Reduced densities and cumulants, bond indices and natural adaptive orbitals

ELECTRONIC SUPPLEMENTARY INFORMATION

Electron counting in position space: from quantum fragments to Lewis structures to multicenter bonds

by

Ángel Martín Pendás* and Evelio Francisco*

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

Email: *ampendas@uniovi.es*
Email: *evelio@uniovi.es*

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1 Calculation of spinless $n^{\text{th}}-$order reduced densities

The spinless $n^{\text{th}}-$order reduced density (nRD) is defined here as

$$\rho^n(\boldsymbol{r}_1 \dots \boldsymbol{r}_n) = \binom{N}{n} n! \int \Psi^\star \Psi \; d\boldsymbol{x}_{i>n} d\sigma_{i\leq n} \tag{1}$$

where $\Psi(1,N)$ is a $N-$ electron wavefunction, $\boldsymbol{x} \equiv \boldsymbol{r}\sigma$ is a spin(σ)-spatial($\boldsymbol{r}$) coordinate, and $d\boldsymbol{x}_{i>n}$ and $d\sigma_{i\leq n}$ mean integration over $\boldsymbol{x}_{n+1} \dots \boldsymbol{x}_N$ and $\sigma_1 \dots \sigma_n$, respectively. We will develop an useful expression for ρ^n in case that Ψ is a multideterminant wavefunction

$$\Psi(1,N) = \sum_K C_K \Psi_K(1,N), \tag{2}$$

where each determinant $\Psi_K(1,N)$ is made of real and orthonormal spin-orbitals ϕ_i:

$$\Psi_K(1,N) = \frac{1}{\sqrt{N!}} \det |\phi_{r_1}(1) \dots \phi_{r_N}(N)| \tag{3}$$

Then, Eq. 1 becomes

$$\rho^n(\boldsymbol{r}_1 \dots \boldsymbol{r}_n) = \sum_{K,L} C_K C_L \rho^n_{KL}(\boldsymbol{r}_1 \dots \boldsymbol{r}_n), \qquad \text{with} \tag{4}$$

$$\rho^n_{KL}(\boldsymbol{r}_1 \dots \boldsymbol{r}_n) = \frac{1}{(N-n)!} \int \Psi_K \Psi_L \; d\boldsymbol{x}_{i>n} d\sigma_{i\leq n}. \tag{5}$$

We will summarize now the main steps necessary to write $\rho^n(\boldsymbol{r}_1 \dots \boldsymbol{r}_n)$ in the form

$$\rho^n(\boldsymbol{r}_1 \dots \boldsymbol{r}_n) = \sum_{a_1 a_2 \dots a_n b_1 b_2 \dots b_n}^{n} c^{b_1 b_2 \dots b_n}_{a_1 a_2 \dots a_n} \prod_k^n \phi_{a_k}(\boldsymbol{r}_k) \phi_{b_k}(\boldsymbol{r}_k). \tag{6}$$

A $r_i > 0$ in Eq. 3 denotes a spin-orbital with a spin function α, and $-r_i < 0$ refers to the spin-orbital with the same spatial part and spin function β. Every r_i satisfies $1 \leq |r_i| \leq M$, where M is the total number of molecular orbitals (MO). We will follow the nomenclature of Löwdin[1] and rename the spin-orbitals $(\phi_{r_1} \dots \phi_{r_N})$ and $(\phi_{s_1} \dots \phi_{s_N})$ (the latter are the spin-orbitals defining $\Psi_L(1,N)$) as $(u_1 \dots u_N)$ and $(v_1 \dots v_N)$, respectively. The overlap between the Slater determinants $U = \det|u_1 \dots u_N|$ and $V = \det|v_1 \dots v_N|$ is given by [1] $\langle U|V\rangle = N! D_{UV} = N! \det|d_{uv}(kl)|$, 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, $|u_1(1) \dots u_N(N)\rangle$ is expanded in terms of its first n rows[1]

$$|u_1(1) \dots u_N(N)\rangle = \sum_{\boldsymbol{k}} \det|u_{k_1}(1) \dots u_{k_n}(n)| \times \det_u(n|\boldsymbol{k}). \tag{7}$$

In this equation, $\boldsymbol{k}$ runs over all possible ordered sets $k_1 < k_2 < \dots < k_n$ and $\det_u(n|\boldsymbol{k})$, that only depends on the coordinates of electrons $n+1$ to N, is the determinant obtained

by elliminating the rows $1 \dots n$ and the columns $k_1 \dots k_n$ from U. If Eq. 7 for U and the analogous one for V are put in Eq. 5, and coordinates $\boldsymbol{x}_{n+1} \dots \boldsymbol{x}_N$ are integrated, we obtain

$$\rho^n_{KL}(\boldsymbol{r}_1 \dots \boldsymbol{r}_n) = \int \sum_{\boldsymbol{k},\boldsymbol{l}} |U_{\mathbf{k}}|\, |V_{\mathbf{l}}|\, D_{UV}(\mathbf{k}|\mathbf{l})\; d\sigma_{i \leq n}, \tag{8}$$

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 $D_{UV}(\mathbf{k}|\mathbf{l})$ 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. 8 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,

$$\rho^n_{KK}(\boldsymbol{r}_1 \dots \boldsymbol{r}_n) = \int \sum_{\mathbf{k}} |U_{\mathbf{k}}|\, |V_{\mathbf{k}}| = \sum_{\mathbf{k}} \sum_{P,Q} (-1)^{P+Q} \prod_{i=1}^{n} \left(\int u_{p_i}(\boldsymbol{x}_i) v_{q_i}(\boldsymbol{x}_i) d\sigma_i \right) \tag{9}$$

where P and Q run over the $n!$ permutations of the indices contained in $\boldsymbol{k}$, and $(p_1 \dots p_n)$ and $(q_1 \dots q_n)$ are the permutation of $\boldsymbol{k}$ associated to P and Q, respectively. The product over i only survives if u_{p_i} and v_{q_i} are both either α or β spin-orbitals. When this condition is met, calling $a_i = |p_i|$ and $b_i = |q_i|$, for $K = L$, the coefficient $c^{b_1 b_2 \dots b_n}_{a_1 a_2 \dots a_n}$ in Eq. 6 has to be increased by $C_K^2 (-1)^{P+Q+R}$.

We consider now the case where Ψ_K and Ψ_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 more than n 0's in the diagonal. 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 $\Psi^\star_K \Psi_L$ will not contribute to ρ^n if both determinants differ in more than n spin-orbitals. The particular cases with $n = 1$ and $n = 2$ are very well known.[2] 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 wich are different in U and V appear in the first d positions. After this has been done, $D_{UV}(\mathbf{k}|\mathbf{k})$ will vanish unless $k_1 = 1$, $k_2 = 2$, ..., $k_d = d$. As a consequence, ρ^n_{KL} for $K \neq L$ is also given by Eq. 9 with the particularity that the first d k_i's are fixed to $1, 2, \dots$, albeit P and Q still 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. 9, with the difference that $c^{b_1 b_2 \dots b_n}_{a_1 a_2 \dots a_n}$ has to be increased by $C_K C_L (-1)^{P+Q+R}$ instead of $C_K^2 (-1)^{P+Q+R}$, as in the $K = L$ case.

Since we are using real spin-orbitals, $\phi_{a_k}(\boldsymbol{r}_k)\phi_{b_k}(\boldsymbol{r}_k) = \phi_{b_k}(\boldsymbol{r}_k)\phi_{a_k}(\boldsymbol{r}_k)$, so that each pair of indices (a_k, b_k) can be condensed to a single index i_k, defined as $i_k = \max(a_k, b_k) \times (\max(a_k, b_k) - 1) + \min(a_k, b_k)$, and ρ^n written also in the form

$$\rho^n(\mathbf{r}_1, \dots, \mathbf{r}_n) = \sum_{i_1, i_2, \dots, i_n}^{n \times (n+1)/2} C_{i_1 i_2 \dots i_n} \prod_{k}^{n} \varphi_{i_k}(\mathbf{r}_k), \tag{10}$$

where the products of pairs of MOs are stored in the order $\varphi_1 = \phi_1\phi_1$, $\varphi_1 = \phi_2\phi_1$, $\varphi_3 = \phi_2\phi_2$, etc. As a consequence of the electron indistinguishability, all $C_{i_1 i_2 \dots i_n}$'s differing

only in the order of i_1,i_2,...,i_n are equal, so that only the those coefficients with $i_1 \geq i_2 \geq \ldots \geq i_n$ need be stored. ρ^{n-1} can be obtained from ρ^n by integrating the over $\boldsymbol{r}_n$:

$$\rho^{n-1}(\mathbf{r}_1,\ldots,\mathbf{r}_{n-1}) = \frac{1}{N-n+1}\int \rho^n(\mathbf{r}_1,\ldots,\mathbf{r}_n)d\mathbf{r}_n, \quad (11)$$

$$= \frac{1}{N-n+1}\sum_{i_1,i_2,\ldots,i_n} C_{i_1 i_2 \ldots i_n}\varphi_{i_1}(\mathbf{r}_1)\varphi_{i_2}(\mathbf{r}_2)\ldots I_{i_n} \quad (12)$$

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

2 Cumulant densities from reduced densities

Equation 10 for n = 1,2, and 3 adopts the form (we suppress the upper limit $n\times(n+1)/2$ in all the following summation symbols):

$$\rho^1(\boldsymbol{r}_1) = \rho(\boldsymbol{r}_1) = \sum_i C_i\varphi_i(\boldsymbol{r}_1) \quad (13)$$

$$\rho^2(\boldsymbol{r}_1,\boldsymbol{r}_2) = \sum_{i,j} C_{ij}\varphi_i(\boldsymbol{r}_1)\varphi_j(\boldsymbol{r}_2) \quad (14)$$

$$\rho^3(\boldsymbol{r}_1,\boldsymbol{r}_2,\boldsymbol{r}_3) = \sum_{i,j,k} C_{ijk}\varphi_i(\boldsymbol{r}_1)\varphi_j(\boldsymbol{r}_2)\varphi_k(\boldsymbol{r}_3), \quad (15)$$

with $_{ij} = C_{ji}$ and $C_{ijk} = C_{ikj} = C_{jik} = C_{jki} = C_{kij} = C_{kji}$. The $n^{\text{th}}-$order cumulant density (nCD), ρ_c^n, is that part of ρ^n that can not be obtained in terms of ρ^m's with $m < n$. It can be obtained following the procedure described in the Appendix of Ref. [3]. The explicit formulas for the first 3 cumulants are

$$\rho_c^1(\boldsymbol{r}_1) = \rho(\boldsymbol{r}_1) \quad (16)$$

$$\rho_c^2(\boldsymbol{r}_1,\boldsymbol{r}_2) = \rho(\boldsymbol{r}_1)\rho(\boldsymbol{r}_2) - \rho^2(\boldsymbol{r}_1,\boldsymbol{r}_2) \quad (17)$$

$$\rho_c^3(\boldsymbol{r}_1,\boldsymbol{r}_2,\boldsymbol{r}_3) = \rho(\boldsymbol{r}_1)\rho(\boldsymbol{r}_2)\rho(\boldsymbol{r}_3) - \frac{1}{2}\hat{S}\rho(\boldsymbol{r}_1)\rho^2(\boldsymbol{r}_2,\boldsymbol{r}_3) + \frac{1}{2}\rho^3(\boldsymbol{r}_1,\boldsymbol{r}_2,\boldsymbol{r}_3) \quad (18)$$

where $\hat{S}\rho(\boldsymbol{r}_1)\rho^2(\boldsymbol{r}_2,\boldsymbol{r}_3) = \rho(\boldsymbol{r}_1)\rho^2(\boldsymbol{r}_2,\boldsymbol{r}_3) + \rho(\boldsymbol{r}_2)\rho^2(\boldsymbol{r}_1,\boldsymbol{r}_3) + \rho(\boldsymbol{r}_3)\rho^2(\boldsymbol{r}_1,\boldsymbol{r}_2)$. The nCDs for $n = 1-9$ are collected in Table 1. Each term $\rho_{p_1}^{s_1}\rho_{p_2}^{s_2}\ldots$ in this table must be actually understood as (the absence of a subindex in ρ^{s_i} means that its value is 1):

$$\rho_{p_1}^{s_1}\rho_{p_2}^{s_2}\ldots \rightarrow \hat{S}\underbrace{\rho^{s_1}\ldots\rho^{s_1}}_{p_1 \text{ times}}\underbrace{\rho^{s_2}\ldots\rho^{s_2}}_{p_2 \text{ times}}\ldots, \quad (19)$$

where $\hat{S}$ is a symmetrizing operator. For instance, $\rho_2^1\rho^2$ that appears for $n = 4$ must be replaced by $\rho^1(\boldsymbol{r}_1)\rho^1(\boldsymbol{r}_2)\rho^2(\boldsymbol{r}_3,\boldsymbol{r}_4) + \rho^1(\boldsymbol{r}_1)\rho^1(\boldsymbol{r}_3)\rho^2(\boldsymbol{r}_2,\boldsymbol{r}_4) + \rho^1(\boldsymbol{r}_1)\rho^1(\boldsymbol{r}_4)\rho^2(\boldsymbol{r}_2,\boldsymbol{r}_3) + \rho^1(\boldsymbol{r}_2)\rho^1(\boldsymbol{r}_3)\rho^2(\boldsymbol{r}_1,\boldsymbol{r}_4) + \rho^1(\boldsymbol{r}_2)\rho^1(\boldsymbol{r}_4)\rho^2(\boldsymbol{r}_1,\boldsymbol{r}_3) + \rho^1(\boldsymbol{r}_3)\rho^1(\boldsymbol{r}_4)\rho^2(\boldsymbol{r}_1,\boldsymbol{r}_2)$.

Using Eqs. 13−15, the cumulants 16−18 can be recast as

$$\rho_c^1(\boldsymbol{r}_1) = \sum_i D_i\varphi_i(\boldsymbol{r}_1) \quad (20)$$

$$\rho_c^2(\boldsymbol{r}_1,\boldsymbol{r}_2) = \sum_{i,j} D_{ij}\varphi_i(\boldsymbol{r}_1)\varphi_j(\boldsymbol{r}_2) \quad (21)$$

$$\rho_c^3(\boldsymbol{r}_1,\boldsymbol{r}_2,\boldsymbol{r}_3) = \sum_{i,j,k} D_{ijk}\varphi_i(\boldsymbol{r}_1)\varphi_j(\boldsymbol{r}_2)\varphi_k(\boldsymbol{r}_3) \quad (22)$$

Table 1: Cumulant of orders $1 \ldots 9$. The number of terms appears in parenthesis.

$n = 1$ (1 term)							
ρ^1							
1							
$n = 2$ (2 terms)							
ρ_2^1	ρ^2						
1	-1						
$n = 3$ (3 terms)							
ρ_3^1	$\rho^1\rho^2$	ρ^3					
1	-1/2	1/2					
$n = 4$ (5 terms)							
ρ_4^1	$\rho_2^1\rho^2$	$\rho^1\rho^3$	ρ^4	ρ_2^2			
1	-1/3	1/6	-1/6	1/6			
$n = 5$ (7 terms)							
ρ_5^1	$\rho_3^1\rho^2$	$\rho_2^1\rho^3$	$\rho^1\rho^4$	$\rho^1\rho_2^2$	$\rho^2\rho^3$	ρ^5	
1	-1/4	1/12	-1/24	1/12	-1/24	1/24	
$n = 6$ (11 terms)							
ρ_6^1	$\rho_4^1\rho^2$	$\rho_3^1\rho^3$	$\rho_2^1\rho^4$	$\rho_2^1\rho_2^2$	$\rho^1\rho^2\rho^3$	$\rho^1\rho^5$	ρ_2^3
1	-1/5	1/20	-1/60	1/20	-1/60	1/120	1/120
ρ^6	$\rho^2\rho^4$	ρ_3^2					
-1/120	1/120	-1/60					
$n = 7$ (15 terms)							
ρ_7^1	$\rho_5^1\rho^2$	$\rho_4^1\rho^3$	$\rho_3^1\rho^4$	$\rho_3^1\rho_2^2$	$\rho_2^1\rho^2\rho^3$	$\rho_2^1\rho^5$	$\rho^1\rho_2^3$
1	-1/6	1/30	-1/120	1/30	-1/120	1/360	1/360
$\rho^1\rho^6$	$\rho^1\rho^2\rho^4$	$\rho^1\rho_3^2$	$\rho^3\rho^4$	$\rho_2^2\rho^3$	$\rho^2\rho^5$	ρ^7	
-1/720	1/360	-1/120	-1/720	1/360	-1/720	1/720	
$n = 8$ (22 terms)							
ρ_8^1	$\rho_6^1\rho^2$	$\rho_5^1\rho^3$	$\rho_4^1\rho^4$	$\rho_4^1\rho_2^2$	$\rho_3^1\rho^2\rho^3$	$\rho_3^1\rho^5$	$\rho_2^1\rho_2^3$
1	-1/7	1/42	-1/210	1/42	-1/210	1/840	1/840
$\rho_2^1\rho^6$	$\rho_2^1\rho^2\rho^4$	$\rho_2^1\rho_3^2$	$\rho^1\rho^3\rho^4$	$\rho^1\rho_2^2\rho^3$	$\rho^1\rho^2\rho^5$	$\rho^1\rho^7$	$\rho^2\rho_2^3$
-1/2520	1/840	-1/210	-1/2520	1/840	-1/2520	1/5040	-1/2520
$\rho^3\rho^5$	ρ^8	$\rho^2\rho^6$	$\rho_2^2\rho^4$	ρ_2^4	ρ_4^2		
1/5040	-1/5040	1/5040	-1/2520	1/5040	1/840		
$n = 9$ (30 terms)							
ρ_9^1	$\rho_7^1\rho^2$	$\rho_6^1\rho^3$	$\rho_5^1\rho^4$	$\rho_5^1\rho_2^2$	$\rho_4^1\rho^2\rho^3$	$\rho_4^1\rho^5$	$\rho_3^1\rho_2^3$
1	-1/8	1/56	-1/336	1/56	-1/336	1/1680	1/1680
$\rho_3^1\rho^6$	$\rho_3^1\rho^2\rho^4$	$\rho_3^1\rho_3^2$	$\rho_2^1\rho^3\rho^4$	$\rho_2^1\rho_2^2\rho^3$	$\rho_2^1\rho^2\rho^5$	$\rho_2^1\rho^7$	$\rho^1\rho^2\rho_2^3$
-1/6720	1/1680	-1/336	-1/6720	1/1680	-1/6720	1/20160	-1/6720
$\rho^1\rho^3\rho^5$	$\rho^1\rho^8$	$\rho^1\rho^2\rho^6$	$\rho^1\rho_2^2\rho^4$	$\rho^1\rho_2^4$	$\rho^1\rho_4^2$	ρ_3^3	$\rho^3\rho^6$
1/20160	-1/40320	1/20160	-1/6720	1/20160	1/1680	1/20160	-1/40320
$\rho^2\rho^3\rho^4$	$\rho_3^2\rho^3$	$\rho^4\rho^5$	$\rho_2^2\rho^5$	$\rho^2\rho^7$	ρ^9		
1/20160	-1/6720	-1/40320	1/20160	-1/40320	1/40320		

with

$$
\begin{aligned}
D_i &= C_i && (23)\\
D_{ij} &= C_iC_j - C_{ij} && (24)\\
D_{ijk} &= C_iC_jC_k + [C_{ijk} - C_iC_{jk} - C_jC_{ik} - C_kC_{ij}]/2 && (25)
\end{aligned}
$$

The symmetries of the $D_{i_1i_2\ldots i_n}$ and $C_{i_1i_2\ldots i_n}$ coefficients are the same. The cumulant ρ_c^{n-1} can be obtained from ρ_c^n by integrating over $\boldsymbol{r}_n$:

$$\rho_c^{n-1}(\boldsymbol{r}_1,\ldots,\boldsymbol{r}_{n-1}) = \int \rho_c^n(\boldsymbol{r}_1,\boldsymbol{r}_2,\ldots,\boldsymbol{r}_n)d\boldsymbol{r}_n. \quad (26)$$

Integrating all the electrons:

$$\int \rho_c^n(\boldsymbol{r}_1,\ldots,\boldsymbol{r}_n)d\boldsymbol{r}_1\ldots d\boldsymbol{r}_n = N. \quad (27)$$

This equation can be inmediately derived by applying n times Eq. 26. In effect, after applying $n-1$ times Eq. 26 we have

$$\rho_c^1(\boldsymbol{r}_1) = \rho(\boldsymbol{r}_1) = \int \rho_c^2(\boldsymbol{r}_1,\boldsymbol{r}_2)d\boldsymbol{r}_2, \quad (28)$$

and integrating one last time

$$\int \rho(\boldsymbol{r}_1)d\boldsymbol{r}_1 = N. \quad (29)$$

3 Bond indices and natural adaptive orbitals

The extensivity of CDs allows for any ρ_c^n to be obtained from the mCDs with $m > n$ (see Eq. 26). We can use this property to obtain a one-basin partition of $\rho(\mathbf{r}) = \rho_c^1(\mathbf{r})$ from the exchange correlation (xc) cumulant, $\rho_{xc}(\mathbf{r}_1,\mathbf{r}_2) = \rho_c^2(\mathbf{r}_1,\mathbf{r}_2)$

$$\rho_c^1(\mathbf{r}) = \sum_a^m \int_{\Omega_a} d\mathbf{r}_2\rho_c^2(\mathbf{r},\mathbf{r}_2) = \sum_a^m \rho_1^a(\mathbf{r}) \equiv \sum_a^m \rho^a(\mathbf{r}), \quad (30)$$

where $\cup_{i=a}^m \Omega_a = \mathcal{R}^3$. The $\rho^a(\mathbf{r})$'s are exactly equivalent to the charge weighted domain averaged Fermi Holes (DAFH) [4, 5] that we have explored in the past [6, 7]. Similarly, $\rho_c^n(\mathbf{r})$ allows for a $(n-1)$-basin partition of $\rho_c^1(\mathbf{r})$:

$$
\begin{aligned}
\rho_c^1(\mathbf{r}) &= \sum_{ab}^m \rho^{ab}(\mathbf{r}) = \sum_{ab}^m \int_{\Omega_a} d\mathbf{r}_2 \int_{\Omega_b} d\mathbf{r}_3\, \rho_c^3(\mathbf{r},\mathbf{r}_2,\mathbf{r}_3), && (31)\\
\rho_c^1(\mathbf{r}) &= \sum_{abc}^m \rho^{abc}(\mathbf{r}) = \sum_{abc}^m \int_{\Omega_a} d\mathbf{r}_2 \int_{\Omega_b} d\mathbf{r}_3 \int_{\Omega_c} d\mathbf{r}_4\, \rho_c^4(\mathbf{r},\mathbf{r}_2,\mathbf{r}_3,\mathbf{r}_4), && (32)\\
&\ldots\\
\rho_c^1(\mathbf{r}) &= \sum_{ab\ldots n-1}^m \rho^{ab\ldots n-1}(\mathbf{r}) = \sum_{ab\ldots n-1}^m \int_{\Omega_a} d\mathbf{r}_2 \int_{\Omega_b} d\mathbf{r}_3 \ldots \int_{\Omega_{n-1}} d\mathbf{r}_n\, \rho_c^4(\mathbf{r},\mathbf{r}_2,\ldots,\mathbf{r}_n). && (33)
\end{aligned}
$$

This partition of $\rho_c^1(\mathbf{r})$ into basins, pairs of basins, etc, can be extended to higher CDs:

$$\rho_c^2(\mathbf{r}_1,\mathbf{r}_2) = \sum_a^m \int_{\Omega_a} d\mathbf{r}_3 \rho_c^3(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3) \quad (34)$$

$$\rho_c^2(\mathbf{r}_1,\mathbf{r}_2) = \sum_{ab}^m \int_{\Omega_a} d\mathbf{r}_3 \int_{\Omega_b} d\mathbf{r}_4 \rho_c^4(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3,\mathbf{r}_4), \quad (35)$$

$$\cdots$$

$$\rho_c^2(\mathbf{r}_1,\mathbf{r}_2) = \sum_{ab\ldots n-2}^m \int_{\Omega_a} d\mathbf{r}_3 \int_{\Omega_b} d\mathbf{r}_4 \ldots \int_{\Omega_{n-2}} d\mathbf{r}_n \rho_c^n(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_n). \quad (36)$$

If instead of integrating all but electron 1 in Eqs. 30-32 to obtain a generalized n-basin density, all the electrons are integrated, the result is a scalar depending only on the definition of the Ω_i basins:

$$\langle N_a\rangle = \int_{\Omega_a} d\mathbf{r}_1\ \rho_c^1(\mathbf{r}_1), \quad (37)$$

$$\langle N_{ab}\rangle = \int_{\Omega_a} d\mathbf{r}_1 \int_{\Omega_b} d\mathbf{r}_2\ \rho_c^2(\mathbf{r}_1,\mathbf{r}_2), \quad (38)$$

$$\langle N_{abc}\rangle = \int_{\Omega_a} d\mathbf{r}_1 \int_{\Omega_b} d\mathbf{r}_2 \int_{\Omega_c} d\mathbf{r}_3\ \rho_c^3(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3), \quad (39)$$

$$\cdots$$

$$\langle N_{ab\ldots n}\rangle = \int_{\Omega_a} d\boldsymbol{r}_1 \int_{\Omega_b} d\boldsymbol{r}_2 \ldots \int_{\Omega_n} d\boldsymbol{r}_n\ \rho_c^n(\boldsymbol{r}_1,\ldots,\boldsymbol{r}_n). \quad (40)$$

Since $\rho_c^1(\mathbf{r}) = \rho(\mathbf{r})$ and $\rho_{xc}(\mathbf{r}_1,\mathbf{r}_2) = \rho_c^2(\mathbf{r}_1,\mathbf{r}_2)$, then $\langle N_a\rangle$ and $2\langle N_{ab}\rangle$ ($a \neq b$) are the average electronic population of basin Ω_a and the delocalization index (DI) between Ω_a and Ω_b, respectively. In general, $n!\langle N_{abcd\ldots}\rangle$ can be identified with a n-center bonding or delocalization index (DI). It is very easy to show by using Eq. 26 that each generalized density $\rho^1_{abc\ldots}(\mathbf{r})$ is normalized to the n-center DI of the same order, i.e.

$$\int \rho^a(\mathbf{r})d\mathbf{r} = \langle N_a\rangle \quad (41)$$

$$\int \rho^{ab}(\mathbf{r})d\mathbf{r} = \langle N_{ab}\rangle \quad (42)$$

$$\int \rho^{abc}(\mathbf{r})d\mathbf{r} = \langle N_{abc}\rangle \quad (43)$$

$$\cdots$$

$$\int \rho^{ab\ldots n}(\mathbf{r})d\mathbf{r} = \langle N_{ab\ldots n}\rangle. \quad (44)$$

Each n-center DI can be recovered from the $(n+1)$-center DIs, $N = \sum_a N_a$, $\langle N_a\rangle = \sum_b \langle N_{ab}\rangle$, $\langle N_{ab}\rangle = \sum_c \langle N_{abc}\rangle$, ..., and the total number of electron, N, can be partitioned into basins, pairs of basins, etc, $N = \sum_a \langle N_a\rangle = \sum_{ab}\langle N_{ab}\rangle = \sum_{abc}\langle N_{abc}\rangle \ldots$.

The n-center generalized densities $\rho^{abc\cdots}(\mathbf{r})$ admit the unified expression

$$\rho^{abc\cdots}(\mathbf{r}) = \boldsymbol{\phi}(\mathbf{r})\mathbf{D}^{abc\cdots}\boldsymbol{\phi}(\mathbf{r})^\dagger, \quad (45)$$

where the row $\boldsymbol{\phi} = (\phi_1,\phi_2,\ldots,\phi_M)$ represents the set of all the MOs of the system and $\mathbf{D}^{abc\cdots}$ is a symmetric matrix. The diagonalization of $\mathbf{D}^a$ (corresponding to taking $n = 1$)

leads to the DAFH eigenvectors (ψ_i^a) and eigenvalues (n_i^a), yielding $\rho^a = \sum n_i^a (\psi_i^a)^2$. This diagonalization has been used many times by Robert Ponec and other authors to analyze chemical bonding issues in relatively large sets of molecules. The ψ_i^a's are called *domain natural orbitals* (DNO) and may be either localized or delocalized, with only the latter contributing significantly to bonding [6]. Similar diagonalizations of further order CDs may be even more important. The two-center partition of ρ coming from ρ_c^3 (Eq. 31) will give rise, after diagonalizing $\mathbf{D}^{ab}$, to orbitals ψ_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 ψ_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* (NAdOs) [8]. In all the cases, the n-center DI is given as the sum of all eigenvalues of these NAdOs, $\langle N_{abc\ldots} \rangle = \sum_i n_i^{abc\ldots}$. As the diagonalization leaves invariant the trace of a matrix we also have $\langle N_{abc\ldots} \rangle = \mathrm{tr}\, \mathbf{D}^{abc\ldots}$. A deeper insight on the meaning of the NAdOs is given in Reference [8].

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