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# A hierarchy of chemical bonding indices in real space from reduced density matrices and cumulants

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## ABSTRACT

Real space techniques in the theory of the chemical bond may in fact be understood as means to obtain chemical information from reduced density matrices (RDMs). Much work has been devoted to examine the one particle density, but the renewed interest in electron correlation effects on bonding has progressively shifted research towards further order densities. Up to date, however, not much work has been carried out to determine higher order RDMs from standard electronic structure packages beyond the single-determinant level. We show in this work a possible efficient route to this end. We discuss how to compute RDMs from multi-determinant wavefunctions, how to construct from them  $n$ th order cumulant density matrices ( $n$ -CDMs), and how to make profit of the recursivity and extensivity of the latter to define a full hierarchy of bonding indices through exhaustive partitions of the physical space. This hierarchy includes a full set of one- to  $n$ -center quantities (multi-center bonding indices) which may be conveniently decomposed into one-electron components, each of them partnered with a one-electron function (natural adaptive orbital, NAdO). Illustrative results are obtained and discussed for a set of simple test molecules.

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## 1. Introduction

John Coleman's classic *Review of Modern Physics* [1] paper clearly identified the  $N$ -representability conditions problem as the big stone precluding, in his own words, that "... the wave function be eliminated from quantum mechanics and its role be taken over, by reduced density matrices". After almost 60 years since these words were uttered, a large amount of outstanding work has taken the problem to a state much closer to a definitive solution [2]. Notwithstanding the great relevance of this problem, it is also interesting to recall Coleman's confidence in the power of reduced density matrices (RDMs) as a means not only to get numbers, but also new insight.

This takes us to the theory of chemical bonding, where it is actually insight what is usually lacking from state of the art calculations. Practicing computational chemists do still analyze their results by appealing to models based on outdated one-electron pictures, that evolve far behind the theoretical levels used to get energies [3], or do not evolve at all.

A route to build new models, insights, and ideas in chemical bonding has been developed that exploits the above-mentioned potential of RDMs. Actually, most of the field that we call today theories of chemical bonding in real space may well be understood

as the study of RDMs in real space regions to understand the chemical bond. The field started in its early days by recognizing the importance of the 1-particle density, giving rise to the quantum theory of atoms in molecules developed by Bader and coworkers [4], but it has now expanded to cover scalars constructed from the non-diagonal 1-particle density, like the electron localization function (ELF) of Becke and Edgecombe [5], or from the 2-RDM, like the electron localizability indicator (ELI) [6], or the interacting quantum atoms approach [7] (IQA). In recent times, further order RDMs have also burst in, as we will show.

One of the most interesting aspects of these real space techniques is that they provide continuous measures across the transition leading from the independent particle model (IPM) to the fully interacting (correlated) description of the system of interest. Namely, they provide a means to generalize existing bond models to the correlated electron regime. This is not an easy task in Fock space, and most of the standard chemical bond indices that work reasonably well close to the IPM, e.g. in simple closed-shell systems near equilibrium configurations, fail in strong correlation conditions, e.g. in  $(2c,2e)$  homolytic dissociations. Another important point is that they are smoothly extended to multi-center bonding, so they will surely play an important role in properly defining slippery concepts such as aromaticity [8].

A problem that is precluding advancing along these lines stems from how to efficiently compute high order RDMs from quantum chemical packages. Until the day comes when variationally

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determined RDMs become available, real space analyses must rest on a previously computed wave function. We show in this contribution the path that we have recently implemented to tackle this problem together with a taxonomy of some of the bond indices and bond objects that may be defined from RDMs or their cumulants.

The layout of the paper is as follows. We will first briefly review some simple concepts related to the structure of RDMs for multi-determinant wave functions. We will then shift to how to compute cumulants from them, and then to the definition of a well-defined hierarchy of (multi-center) bonding indices. Finally we will consider a limited set of toy molecular system to illustrate our techniques.

## 2. Reduced density matrices for multi-determinant wavefunctions

We define here the diagonal and spinless  $n$ -order reduced density matrix ( $n$ -RDM),  $\rho^n(\mathbf{r}_1, \dots, \mathbf{r}_n)$ , for a  $N$ -electron system as [9]

$$\rho^n(\mathbf{r}_1, \dots, \mathbf{r}_n) = \binom{N}{n} n! \int |\Psi(1, N)|^2 ds_{i \leq n} d\mathbf{x}_{i > n} \quad (1)$$

where  $\mathbf{x} = \mathbf{r}s$  and  $s$  denote space-spin and spin coordinates, respectively,  $d\mathbf{x}_{i > n}$  means integration over  $\mathbf{x}_{n+1}, \dots, \mathbf{x}_N$ , and  $ds_{i \leq n}$  means integration over  $s_1, \dots, s_n$ . Our main interest in this section is to show how  $\rho^n$  may be obtained for multi-determinant  $\Psi$ 's:

$$\Psi(1, N) = \sum_K C_K \Psi_K(1, \dots, N), \quad (2)$$

$$\Psi_K(1, N) = \frac{1}{\sqrt{N!}} \det |\phi_{K_1}, \dots, \phi_{K_N}| \equiv \frac{1}{\sqrt{N!}} |K_1, \dots, K_N\rangle, \quad (3)$$

where the  $\phi_i$ 's are assumed to be orthonormal and real,  $\langle \phi_i | \phi_j \rangle = \delta_{ij}$ . A major problem that one faces in this respect is the computational complexity of these objects, which quickly transform into storage monsters. For the smallest values of  $n$  ( $n \leq 4$ ), brute force algorithms offer no particular difficulties, even though  $\rho^n$  for  $n > 1$  does not usually appear routinely on the output of the most frequently used electronic structure computational codes. Although we will closely follow here the classical article of Löwdin [10], so that no new theoretical knowledge is actually involved, we believe it instructive to detail the main steps that are necessary to derive an efficient computational scheme to obtain the  $n$ -RDM for small  $n$ 's ( $n \leq 4$ ) and  $N$ 's. As far as we know, no other general code with these capabilities presently exists in the market.

From Eqs. (2) and (3),  $\rho^n(\mathbf{r}_1, \dots, \mathbf{r}_n)$  in Eq. (1) becomes

$$\rho^n(\mathbf{r}_1, \dots, \mathbf{r}_n) = \sum_{K \geq L} C_K C_L \int \rho_{KL}^n(1, \dots, n) ds_{i \leq n} d\mathbf{x}_{i > n}, \quad \text{where} \quad (4)$$

$$\rho_{KL}^n(1, \dots, n) = \frac{1}{(N-n)!} \langle K_1, \dots, K_N | L_1, \dots, L_N \rangle. \quad (5)$$

To simplify the notation, the spin-orbitals ( $K_1, \dots, K_N$ ) and ( $L_1, \dots, L_N$ ) in Eq. (5) are renamed ( $u_1, \dots, u_N$ ) and ( $v_1, \dots, v_N$ ), respectively [10]. The overlap between the Slater determinants  $U = \det |u_1, \dots, u_N|$  and  $V = \det |v_1, \dots, v_N|$  is given by [10]  $\langle U | V \rangle = N! D_{UV} = N! \det |d_{uv}(kl)|$ , where  $d_{uv}(kl) = \langle u_k | v_l \rangle$ . For the present case, with an orthonormal MO basis,  $d_{uv}(kl)$  is either 1 or 0 depending on whether  $u_k = v_l$  or  $u_k \neq v_l$ , respectively. If the spin-orbitals ( $v_1, \dots, v_N$ ) in  $V$  are re-ordered such that  $D_{UV}$  is diagonal, the coefficient  $C_L$  of the Slater determinant remains unchanged or changes its sign depending if the number of transpositions needed to put these spin-orbitals back to their original situation ( $R$ ) is even or odd, respectively. Now,  $|u_1(1), \dots, u_N(N)\rangle$  may be expanded in terms of its first  $n$  rows [10]

$$|u_1(1), \dots, u_N(N)\rangle = \sum_{\substack{k_1 < k_2 < \dots < k_n \\ l_1 < l_2 < \dots < l_n}} \det |u_{k_1}(1), \dots, u_{k_n}(n)| \times \det_u(1, \dots, n | k_1, \dots, k_n). \quad (6)$$

In this equation,  $\det_u(1, \dots, n | k_1, \dots, k_n)$  is the determinant obtained by eliminating the rows  $1, \dots, n$  and the columns  $k_1, \dots, k_n$  from  $U$ . It is relevant to stress that it only contains coordinates of electrons  $n+1$  to  $N$ . If Eq. (6) for  $U$  and the analogous one for  $V$  are substituted in Eq. (5), and the space-spin coordinates of electrons  $n+1, \dots, N$  are integrated, we obtain

$$\rho_{KL}^n(1, \dots, n) = \sum_{\substack{k_1 < k_2 < \dots < k_n \\ l_1 < l_2 < \dots < l_n}} |U_{\mathbf{k}}^*| |V_{\mathbf{l}}| D_{UV}(\mathbf{k} | \mathbf{l}), \quad (7)$$

where  $|U_{\mathbf{k}}^*| = \det |u_{k_1}^*(1), \dots, u_{k_n}^*(n)|$ ,  $|V_{\mathbf{l}}| = \det |v_{l_1}(1), \dots, v_{l_n}(n)|$ , and  $D_{UV}(\mathbf{k} | \mathbf{l}) \equiv D_{UV}(k_1, \dots, k_n | l_1, \dots, l_n)$  is the minor of order  $(N-n)$  built by deleting the rows  $k_1, \dots, k_n$  and the columns  $l_1, \dots, l_n$  from  $D_{UV}$ . Since  $D_{UV}$  is already a diagonal determinant with only 1's and 0's in the diagonal, each  $D_{UV}(\mathbf{k} | \mathbf{l})$  in Eq. (7) can only be 1 or 0.  $D_{UV}(\mathbf{k} | \mathbf{l})$  will thus vanish for  $\mathbf{k} \neq \mathbf{l}$  regardless  $K=L$  or  $K \neq L$ . When  $K=L$ ,  $D_{UV} = \det |\mathbf{I}_N| = 1$ , where  $\mathbf{I}_N$  is the  $(N \times N)$  unit matrix, and all the  $D_{UV}(\mathbf{k} | \mathbf{k})$  are 1. Hence,

$$\begin{aligned} \rho_{KK}^n(1, \dots, n) &= \sum_{\mathbf{k}} |U_{\mathbf{k}}^*| |V_{\mathbf{k}}| \\ &= \sum_{\mathbf{k}} \sum_{P, Q} (-1)^{P+Q} u_{p_1}^*(1) v_{q_1}(1), \dots, u_{p_n}^*(n) v_{q_n}(n), \end{aligned} \quad (8)$$

where  $P$  and  $Q$  run over the  $n!$  permutations of the indices  $(k_1, \dots, k_n)$ ,  $(p_1, \dots, p_n)$  is the permutation of  $(k_1, \dots, k_n)$  associated to  $P$  and  $(q_1, \dots, q_n)$  is the permutation of  $(k_1, \dots, k_n)$  associated to  $Q$ . The spin coordinates in Eq. (4) can be immediately integrated, so that  $|U_{\mathbf{k}}^*| |V_{\mathbf{k}}|$  only contributes to  $\rho_{KK}^n$  if  $\text{sgn}(p_1) = \text{sgn}(q_1), \dots, \text{sgn}(p_n) = \text{sgn}(q_n)$ , i.e. if every  $p_i$  has the same spin part than  $q_i$ . When this condition is met, calling  $a_i = |p_i|$ , and  $b_i = |q_i|$ , for  $K=L$ , the coefficient of  $u_{a_1}^*(\mathbf{r}_1) v_{b_1}(\mathbf{r}_1), \dots, u_{a_n}^*(\mathbf{r}_n) v_{b_n}(\mathbf{r}_n)$  in  $\rho^n(\mathbf{r}_1, \dots, \mathbf{r}_n)$  is to be increased by  $C_K^2 (-1)^{P+Q+R}$ . Given that MOs are real, it is convenient to condense each pair  $(a_i, b_i)$  to a single index (see below)  $i_i$  defined as  $i_i = j_i^{\max} \times (j_i^{\max} - 1)/2 + j_i^{\min}$ , where  $j_i^{\max} = \max(a_i, b_i)$  and  $j_i^{\min} = \min(a_i, b_i)$ , and to work directly with orbital products  $\varphi_{i_i}(\mathbf{r}_i) = u_{a_i}(\mathbf{r}_i) v_{b_i}(\mathbf{r}_i)$ , instead of using  $u_{a_i}(\mathbf{r}_i)$  and  $v_{b_i}(\mathbf{r}_i)$  independently.

We consider now the case where  $\Psi_K$  and  $\Psi_L$  differ in  $d$  spin-orbitals. When  $d > n$  the determinant  $D_{UV}$  (after re-ordering the columns of  $V$  such that  $D_{UV}$  be diagonal) will contain in the diagonal more than  $n$  0's. Consequently, all the minors  $D_{UV}(\mathbf{k} | \mathbf{k})$  obtained by deleting  $n$  rows and (the same)  $n$  columns from  $D_{UV}$  will still contain one or more 0's in the diagonal and will be 0. In other words, the product  $\Psi_K^* \Psi_L$  will not contribute to  $\rho^n$  if both determinants differ in more than  $n$  spin-orbitals. The particular cases with  $n=1$  and  $n=2$  are very well known [9]. On the other hand, since a determinant remains unchanged if the same series of rows and columns exchanges are performed, we can always put  $D_{UV}$  into a form such that the  $d \leq n$  spin-orbitals which are different in  $U$  and  $V$  appear in the first  $d$  positions. After this has been done, it is clear that  $D_{UV}(\mathbf{k} | \mathbf{k})$  will vanish unless  $k_1=1, k_2=2, \dots, k_d=d$ . As a consequence,  $\rho_{KL}^n$  with  $K \neq L$  is also given by Eq. (8) with the particularity that the first  $d$   $k_i$ 's are fixed to the above values. Now, however,  $P$  and  $Q$  in that equation run over the  $n!$  permutations of the indices  $1, 2, \dots, d, k_{d+1}, \dots, k_n$ , and  $p_1, \dots, p_n$  and  $q_1, \dots, q_n$  are the permutations of  $1, 2, \dots, d, k_{d+1}, \dots, k_n$  associated to  $P$  and  $Q$ , respectively. The rest of arguments are analogous to those given after Eq. (8), with the difference that the coefficient of  $\varphi_{i_1}(\mathbf{r}_1), \dots, \varphi_{i_n}(\mathbf{r}_n)$  is to be increased by  $2C_K C_L (-1)^{P+Q+R}$  instead of  $C_K^2 (-1)^{P+Q+R}$ , as in the  $K=L$  case.

To end this section, and returning to the  $\varphi$  orbital products defined before,  $\rho^n(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_n)$  may finally be written as

$$\rho^n(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_n) = \sum_{i_1, i_2, \dots, i_n} C_{i_1, i_2, \dots, i_n} \varphi_{i_1}(\mathbf{r}_1) \varphi_{i_2}(\mathbf{r}_2), \dots, \varphi_{i_n}(\mathbf{r}_n), \quad (9)$$

where as a consequence of the electron indistinguishability, all the coefficients  $C_{i_1, i_2, \dots, i_n}$  differing only in the order of  $i_1, i_2, \dots, i_n$  are equal, so that only the  $C_{i_1, i_2, \dots, i_n}$ 's with  $i_1 \geq i_2 \geq \dots \geq i_n$  need be stored. Finally,  $\rho^{n-1}$  is obtained from  $\rho^n$  by integrating the coordinates of electron  $n$  over  $\mathcal{R}^3$ :

$$\rho^{n-1}(\mathbf{r}_1, \dots, \mathbf{r}_{n-1}) = \frac{1}{N-n+1} \int \rho^n(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_n) d\mathbf{r}_n, \quad (10)$$

$$= \frac{1}{N-n+1} \sum_{i_1, i_2, \dots, i_n} C_{i_1, i_2, \dots, i_n} \varphi_{i_1}(\mathbf{r}_1) \varphi_{i_2}(\mathbf{r}_2), \dots, I_{i_n} \quad (11)$$

where  $I_{i_n} = \int \varphi_{i_n}(\mathbf{r}_n) d\mathbf{r}_n = 1$  for  $i_n = 1, 3, 6, \dots$  and  $I_{i_n} = 0$  otherwise.

### 3. Cumulants from $n$ -RDMs

The  $n$ th-order cumulant density ( $n$ -CDM) [11],  $\rho_c^n$ , represents that part of  $\rho^n$  that cannot be expressed in terms of RDMs of orders lower than  $n$ , and provides an appropriate measure of the true  $n$ -particle correlations existing in the system.  $n$ -CDMs are the key objects to generalize bonding analyses in real space to arbitrarily correlated wavefunctions. However, up to now, they have been only obtained at the Hartree-Fock (HF) level and condensed (i.e., all their electrons integrated) over three-dimensional (3D) basins to obtain the standard  $n$ -center bonding or delocalization indices (DI) [12,13]. However, Ziesche [14] has nicely shown how they actually are the generators of the  $n$ -particle fluctuations of the electron distribution. This uncovers a deep theoretical link between  $n$ -CDMs and electron number distribution functions (EDF) [15–19] that has not been explored yet. The  $n$ -CDM for both single- (SDW) and MDWs can be obtained from  $\rho^1, \rho^2, \dots, \rho^n$  by using the procedure described in Appendix A. The explicit formulas for the first 4 CDMs are:  $\rho_c^1(\mathbf{r}_1) = \rho^1(\mathbf{r}_1)$ ,  $\rho_c^2(\mathbf{r}_1, \mathbf{r}_2) = \rho^1(\mathbf{r}_1)\rho^1(\mathbf{r}_2) - \rho^2(\mathbf{r}_1, \mathbf{r}_2)$ ,

$$\rho_c^3(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) = \rho_1 \rho_2 \rho_3 - \frac{1}{2} \hat{S} \rho_{123} + \frac{1}{2} \rho_{123}, \text{ and} \quad (12)$$

$$\rho_c^4(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4) = \rho_1 \rho_2 \rho_3 \rho_4 - \frac{1}{3} \hat{S} \rho_{1234} + \frac{1}{6} \hat{S} \rho_{1234} + \frac{1}{6} \hat{S} \rho_{1234} - \frac{1}{6} \rho_{1234}, \quad (13)$$

where

$$\hat{S} \rho_{123} = \rho_1 \rho_{23}^2 + \rho_2 \rho_{13}^2 + \rho_3 \rho_{12}^2 \quad (14)$$

$$\hat{S} \rho_{1234} = \rho_1 \rho_2 \rho_{34} + \rho_1 \rho_3 \rho_{24} + \rho_1 \rho_4 \rho_{23} + \rho_2 \rho_3 \rho_{14} + \rho_2 \rho_4 \rho_{13} + \rho_3 \rho_4 \rho_{12} \quad (15)$$

$$\hat{S} \rho_{1234} = \rho_1 \rho_{234} + \rho_2 \rho_{134} + \rho_3 \rho_{124} + \rho_4 \rho_{123} \quad (16)$$

$$\hat{S} \rho_{1234} = \rho_{12} \rho_{34} + \rho_{13} \rho_{24} + \rho_{14} \rho_{23} \quad (17)$$

are fully symmetrized products, and  $\rho_i$ ,  $\rho_{ij}$ ,  $\rho_{ijk}$ , and  $\rho_{ijkl}$  abbreviations for  $\rho^1(\mathbf{r}_i)$ ,  $\rho^2(\mathbf{r}_i, \mathbf{r}_j)$ ,  $\rho^3(\mathbf{r}_i, \mathbf{r}_j, \mathbf{r}_k)$ , and  $\rho^4(\mathbf{r}_i, \mathbf{r}_j, \mathbf{r}_k, \mathbf{r}_l)$ , respectively. The expressions  $\rho_c^1 = \rho_1$  and  $\rho_c^2 = \rho_1 \rho_2 - \rho_{12}$  simply highlight the well known fact that  $\rho_c^1$  and  $\rho_c^2$  coincide with electron density  $\rho$  and the exchange-correlation density  $\rho_{xc}$ , respectively. Using Eq. (9), any  $\rho_c^n$  can be recast as

$$\rho_c^n(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_n) = \sum_{i_1, i_2, \dots, i_n} D_{i_1, i_2, \dots, i_n} \varphi_{i_1}(\mathbf{r}_1) \varphi_{i_2}(\mathbf{r}_2), \dots, \varphi_{i_n}(\mathbf{r}_n). \quad (18)$$

For  $1 \leq n \leq 4$  the  $D_{i_1, i_2, \dots, i_n}$ 's are given from the  $C_{i_1, i_2, \dots, i_n}$ 's by  $D_i = C_i$ ,  $D_{ij} = C_{ij} - C_{ij}$ , and

$$D_{ijk} = C_{ij} C_{ik} + \frac{1}{2} [C_{ijk} - C_{ij} C_{jk} - C_{ij} C_{ik} - C_{jk} C_{ik}] \quad (19)$$

$$D_{ijkl} = C_{ij} C_{kl} - \frac{1}{3} [C_{ij} C_{kl} + C_{ij} C_{kl} + C_{ij} C_{kl} + C_{ij} C_{kl}] + C_{ij} C_{kl} + C_{kl} C_{ij} + \frac{1}{6} [C_{ij} C_{kl} + C_{ij} C_{kl} + C_{kl} C_{ij} + C_{kl} C_{ij}] + \frac{1}{6} [C_{ij} C_{kl} + C_{kl} C_{ij} + C_{ij} C_{kl} - C_{ijkl}], \quad (20)$$

and symmetries of both types of coefficients are the same. It must be stressed here that  $\rho_c^n$  is defined when  $n > N$ , even though  $\rho^n$  is not. In these cases, to obtain  $\rho_c^n$  from RDMs, we simply ignore the contributions depending on  $\rho^n$ 's with  $n > N$ . Equivalently, we set  $C_{ij} = 0$  when computing  $D_{ij}$  if  $N = 1$ ,  $C_{ijk} = 0$  when computing  $D_{ijk}$  if  $N = 2$ , etc.

An important property of  $n$ -CDMs is their extensivity, which allows  $\rho_c^{n-1}$  to be obtained from  $\rho_c^n$  by integrating out the  $n$ th electron:

$$\rho_c^{n-1}(\mathbf{r}_1, \dots, \mathbf{r}_{n-1}) = \int \rho_c^n(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_n) d\mathbf{r}_n. \quad (21)$$

Applying successively these equations to electrons  $n, n-1, \dots, 1$  one has

$$\int \rho_c^n(\mathbf{r}_1, \dots, \mathbf{r}_n) d\mathbf{r}_1, \dots, d\mathbf{r}_n = N. \quad (22)$$

As we will see, Eq. (22) warrants that  $(n-1)$ -center bonding indices may be obtained applying sum rules to  $n$ -center ones, while Eq. (21) implies that a partition of a given CDM into basin contributions may always be obtained from any other larger order CDM. Integrations appearing in this equation are trivial after the coefficients  $D_{i_1, i_2, \dots, i_n}$  are available (see Eq. (11)).

Despite that Eq. (18) for  $\rho_c^n$  is valid for both SDWs and MDWs, it is instructive to express it in a more familiar way in the first case. This may help us to see clearly its connection to the  $n$ -center bonding indices extensively used in recent years [20–29]. We recall that the  $n$ -RDM for a SDW before the spin coordinates are integrated can be expressed in terms of all non-diagonal 1-RDMs  $\rho^1(\mathbf{x}_i, \mathbf{x}_j)$ , as:

$$\rho^n(\mathbf{x}_1, \dots, \mathbf{x}_n) = \begin{vmatrix} (1,1) & (1,2) & \dots & (1,n) \\ (2,1) & (2,2) & \dots & (2,n) \\ \vdots & \vdots & \ddots & \vdots \\ (n,1) & (n,2) & \dots & (n,n) \end{vmatrix}, \quad (23)$$

where the simplified notation  $(i,j) \equiv \rho^1(\mathbf{x}_i, \mathbf{x}_j)$  has been used. Each of the  $n!$  products is of the form  $\pm(1, i_1)(2, i_2) \dots (n, i_n)$ , where  $(i_1, \dots, i_n)$  is a permutation of  $(1, \dots, n)$ , and only the subset of  $(n-1)!$  of these products that cannot be expressed in terms of RDMs of orders lower than  $n$  contribute to the irreducible part of  $\rho^n(\mathbf{r}_1, \dots, \mathbf{r}_n)$ . For instance, the 3-RDM is given by

$$\rho^3(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3) = (1,1)(2,2)(3,3) + (1,2)(2,3)(3,1) + (1,3)(3,2)(2,1) - (1,3)(2,2)(3,1) - (1,2)(2,1)(3,3) - (1,1)(2,3)(3,2) \quad (24)$$

From these, only the 2nd and the 3rd ones contribute to  $\rho_c^3$ :

$$\rho_c^3(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3) = \frac{1}{2!} [(1,2)(2,3)(3,1) + (1,3)(3,2)(2,1)]. \quad (25)$$

The numerical factor is always  $1/(n-1)!$ , which coincides (in absolute value) with the coefficient of  $\rho^n$  in the expansion of  $\rho_c^n$  (see Table 4).  $\rho_c^n$  never contains diagonal elements  $\rho^1(\mathbf{x}_i, \mathbf{x}_i)$  but is exclusively formed by products of non-diagonal  $\rho^1(\mathbf{x}_i, \mathbf{x}_j)$ 's ( $i \neq j$ ) that

cover, travelling a complete circuit, all the electrons of the system. The factor  $(n-1)!$  is the number of forms in which the circuit  $1 \rightarrow a \rightarrow b \rightarrow \dots \rightarrow 1$  can be travelled. For  $n=3$ , there are only the  $2! = 2$  possibilities that appear in Eq. (25):  $1 \rightarrow 2 \rightarrow 3 \rightarrow 1$  (clockwise) and  $1 \rightarrow 3 \rightarrow 2 \rightarrow 1$  (anti-clockwise). However, for  $n=4$  we have  $(1 \rightarrow 2 \rightarrow 3 \rightarrow 4 \rightarrow 1)$ ,  $(1 \rightarrow 2 \rightarrow 4 \rightarrow 3 \rightarrow 1)$ ,  $(1 \rightarrow 3 \rightarrow 2 \rightarrow 4 \rightarrow 1)$ ,  $(1 \rightarrow 3 \rightarrow 4 \rightarrow 2 \rightarrow 1)$ ,  $(1 \rightarrow 4 \rightarrow 2 \rightarrow 3 \rightarrow 1)$ , and  $(1 \rightarrow 4 \rightarrow 3 \rightarrow 2 \rightarrow 1)$ . Indeed, for each  $n$  (except  $n=2$ ) there are only  $(n-1)!/2$  independent circuits if the direction of the arrows is irrelevant.

In the following section, we will see how  $n$ -center delocalization indices can be easily derived from the general expression for  $\rho_C^n$  (Eq. (18)) and how their analogues in the SDW case arise.

#### 4. Generalized bonding indices in real space

We have seen that the extensivity of CDMs allows for any  $\rho_C^n$  to be obtained from  $m$ -CDMs with  $m > n$  (see Eq. (21)). This property has been used, for instance, to obtain a one-basin partition of the electron density  $\rho(\mathbf{r}) = \rho_C^1(\mathbf{r})$  from the exchange correlation cumulant  $\rho_{xc}(\mathbf{r}_1, \mathbf{r}_2) \equiv \rho_C^2(\mathbf{r}_1, \mathbf{r}_2)$

$$\rho_C^1(\mathbf{r}) = \sum_a^M \int_{\Omega_a} d\mathbf{r}_2 \rho_C^2(\mathbf{r}, \mathbf{r}_2) = \sum_a^M \rho_a^1(\mathbf{r}), \quad (26)$$

where  $\cup_{i=a}^M \Omega_a = \mathcal{R}^3$ . The  $\rho_a^1(\mathbf{r})$ 's are exactly equivalent to the charge weighted domain averaged Fermi holes (DAFHs) [30–35], that have provided an important number of insights about bonding [35–41] and that we have explored in the past [32,42]. Similarly,  $\rho_C^n(\mathbf{r})$  allows for a  $(n-1)$ -basin partition of  $\rho_C^1(\mathbf{r})$ :

$$\rho_C^1(\mathbf{r}) = \sum_{ab}^M \rho_{ab}^1(\mathbf{r}) = \sum_{ab}^M \int_{\Omega_a} d\mathbf{r}_2 \int_{\Omega_b} d\mathbf{r}_3 \rho_C^3(\mathbf{r}, \mathbf{r}_2, \mathbf{r}_3), \quad (27)$$

$$\rho_C^1(\mathbf{r}) = \sum_{abc}^M \rho_{abc}^1(\mathbf{r}) = \sum_{abc}^M \int_{\Omega_a} d\mathbf{r}_2 \int_{\Omega_b} d\mathbf{r}_3 \int_{\Omega_c} d\mathbf{r}_4 \rho_C^4(\mathbf{r}, \mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4), \dots \quad (28)$$

This partition of  $\rho_C^1(\mathbf{r})$  into basins, pairs of basins, etc., may also be extended to higher CDMs:

$$\rho_C^2(\mathbf{r}_1, \mathbf{r}_2) = \sum_a^M \rho_{C,a}^2(\mathbf{r}_1, \mathbf{r}_2) = \sum_a^M \int_{\Omega_a} d\mathbf{r}_3 \rho_C^3(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \quad (29)$$

$$\rho_C^2(\mathbf{r}_1, \mathbf{r}_2) = \sum_{ab}^M \rho_{C,ab}^2(\mathbf{r}_1, \mathbf{r}_2) = \sum_{ab}^M \int_{\Omega_a} d\mathbf{r}_3 \int_{\Omega_b} d\mathbf{r}_4 \rho_C^4(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4), \dots \quad (30)$$

In Eqs. (26)–(28) all electrons but electron 1 are condensed over domains, yielding as a result a generalized  $n$ -basins density. However, for each  $\rho_C^n$ , we can also integrate the  $n$ th electron such that the result is a scalar depending only on the definition of the  $\Omega_i$  basins:

$$\langle N_a \rangle = \int_{\Omega_a} d\mathbf{r}_1 \rho_C^1(\mathbf{r}_1), \quad (31)$$

$$\langle N_{ab} \rangle = \int_{\Omega_a} d\mathbf{r}_1 \int_{\Omega_b} d\mathbf{r}_2 \rho_C^2(\mathbf{r}_1, \mathbf{r}_2), \quad (32)$$

$$\langle N_{abc} \rangle = \int_{\Omega_a} d\mathbf{r}_1 \int_{\Omega_b} d\mathbf{r}_2 \int_{\Omega_c} d\mathbf{r}_3 \rho_C^3(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3), \quad (33)$$

$$\langle N_{abcd} \rangle = \int_{\Omega_a} d\mathbf{r}_1 \int_{\Omega_b} d\mathbf{r}_2 \int_{\Omega_c} d\mathbf{r}_3 \int_{\Omega_d} d\mathbf{r}_4 \rho_C^4(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4), \dots \quad (34)$$

Since  $\rho_C^n$  is well defined for any  $n$  regardless of the number of electrons  $N$  (see the discussion after Eq. (19)), the above indices can be defined even though the number of centers is greater than  $N$ . Given that  $\rho_C^1(\mathbf{r}) = \rho(\mathbf{r})$ ,  $\langle N_a \rangle$  is immediately recognized as the average number of electrons in basin  $\Omega_a$ . In the same way, since  $\rho_{xc}(\mathbf{r}_1, \mathbf{r}_2) = \rho_C^2(\mathbf{r}_1, \mathbf{r}_2)$ ,  $2\langle N_{ab} \rangle$  with  $a \neq b$  coincides with the delocalization index between basins  $\Omega_a$  and  $\Omega_b$  [43–51], and, in general, we identify  $n!\langle N_{abcd\dots} \rangle$  with a  $n$ -center bonding or delocalization index

(DI). It is important to stress that all the above indices, as well as the generalized  $n$ -basin densities, are immediately available once the expansion coefficients  $D_{i_1, i_2, \dots, i_n}$  of  $\rho_C^n$  in terms of orbital products (Eq. (18)) are known. It is also very easy to show by using the recursivity property of  $\rho_C^n$  (Eq. (21)) that each generalized density  $\rho_{abc\dots}^1(\mathbf{r})$  is normalized to the  $n$ -center DI of the same order, i.e.

$$\int \rho_a^1(\mathbf{r}) d\mathbf{r} = \langle N_a \rangle \quad (35)$$

$$\int \rho_{ab}^1(\mathbf{r}) d\mathbf{r} = \langle N_{ab} \rangle \quad (36)$$

$$\int \rho_{abc}^1(\mathbf{r}) d\mathbf{r} = \langle N_{abc} \rangle, \dots \quad (37)$$

Any  $n$ -center DI can be recovered from the appropriate sum of  $(n+1)$ -center DI's,  $N = \sum_a N_a$ ,  $\langle N_a \rangle = \sum_b \langle N_{ab} \rangle$ ,  $\langle N_{ab} \rangle = \sum_c \langle N_{abc} \rangle, \dots$ , and the total number of electron,  $N$ , can be partitioned into basins, pairs of basins,  $N = \sum_{ab} \langle N_{ab} \rangle$ , trios of basins,  $N = \sum_{abc} \langle N_{abc} \rangle$ , etc. The above relations are simply the generalization to real space of simpler orbital procedures used to distribute the total number of electrons of a molecule,  $N$ , into centers. In Mulliken approach, for instance, each basis set primitive is naively associated to the nucleus it is centered on. In this way, the atomic population of center  $a$  becomes  $\langle N_a \rangle = \sum_{\mu \in a} (PS)_{\mu\mu}$ , where  $P$  and  $S$  are the density and overlap matrices over primitives, respectively. Given the idempotence of  $Q = PS$ ,  $Q^n = Q$ , it follows that  $N = \text{tr} Q^n$ , so for any integer  $n$  there exists a partition of  $N$  into  $n$  center contributions.

If the physical space is exhaustively partitioned into only two fragments  $\Omega_a$  and  $\Omega_b$  ( $\Omega_a \cup \Omega_b = \mathcal{R}^3$ ) we then have  $\langle N_a \rangle = \langle N_{aa} \rangle + \langle N_{ab} \rangle$ , so that  $\langle N_a \rangle = \langle N_{aa} \rangle$  when  $\langle N_{ab} \rangle = 0$ . This happens when the number of electrons in  $\Omega_a$  is fixed, i.e. the variance of the number of electrons in  $\Omega_a$  (or equivalently when the covariance between the  $a, b$  electron populations) is zero. Generalizing to  $n$  centers, it can be shown [17,19] that  $\langle N_{abc\dots} \rangle \sim \langle (N_a - \langle N_a \rangle)(N_b - \langle N_b \rangle)(N_c - \langle N_c \rangle) \dots \rangle$ , where  $N_a$  denotes the instantaneous value of the number of electrons in  $\Omega_a$ . Consequently, a  $n$ -center index  $\langle N_{abc\dots} \rangle$  only differs from 0 when neither of the electron populations in  $\Omega_a, \Omega_b, \Omega_c, \dots$  is fixed.

The  $n$ -center generalized densities  $\rho_{abc\dots}^1(\mathbf{r})$  obtained by condensing the electrons  $2, 3, \dots, n$  of  $\rho_C^n(\mathbf{r}_1, \dots, \mathbf{r}_n)$  (Eq. (18)) into  $\Omega_a, \Omega_b, \dots$ , may be re-written by using the unified expression

$$\rho_{abc\dots}^1(\mathbf{r}) = \phi(\mathbf{r}) \mathbf{D}^{abc\dots} \phi(\mathbf{r})^\dagger, \quad (38)$$

where  $\phi$  collects the set of occupied MOs of the system and  $\mathbf{D}^{abc\dots}$  is a symmetric matrix. The diagonalization of  $\mathbf{D}^n$  in the case  $n=1$  leads to a set of eigenvectors  $(\psi_i^a)$  and eigenvalues  $(n_i^a)$ , yielding  $\rho_a^1 = \sum n_i^a (\psi_i^a)^2$ , an expression entirely equivalent to the molecular orbitals (MOs) and occupation numbers arising from the diagonalization of the previously mentioned DAFH. This diagonalization has been explored number of times by Robert Ponec and other authors to analyze chemical bonding issues in relatively large sets of molecules [30–41]. In this way, diagonalizing  $\mathbf{D}^n$ , we obtain a decomposition of the density associated to a basin into a set of orthonormal one-electron functions  $\psi_i^a$ , that have been called *domain natural orbitals* (DNOs). From Eq. (35), the  $n_i^a$  eigenvalues add to  $\langle N_a \rangle$ , the electron population of basin  $\Omega_a$ . DNOs may be either localized or delocalized, and we have shown [32] that only delocalized ones contribute to bonding, describing effective quasiparticles that behave as statistically independent objects. It is remarkable that DNOs recover the ordinary insights provided by the standard MO theory [32].

Similar diagonalizations for further order CDMs may be even more important. The two-center partition of  $\rho$  coming from the third order cumulant (Eq. (27)) will give rise, after diagonalizing  $\mathbf{D}^{ab}$ , to orbitals  $\psi_i^{ab}$  which describe the two-center bonds between two given basins. Each of these orbitals will contribute additively



to the bond order with the quantity  $n_i^{ab}$ , the eigenvalue associated to  $\psi_i^{ab}$ . In a similar way, we can decompose 3-, 4- and, in general,  $n$ -center bonds. We call these effective one-electron functions *Natural Adaptive Orbitals* (NAOs). In all the cases, the  $n$ -center DI is given as the sum of all eigenvalues of these NAOs,  $\langle N_{abc\dots} \rangle = \sum_i n_i^{abc\dots}$ . As the diagonalization leaves invariant the trace of a matrix we also have  $\langle N_{abc\dots} \rangle = \text{tr} \mathbf{D}^{abc\dots}$ .

As in the previous section, it is convenient at this moment to illustrate how the general expressions for  $n$ -center bonding indices,  $\langle N_{abc\dots} \rangle$ , densities,  $\rho_{abc\dots}^1(\mathbf{r})$ , etc., acquire relatively familiar forms in the case of SDWs. The spinless non-diagonal 1-RDM for a closed-shell SDW is given by

$$\rho^1(\mathbf{r}_i, \mathbf{r}_j) = \sum_{k=1}^{N/2} 2\phi_k(\mathbf{r}_i)\phi_k(\mathbf{r}_j). \quad (39)$$

Taking into account this expression and the orthogonality of  $\alpha$  and  $\beta$  spin functions, the spinless 2-CDM,  $\rho_c^2(\mathbf{r}_1, \mathbf{r}_2)$ , is given by the well known expression

$$\rho_c^2(\mathbf{r}_1, \mathbf{r}_2) = \int \rho_c^2(\mathbf{x}_1, \mathbf{x}_2) d\mathbf{s}_1 d\mathbf{s}_2 \quad (40)$$

$$= \frac{1}{2} \rho^1(\mathbf{r}_1, \mathbf{r}_2) \rho^1(\mathbf{r}_2, \mathbf{r}_1) \\ = \sum_{k,l}^{N/2} 2\phi_k(\mathbf{r}_1)\phi_k(\mathbf{r}_2)\phi_l(\mathbf{r}_2)\phi_l(\mathbf{r}_1), \quad (41)$$

from which it is evident that the  $D_{ij}$  coefficients of Eq. (18) are given in the case of a closed-shell SDW by  $D_{ij} = 0$  for  $i \neq j$ ,  $D_{ii} = 2$  for  $i = 1, 3, \dots, k(k+1)/2$ , and  $D_{ii} = 4$  for  $i \neq k(k+1)/2$ . The  $n$ -CDM with  $n > 2$  including spin for SDWs is given by a linear combination of  $(n-1)!$  terms of the form  $(1ab, \dots, 1) = (1, a)(a, b), \dots, (c, 1)$  (see Eq. (25)). Integrating the spin coordinates one has

$$\int (1ab, \dots, 1) d\mathbf{s}_{i \leq n} = 2 \sum_{k,l,\dots,m} \phi_k(\mathbf{r}_1)\phi_k(\mathbf{r}_a)\phi_l(\mathbf{r}_a)\phi_l(\mathbf{r}_b), \dots, \phi_m(\mathbf{r}_c)\phi_m(\mathbf{r}_1) \quad (42)$$

$$= 2^{1-n} \rho^1(\mathbf{r}_1, \mathbf{r}_a) \rho^1(\mathbf{r}_a, \mathbf{r}_b), \dots, \rho^1(\mathbf{r}_c, \mathbf{r}_1). \quad (43)$$

Finally, condensing the electrons  $2, 3, \dots, n$  into  $\Omega_a, \Omega_b, \dots$ , Eq. (38) is obtained, with  $\mathbf{D}^a, \mathbf{D}^{ab}, \mathbf{D}^{abc}, \dots$ , given now by

$$(\mathbf{D}^a)_{ij} = 2(\mathbf{S}^a)_{ij} \quad (44)$$

$$(\mathbf{D}^{ab})_{ij} = \sum_{l=1}^{N/2} [\mathbf{S}_{il}^a \mathbf{S}_{lj}^b + \mathbf{S}_{il}^b \mathbf{S}_{lj}^a] \quad (45)$$

$$(\mathbf{D}^{abc})_{ij} = \frac{1}{3} \sum_{l,m=1}^{N/2} [\mathbf{S}_{il}^a \mathbf{S}_{lm}^b \mathbf{S}_{mj}^c + \mathbf{S}_{il}^a \mathbf{S}_{lm}^c \mathbf{S}_{mj}^b + \dots], \quad (46)$$

where  $\mathbf{S}_{kl}^\Omega$  are the elements of the atomic overlap matrix (AOM)

$$\mathbf{S}_{kl}^\Omega = \int_{\Omega} \phi_k(\mathbf{r})\phi_l(\mathbf{r}) d\mathbf{r}. \quad (47)$$

For the general case, we have

$$(\mathbf{D}^{\Omega_1, \dots, \Omega_p})_{ij} = \frac{2}{p!} \sum_{i_1, i_2, \dots, i_{p-1}} \hat{S}_{\Omega_1, \dots, \Omega_p} [\mathbf{S}_{ii_1}^{\Omega_1} \mathbf{S}_{i_1 i_2}^{\Omega_2} \mathbf{S}_{i_2 i_3}^{\Omega_3}, \dots, \mathbf{S}_{i_{p-1} j}^{\Omega_p}]. \quad (48)$$

As we can see,  $\mathbf{D}^{abc\dots}$  is given in all the cases by a normalized and symmetrized product of AOMs.

## 5. Examples and computational details

We have selected a set of very simple toy molecules to illustrate the type of results that can be derived from the above methodology. Specifically, we have carried out restricted Hartree–Fock (RHF) and complete active space (CAS) calculations with the GAMESS code [52] for the LiH, BeH<sub>2</sub>, and H<sub>2</sub>O second row hydrides using standard 6-311G(d,p) basis sets at the theoretical equilib-

rium geometries. We included in the CAS calculations for LiH and BeH<sub>2</sub> all the electrons in the valence segment using 12 and 14 valence MOs, respectively. In H<sub>2</sub>O, the 1s electrons of oxygen were kept in the core and the remaining 8 electrons placed in 10 valence MOs. The AOMs defined in Eq. (47), needed in both RHF and CAS calculations, have been obtained with our PROMOLDEN program [53]. Although different space partitionings in 3D regions are possible [54], based either in fuzzy [55–58] or in exhaustive atomic definitions [4], we will restrict in this work to QTAIM  $\Omega_i$  domains. Reduced density matrices,  $\rho^n$ , cumulants,  $\rho_c^n$ ,  $n$ -center bonding indices,  $N_{abc\dots}$ , and generalized densities,  $\rho_{abc\dots}$ , have been obtained with our DENMAT code, developed explicitly for this work.

## 6. Illustrative results

As discussed in the text, the diagonalization of the orbital representation of the generalized density  $\rho_{ab}^1$ , obtained from the 3-CDM, gives the 2-center NAOs,  $\phi_i^{ab}$ , and their eigenvalues,  $n_i^{ab}$ , that describe two-center bonds. In the same way, three-center bonds rest on the  $\phi_i^{abc}$  NAOs and the  $n_i^{abc}$  eigenvalues obtained after diagonalizing  $\rho_{abc}^1$ . The computed  $n_i^{ab}$  and  $n_i^{abc}$ , as well as the  $n$ -center bonding indices  $\langle N_{ab\dots} \rangle$  values for the LiH, BeH<sub>2</sub>, and H<sub>2</sub>O molecules are collected in Tables 1–3, respectively. The two-center indices  $\langle N_{ab} \rangle$  in these tables can be obtained from the 2-RDM (Eq. (32)), and exact [7] and (most times) approximated [59–64] 2-RDMs have been used many times for this purpose. However, an orbital decomposition of  $\langle N_{ab} \rangle$  requires also the 3-RDM. We can see in these tables that, even though  $\langle N_{ab} \rangle$  is given by the sum of several  $n_i^{ab}$  values, a single  $n_i^{ab}$  recovers more than 92%, 97%, and 93% (94%, 98%, and 93%) of the  $\langle N_{ab} \rangle$  value in the RHF (CAS) calculation of LiH, BeH<sub>2</sub>, and H<sub>2</sub>O, respectively, confirming that, as expected, Li–H, Be–H, and O–H are single (2c, 2e) bonds. Comparing the RHF and CAS values of  $\langle N_{ab} \rangle$  and  $\langle N_{aa} \rangle$  we observe that correlation increases a little  $\langle N_{\text{LiH}} \rangle$ ,  $\langle N_{\text{BeH}} \rangle$ ,  $\langle N_{\text{LiLi}} \rangle$ , and  $\langle N_{\text{BeBe}} \rangle$ , and decreases  $\langle N_{\text{OH}} \rangle$  and  $\langle N_{\text{OO}} \rangle$ . As a consequence,  $\langle N_{\text{HH}} \rangle$  decreases in LiH and BeH<sub>2</sub> and increases in H<sub>2</sub>O. The total charge of the H atom in LiH, BeH<sub>2</sub>, and H<sub>2</sub>O passes from –0.9134, –0.8527, and +0.6015 in the HF calculation to –0.9026, –0.8391, and +0.5538 in the CAS calculation. It is interesting to observe that, when an equivalent analysis using the definitions  $a = \text{H}_1$  and  $b = \text{H}_2$  is performed, correlation changes very little  $\langle N_{ab} \rangle$  in BeH<sub>2</sub> (0.0421(RHF) → 0.0462(CAS)) while multiplies it by 4 in H<sub>2</sub>O (0.0038(RHF) → 0.0155(CAS)). Regarding 3-center indices  $\langle N_{abc} \rangle$  and eigenvalues  $\langle n_i^{abc} \rangle$ , we observe in Table 2 that a bonding and an antibonding (we will use this notation for a NAO that decreases the bond indices) 3-center orbital exists in BeH<sub>2</sub>, with RHF eigenvalues (0.0053, –0.0027) that hardly change in the CAS calculation (0.0057, –0.0028), thus leaving  $\langle N_{abc} \rangle$  almost unaltered (0.0026 (RHF) and 0.0030 (CAS)). In H<sub>2</sub>O, there are also a bonding and an antibonding 3-center orbital in the RHF calculation, with eigenvalues 0.0052 and –0.0026, yielding  $\langle N_{abc} \rangle = 0.0028$ . However, correlation alters seriously this image giving rise to at least three 3-center orbitals, two bonding and one antibonding, that contribute significantly to  $\langle N_{abc} \rangle$ . This index has a value of 0.0092, more than three times larger than in the RHF calculation.

**Table 1**

Two-center eigenvalues ( $n_i^{ab}$ ) and  $n$ -center bonding indices ( $\langle N_{ab\dots} \rangle$ ) for the LiH molecule. Labels  $a$  and  $b$  are for Li and H atoms, respectively.

$n_i^{ab}$	RHF	CAS	$n_i^{ab}$	CAS	$\langle N_{ab\dots} \rangle$	RHF	CAS
$n_1^{ab}$	0.0074	0.0075	$n_7^{ab}$	–0.0000	$N_{ab}$	0.0970	0.1042
$n_2^{ab}$	0.0896	0.0986	$n_8^{ab}$	0.0002	$N_{aa}$	1.9896	1.9932
$n_3^{ab}$		–0.0024	$n_9^{ab}$	0.0002	$N_{bb}$	1.8164	1.7984
$n_4^{ab}$		0.0005	$n_{10}^{ab}$	0.0000	$N_a$	2.0866	2.0974
$n_5^{ab}$		–0.0001	$n_{11}^{ab}$	0.0000	$N_b$	1.9134	1.9026
$n_6^{ab}$		–0.0001	$n_{12}^{ab}$	–0.0001			

**Table 2**  
Two-center and three-center eigenvalues ( $n_i^{ab}, n_i^{abc}$ ) and  $n$ -center bonding indices ( $N_{ab...}$ ) for the BeH<sub>2</sub> molecule. Labels  $a$ ,  $b$ , and  $c$  are for Be, H<sub>1</sub>, and H<sub>2</sub>, atoms, respectively. The CAS  $n_i^{abc}$  values with  $i > 7$  (not printed), are lower than 0.0001.

$n_i^{ab}$	RHF	CAS	$n_i^{ab}$	CAS	$n_i^{abc}$	RHF	CAS	$\langle N_{ab...} \rangle$	RHF	CAS
$n_1^{ab}$	0.0043	0.0042	$n_8^{ab}$	−0.0008	$n_1^{abc}$	0.0000	0.0001	$\langle N_{aaa} \rangle$	1.9764	1.9813
$n_2^{ab}$	0.1397	0.1459	$n_9^{ab}$	0.0005	$n_2^{abc}$	0.0053	0.0057	$\langle N_{bbb} \rangle$	1.5214	1.5036
$n_3^{ab}$	−0.0003	0.0025	$n_{10}^{ab}$	0.0005	$n_3^{abc}$	−0.0027	−0.0028	$\langle N_{abc} \rangle$	0.0026	0.0030
$n_4^{ab}$		−0.0000	$n_{11}^{ab}$	−0.0000	$n_4^{abc}$		−0.0000	$\langle N_{aa} \rangle$	2.0071	2.0251
$n_5^{ab}$		−0.0000	$n_{12}^{ab}$	−0.0000	$n_5^{abc}$		−0.0000	$\langle N_{ab} \rangle$	0.1437	0.1484
$n_6^{ab}$		−0.0052	$n_{13}^{ab}$	−0.0000	$n_6^{abc}$		−0.0000	$\langle N_{bb} \rangle$	1.6669	1.6473
$n_7^{ab}$		0.0009	$n_{14}^{ab}$	−0.0000	$n_7^{abc}$		0.0002	$\langle N_a \rangle$	2.2946	2.3219
								$\langle N_b \rangle$	1.8527	1.8391

**Table 3**  
Two-center and three-center eigenvalues ( $n_i^{ab}, n_i^{abc}$ ) together with  $n$ -center bonding indices ( $N_{ab...}$ ) for the H<sub>2</sub>O molecule. Labels  $a$ ,  $b$ , and  $c$  stand for the O, H<sub>1</sub>, and H<sub>2</sub> atoms, respectively. The CAS  $n_i^{abc}$  values with  $i > 8$  (not printed), are lower than 0.0001.

$n_i^{ab}$	RHF	CAS	$n_i^{ab}$	CAS	$n_i^{abc}$	RHF	CAS	$\langle N_{ab...} \rangle$	RHF	CAS
$n_1^{ab}$	0.0000	0.0000	$n_9^{ab}$	−0.0119	$n_1^{abc}$	0.0000	0.0000	$\langle N_{aaa} \rangle$	8.0267	8.0065
$n_2^{ab}$	0.0021	0.0130	$n_{10}^{ab}$	0.0004	$n_2^{abc}$	−0.0026	−0.0012	$\langle N_{bbb} \rangle$	0.0133	0.0333
$n_3^{ab}$	0.3027	0.2990	$n_{11}^{ab}$	0.0002	$n_3^{abc}$	0.0052	0.0078	$\langle N_{abc} \rangle$	0.0028	0.0092
$n_4^{ab}$	0.0074	0.0208			$n_4^{abc}$	0.0001	0.0019	$\langle N_{aa} \rangle$	8.5550	8.4714
$n_5^{ab}$	0.0117	0.0290			$n_5^{abc}$	0.0000	0.0007	$\langle N_{ab} \rangle$	0.3240	0.3181
$n_6^{ab}$		−0.0156			$n_6^{abc}$		−0.0002	$\langle N_{bb} \rangle$	0.0708	0.1127
$n_7^{ab}$		−0.0009			$n_7^{abc}$		−0.0002	$\langle N_a \rangle$	9.2029	9.1075
$n_8^{ab}$		−0.0158			$n_8^{abc}$		0.0003	$\langle N_b \rangle$	0.3985	0.4462

## 7. Final considerations

More than half a century ago the inspiring work of a set of great scientists, Charles Coulson, John Coleman, Per-Olov Löwdin, and Roy McWeeny being among them, laid the ground for an important change of focus in theoretical chemistry, from wave functions to reduced density matrices. Consideration of the latter within the theory of chemical bonding has given rise to modern real space approaches, generally tied to the 1-RDM, the electron density. The importance of the 2- and further order RDMs in these methods has recently been started to be fully recognized.

In this work we have shown how a number of widely used bonding indices, usually obtained at the single determinant level, may be hierarchically defined and generalized from  $n$ th order

cumulants. We have also paid attention to how to automate the construction of RDMs and CDMs from standard electronic calculations, and shown some toy results in very simple systems. We firmly think that there is much room in real space approaches for these (and surely other) ideas, and that advance along these lines should be actively pursued.

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## Appendix A

Efficient computation of  $\rho_c^n$ 's depends on simple algorithms to obtain their algebraic expressions. One of the most efficient starts by recalling that the  $r$ th central moment  $\rho_r$  of a probability distribution function  $f(x)$  is the  $r$ th derivative of its moment generating function  $M(\xi) = E(e^{\xi x})$ . The cumulants  $c_r$  are the coefficients in the Taylor expansion of the generating function  $\ln M(\xi)$ , i.e.  $\ln M(\xi) = \sum_{r=0}^{\infty} c_r \xi^r / r!$ . A closed form that gives the  $c_l$ 's in terms of the first  $l$  moments is

$$c_l = (-1)^{l+1} \begin{vmatrix} \rho_1 & 1 & 0 & 0 & 0 & 0 & \dots & 0 \\ \rho_2 & \rho_1 & 1 & 0 & 0 & 0 & \dots & 0 \\ \rho_3 & \rho_2 & \binom{2}{1}\rho_1 & 1 & 0 & 0 & \dots & 0 \\ \rho_4 & \rho_3 & \binom{3}{1}\rho_2 & \binom{3}{2}\rho_1 & 1 & 0 & \dots & 0 \\ \rho_5 & \rho_4 & \binom{4}{1}\rho_3 & \binom{4}{2}\rho_2 & \binom{4}{3}\rho_1 & 1 & \dots & 0 \\ \vdots & \vdots & \vdots & \vdots & \vdots & \ddots & \ddots & \vdots \\ \rho_{l-1} & \rho_{l-2} & \dots & \dots & \dots & \dots & \ddots & 1 \\ \rho_l & \rho_{l-1} & \dots & \dots & \dots & \dots & \dots & \binom{l-1}{l-2}\rho_1 \end{vmatrix}. \quad (49)$$

**Table 4**

Cumulant of orders 1,...,9. The number of terms appears in parenthesis.

$l = 1$ (1)							
$\rho_1$							
1							
$l = 2$ (2)							
$\rho_1^2$	$\rho_2$						
1	-1						
$l = 3$ (3)							
$\rho_1^3$	$\rho_1\rho_2$	$\rho_3$					
1	-1/2	1/2					
$l = 4$ (5)							
$\rho_1^4$	$\rho_1^2\rho_2$	$\rho_1\rho_3$	$\rho_4$	$\rho_2^2$			
1	-1/3	1/6	-1/6	1/6			
$l = 5$ (7)							
$\rho_1^5$	$\rho_1^3\rho_2$	$\rho_1^2\rho_3$	$\rho_1\rho_4$	$\rho_1\rho_2^2$	$\rho_2\rho_3$	$\rho_5$	
1	-1/4	1/12	-1/24	1/12	-1/24	1/24	
$l = 6$ (11)							
$\rho_1^6$	$\rho_1^4\rho_2$	$\rho_1^3\rho_3$	$\rho_1^2\rho_4$	$\rho_1^2\rho_2^2$	$\rho_1\rho_2\rho_3$	$\rho_1\rho_5$	$\rho_3^2$
1	-1/5	1/20	-1/60	1/20	-1/60	1/120	1/120
$\rho_6$	$\rho_2\rho_4$	$\rho_2^2$					
-1/120	1/120	-1/60					
$l = 7$ (15)							
$\rho_1^7$	$\rho_1^5\rho_2$	$\rho_1^4\rho_3$	$\rho_1^3\rho_4$	$\rho_1^3\rho_2^2$	$\rho_1^2\rho_2\rho_3$	$\rho_1^2\rho_5$	$\rho_1\rho_3^2$
1	-1/6	1/30	-1/120	1/30	-1/120	1/360	1/360
$\rho_1\rho_6$	$\rho_1\rho_2\rho_4$	$\rho_1\rho_3^2$	$\rho_3\rho_4$	$\rho_2^2\rho_3$	$\rho_2\rho_5$	$\rho_7$	
-1/720	1/360	-1/120	-1/720	1/360	-1/720	1/720	
$l = 8$ (22)							
$\rho_1^8$	$\rho_1^6\rho_2$	$\rho_1^5\rho_3$	$\rho_1^4\rho_4$	$\rho_1^4\rho_2^2$	$\rho_1^3\rho_2\rho_3$	$\rho_1^3\rho_5$	$\rho_1^2\rho_3^2$
1	-1/7	1/42	-1/210	1/42	-1/210	1/840	1/840
$\rho_1^2\rho_6$	$\rho_1^2\rho_2\rho_4$	$\rho_1^2\rho_3^2$	$\rho_1\rho_3\rho_4$	$\rho_1\rho_2^2\rho_3$	$\rho_1\rho_2\rho_5$	$\rho_1\rho_7$	$\rho_2\rho_3^2$
-1/2520	1/840	-1/210	-1/2520	1/840	-1/2520	1/5040	-1/2520
$\rho_3\rho_5$	$\rho_8$	$\rho_2\rho_6$	$\rho_2^2\rho_4$	$\rho_4^2$	$\rho_4^2$		
1/5040	-1/5040	1/5040	-1/2520	1/5040	1/840		
$l = 9$ (30)							
$\rho_1^9$	$\rho_1^7\rho_2$	$\rho_1^6\rho_3$	$\rho_1^5\rho_4$	$\rho_1^5\rho_2^2$	$\rho_1^4\rho_2\rho_3$	$\rho_1^4\rho_5$	$\rho_1^3\rho_3^2$
1	-1/8	1/56	-1/336	1/56	-1/336	1/1680	1/1680
$\rho_1^3\rho_6$	$\rho_1^3\rho_2\rho_4$	$\rho_1^3\rho_3^2$	$\rho_1^2\rho_3\rho_4$	$\rho_1^2\rho_2^2\rho_3$	$\rho_1^2\rho_2\rho_5$	$\rho_1^2\rho_7$	$\rho_1\rho_2\rho_3^2$
-1/6720	1/1680	-1/336	-1/6720	1/1680	-1/6720	1/20160	-1/6720
$\rho_1\rho_3\rho_5$	$\rho_1\rho_8$	$\rho_1\rho_2\rho_6$	$\rho_1\rho_2^2\rho_4$	$\rho_1\rho_4^2$	$\rho_1\rho_2^2$	$\rho_3^3$	$\rho_3\rho_6$
1/20160	-1/40320	1/20160	-1/6720	1/20160	1/1680	1/20160	-1/40320
$\rho_2\rho_3\rho_4$	$\rho_2^3\rho_3$	$\rho_4\rho_5$	$\rho_2^2\rho_5$	$\rho_2\rho_7$	$\rho_9$		
1/20160	-1/6720	-1/40320	1/20160	-1/40320	1/40320		

When this determinant is algebraically computed,  $c_l$  is given by a sum of  $N_l$  terms of the form  $d_k \rho_{s_1}^{p_1} \rho_{s_2}^{p_2} \dots \rho_{s_{n_k}}^{p_{n_k}}$ , being  $N_l$  equal to the number of forms in which  $l$  can be decomposed into a sum of positive integers. These terms for  $l = 1, \dots, 9$  are collected in Table 4.

Each of them satisfies  $\sum_{i=1}^{n_k} s_i \times p_i = l$ . The  $d_k$ 's in Table 4 are not directly those resulting from the expansion of determinant (49). They have been modified as follows in order that the  $c$ 's satisfy properties (21) and (22): (i) If the coefficient of  $\rho_1^l$  (always present) is negative we change the sign of all the  $d_k$ 's. (ii) We divide each  $d_k$  by the coefficient of the term  $\rho_1^l$ . (iii) We divide further each  $d_k$  by the factor  $l!/[l! \prod_{i=1}^{n_k} p_i! (s_i!)^{p_i}]$ . This last normalization is pertinent because each  $\rho_{s_1}^{p_1} \rho_{s_2}^{p_2} \dots$  term in Table 4 must be replaced by its symmetrized expression. For instance, the term  $\rho_1^2 \rho_2$  that appears for  $l = 4$  must be replaced by  $\rho_1(1)\rho_1(2)\rho_2(3,4) + \rho_1(1)\rho_1(3)\rho_2(2,4) + \rho_1(1)\rho_1(4)\rho_2(1,3) + \rho_1(2)\rho_1(3)\rho_2(2,4) + \rho_1(2)\rho_1(4)\rho_2(1,3) + \rho_1(3)\rho_1(4)\rho_2(1,2)$ , so that  $\rho_1^2 \rho_2$  actually has  $4!/[2!1!(1!)^2(2!)^1] = 6$  components.

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