1)\phi_{j_l}(\boldsymbol{x}_2)\phi^\star_{k_i}(\boldsymbol{x}'_1)\phi^\star_{j_l}(\boldsymbol{x}'_2)\,n^{A,2}_{j_i j_l k_i j_l} \tag{25}$$

If $\chi_{\boldsymbol{j}}$ and $\chi_{\boldsymbol{k}}$ differ in two MSO's $u^p_{j_i} \neq u^p_{k_i}$ (or $\phi_{j_i} \neq \phi_{k_i}$) and $u^p_{j_l} \neq u^p_{k_l}$ (or $\phi_{j_l} \neq \phi_{k_l}$), we obtain

$$I^2_{\boldsymbol{jk}}(\boldsymbol{x}_1,\boldsymbol{x}_2;\boldsymbol{x}'_1,\boldsymbol{x}'_2) \;=\; \hat{A}_{12}\phi_{j_i}(\boldsymbol{x}_1)\phi_{j_l}(\boldsymbol{x}_2)\phi^\star_{k_i}(\boldsymbol{x}'_1)\phi^\star_{k_l}(\boldsymbol{x}'_2)\,n^{A,2}_{j_i j_l k_i k_l}. \tag{26}$$

Finally, $I^2_{\boldsymbol{jk}} = 0$ if $\chi_{\boldsymbol{j}}$ and $\chi_{\boldsymbol{k}}$ 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 $n^{A,1}_{j_ik_i}$ and $n^{A,1}_{j_ij_lk_ik_l}$.

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 $\chi_{\boldsymbol{j}}$, compute the probabilities $p^{j_i}(n-1)$ and $p^{j_ij_l}(n-2)$. Clearly, we can obviate the sector $n=0$, since the 1RDM and 2RDM are zero in this case, $\rho^{A,1}_0 = \rho^{A,2}_0 = 0$. Similarly, only $p^{j_i}(n-1)$ is needed for $n=1$, since $\rho^{A,2}_1 = 0$. Once these calculations have been performed, $\rho^{A,1}_n$ and $\rho^{A,2}_n$ in the $|\phi\rangle$ basis can be written as

$$\rho^{A,1}_n(\boldsymbol{x}_1;\boldsymbol{x}'_1) \;=\; \mathbf{1}^{\prime A}_1\mathbf{1}^A_1\sum_{i,k}\gamma^n_{ik}\phi_i(\boldsymbol{x}_1)\phi_k(\boldsymbol{x}'_1), \qquad (n\geq 1), \tag{27}$$

$$\rho^{A,2}_n(\boldsymbol{x}_1,\boldsymbol{x}_2;\boldsymbol{x}'_1,\boldsymbol{x}'_2) \;=\; \mathbf{1}^{\prime A}_2\mathbf{1}^A_2\sum_{i,j,k,l}\Gamma^n_{ijkl}\phi_i(\boldsymbol{x}_1)\phi_j(\boldsymbol{x}_2)\phi^\star_k(\boldsymbol{x}'_1)\phi^\star_l(\boldsymbol{x}'_2) \qquad (n\geq 2). \tag{28}$$

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 $\gamma^n_{ik}$ and $\Gamma^n_{ijkl}$ for the coefficient that multiplies $\phi_i(\boldsymbol{r}_1)\phi_k(\boldsymbol{r}'_1)$ and $\phi_i(\boldsymbol{r}_1)\phi_j(\boldsymbol{r}_2)\phi^\star_k(\boldsymbol{r}_1)\phi^\star_l(\boldsymbol{r}_2)$, 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 ($m=1,2,\cdots$) 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 $\boldsymbol{j}=\boldsymbol{k}=\{1,\cdots,N\}$ 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 $\langle \hat{S}_A^2\rangle = \mathrm{Tr}\left(\hat{S}^2\hat{\rho}^A\right)$, 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 contributes 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

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

$$\begin{aligned}
\langle \hat{S}_A^2\rangle &= \langle \hat{S}_{1,A}^2\rangle + \langle \hat{S}_{2,A}^2\rangle, \qquad \text{with} && (30)\\
\langle \hat{S}_{1,A}^2\rangle &= \sum_n \langle \hat{S}_{1,A,n}^2\rangle = \sum_n \mathrm{Tr}\left(\hat{S}_1^2 \rho_n^{A,1}(\boldsymbol{x};\boldsymbol{x}')\right), && (31)\\
\langle \hat{S}_{2,A}^2\rangle &= \sum_n \langle \hat{S}_{2,A,n}^2\rangle = \sum_n \mathrm{Tr}\left(\hat{S}_2^2 \rho_n^{A,2}(\boldsymbol{x}_1,\boldsymbol{x}_2;\boldsymbol{x}_1',\boldsymbol{x}_2')\right). && (32)
\end{aligned}$$

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)

$$\langle \hat{S}^2 \rangle_{A,n} = \sum_{\boldsymbol{k}} p_n^{\boldsymbol{k}} \left[ n/2 + M_{\boldsymbol{k}}^2 - S_{\boldsymbol{k}} \right] = \sum_{\boldsymbol{k}} p_n^{\boldsymbol{k}} \langle \hat{S}^2 \rangle_{A,n,\boldsymbol{k}} \tag{33}$$

In eq 33, $M_{\boldsymbol{k}} = (n^\alpha - n^\beta)/2$ is the eigenvalue of $\hat{S}_z$ for the determinant $|\phi_{\boldsymbol{k}}\rangle$, with $n^\alpha + n^\beta = n$, and $S_{\boldsymbol{k}} = \sum_{k_i \in \alpha} \sum_{k_j \in \beta} |\langle k_i^\alpha | k_j^\beta \rangle_A|^2$, where $k_i^\alpha$ and $k_j^\beta$ are the real parts of MSO's $k_i$ and $k_j$, respectively.[2] 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. $|\phi_{\boldsymbol{k}}\rangle$ in the general case is a spin-unrestricted Slater determinant. Particular cases of eq 33 deserve to to commented. (i) A single $\alpha$ or $\beta$ electron in $A$ has $n/2 = \frac{1}{2}$, $M_{\boldsymbol{k}}^2 = \frac{1}{4}$ and $S_{\boldsymbol{k}} = 0$, so that $\langle \hat{S}^2 \rangle_{A,n,\boldsymbol{k}} = \frac{3}{4}$. (ii) An arbitrary $|\phi_{\boldsymbol{k}}\rangle$ with $n^\alpha = n^\beta$ has $M_{\boldsymbol{k}} = 0$, so that $\langle \hat{S}^2 \rangle_{A,n,\boldsymbol{k}} = n/2 - S_{\boldsymbol{k}}$. (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 $S_{\boldsymbol{k}} = n^\beta$ and $n/2 - S_{\boldsymbol{k}} = M_{\boldsymbol{k}} = |M_{\boldsymbol{k}}|$. 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 $S_{\boldsymbol{k}} = n^\alpha$ and $n/2 - S_{\boldsymbol{k}} = -M_{\boldsymbol{k}} = |M_{\boldsymbol{k}}|$. Since $M_{\boldsymbol{k}}^2 = |M_{\boldsymbol{k}}|^2$, we obtain in both cases $\langle \hat{S}_{A,n,\boldsymbol{k}}^2 \rangle = |M_{\boldsymbol{k}}|(1 + |M_{\boldsymbol{k}}|)$. If, in addition, $n^\alpha = n^\beta$, $\langle \hat{S}_{A,n,\boldsymbol{k}}^2 \rangle = 0$, that correspondonds 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 $n_c \leq n_\beta$), $S_{\boldsymbol{k}} = n_c$, and $\langle \hat{S}_{A,n,\boldsymbol{k}}^2 \rangle = M_{\boldsymbol{k}}^2 + n_d/2$, where $n_d = n_\alpha + n_\beta - 2n_c$ is the number of not-matched orbitals from either spin.[5] For instance, if $\boldsymbol{k} = \{\phi_1, \phi_2, \phi_3, \phi_4, \phi_5, \bar{\phi}_4, \bar{\phi}_5, \phi_6, \phi_7\}$, 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[5], $n_d$ is the trace of the effectively unpaired density $u(\boldsymbol{r})$. 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

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[2] The meaning of $S_{\boldsymbol{k}}$ is the following. The set of spin-orbitals in $\boldsymbol{k}$ 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 $S_{\boldsymbol{k}}$.

except that $\tilde{p}_n^{\boldsymbol{k}}$ must replace $p_n^{\boldsymbol{k}}$. 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 $N!/[n!(N-n)!]$ choices of $\boldsymbol{k}$. Given that $p_n^{\boldsymbol{k}} = \prod_i^N p_i$ with $p_i = s_i$ if $i \in \boldsymbol{k}$ and $p_i = 1 - s_i$ if $i \notin \boldsymbol{k}$, it is clear that only $\boldsymbol{k}$'s with all of its MSO's partially localized in $A$ will contribute significantly to $\langle \hat{S}^2_{A,n} \rangle$.

The $\boldsymbol{k}$ 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. $\langle \hat{S}^2_{A,n} \rangle = \sum'_{n^\alpha, n^\beta} \sum'_{\boldsymbol{k}} p_n^{\boldsymbol{k}} \left[ n/2 + M_{\boldsymbol{k}}^2 - S_{\boldsymbol{k}} \right]$, where the prime ($'$) in the first sum means than only terms with $n^A_\alpha + n^A_\beta = n$ are included, and the $'$ in the second that only $\boldsymbol{k}$'s associated to these $n^\alpha$ and $n^\beta$ have to be considered. All these restricted $\boldsymbol{k}$'s have $n/2 = (n^\alpha + n^\beta)/2$ and $M_{\boldsymbol{k}} = (n^\alpha - n^\beta)/2$, so that

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

where $p^A(n^\alpha, n^\beta) = \sum'_{\boldsymbol{k}} p_n^{\boldsymbol{k}}$ is probability of having $n^\alpha$ $\alpha$ and $n^\beta$ $\beta$ electrons in the domain $A$, and we have defined $S^n_{\boldsymbol{k}} = p^A(n^\alpha, n^\beta)^{-1} \sum'_{\boldsymbol{k}} p_n^{\boldsymbol{k}} S_{\boldsymbol{k}}$. The quantity $\left[ n/2 + (n_\alpha - n_\beta)^2/4 - S^n_{\boldsymbol{k}} \right]$ can be understood as $\langle \hat{S}^2_{A,n_\alpha,n_\beta} \rangle$, 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

$$\langle \hat{S}^2 \rangle_{A,n} = \frac{3}{4} \sum_i \gamma^n_{ii} - \frac{1}{4} \sum_{i,j} \left( \Gamma^n_{ijij} + 2\Gamma^n_{ijji} \right). \tag{35}$$

In some way, the expresion 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 $\gamma^n_{ij}$ and $\Gamma^n_{ijkl}$ 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 $\langle \hat{S}^2_{A,n^A_\alpha,n^A_\beta} \rangle$ 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

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

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

$$\begin{aligned}
\rho^2(\boldsymbol{r}_1,\boldsymbol{r}_2;\boldsymbol{r}_1,\boldsymbol{r}_2) &= \rho(\boldsymbol{r}_1)\rho(\boldsymbol{r}_2) - \frac{1}{2}\rho(\boldsymbol{r}_1;\boldsymbol{r}_2)\rho(\boldsymbol{r}_2;\boldsymbol{r}_1) - \frac{1}{2}\rho^s(\boldsymbol{r}_1;\boldsymbol{r}_2)\rho^s(\boldsymbol{r}_2;\boldsymbol{r}_1), && (37)\\
\rho^2(\boldsymbol{r}_1,\boldsymbol{r}_2;\boldsymbol{r}_2,\boldsymbol{r}_1) &= \rho(\boldsymbol{r}_1;\boldsymbol{r}_2)\rho(\boldsymbol{r}_2;\boldsymbol{r}_1) - \frac{1}{2}\rho(\boldsymbol{r}_1)\rho(\boldsymbol{r}_2) - \frac{1}{2}\rho^s(\boldsymbol{r}_1;\boldsymbol{r}_1)\rho^s(\boldsymbol{r}_2;\boldsymbol{r}_2), && (38)
\end{aligned}$$

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

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

The integration of $\rho^2(\boldsymbol{r}_1,\boldsymbol{r}_2;\boldsymbol{r}_2,\boldsymbol{r}_1)$ is as follows. First, $\int_A\int_A \rho(\boldsymbol{r}_1;\boldsymbol{r}_2)\rho(\boldsymbol{r}_2;\boldsymbol{r}_1)\, d\boldsymbol{r}_1 d\boldsymbol{r}_2 = \alpha\alpha + \beta\beta + \alpha\beta + \beta\alpha$, where $\sigma\sigma' = \int_A\int_A \rho^\sigma(\boldsymbol{r}_1;\boldsymbol{r}_2)\rho^{\sigma'}(\boldsymbol{r}_2;\boldsymbol{r}_1)\, d\boldsymbol{r}_1 d\boldsymbol{r}_2$. 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 $\alpha\beta = \sum_{k_i\in\alpha}\sum_{k_j\in\beta}|\langle k^\alpha_i|k^\beta_j\rangle_A|^2 = |S^{\alpha\beta}_{ij}|^2 = S_{\boldsymbol{k}}$, 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 $S_{\boldsymbol{k}} = n_p^{\boldsymbol{k}}$, where $n_p^{\boldsymbol{k}}$ is the number $\phi_i$'s in $\boldsymbol{k}$ that appear simultaneously in the $\alpha$ and $\beta$ sets. For instance, for the five-components $\boldsymbol{k}$ 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 $n_p^{\boldsymbol{k}} = 2$. 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 $\beta\alpha = S_{\boldsymbol{k}}$. In summary, we have $\int_A \int_A \rho(\boldsymbol{r}_1;\boldsymbol{r}_2)\rho(\boldsymbol{r}_2;\boldsymbol{r}_1)\, d\boldsymbol{r}_1 d\boldsymbol{r}_2 = n + 2S_{\boldsymbol{k}}$. From $\int_A \rho(\boldsymbol{r}) d\boldsymbol{r} = n$, we trivially obtain $-\frac{1}{2}\int_A \int_A \rho(\boldsymbol{r}_1)\rho(\boldsymbol{r}_2)\, d\boldsymbol{r}_1 d\boldsymbol{r}_2 = -\frac{1}{2}n^2$. Finally, from $\rho^s(\boldsymbol{r};\boldsymbol{r}') = \rho^\alpha(\boldsymbol{r};\boldsymbol{r}') - \rho^\beta(\boldsymbol{r};\boldsymbol{r}')$ we have $-\frac{1}{2}\int_A \int_A \rho^s(\boldsymbol{r}_1;\boldsymbol{r}_1)\rho^s(\boldsymbol{r}_2;\boldsymbol{r}_2)\, d\boldsymbol{r}_1 d\boldsymbol{r}_2 = -\frac{1}{2}(n^\alpha - n^\beta)^2 = -2M_{\boldsymbol{k}}^2$. Adding these three contributions

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

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.