

# Topological population analysis from higher order densities. I. Hartree–Fock level

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In this work we present the formulation of a topological population analysis derived from reduced density matrices of arbitrary order. We describe the construction of a mathematical framework which is suitable for handling any number of physical atomic regions. The procedure provides appropriate tools for enabling the detection and direct localization of multicenter bondings in molecules.

**KEY WORDS:** population analysis, multicenter bonds

## 1. Introduction

The formalism of population analysis has played an important role in the description and visualization of molecular structures and chemical bondings. The complexity which usually features the wavefunction of an  $N$ -electron system is in part overcome by the use of this procedure which extracts from the cumbersome wavefunction simple quantities of chemical interest. Concepts such as bond order, valence, charge density etc., which are so popular in chemical language, are directly obtained from this treatment. Since the early studies of McWeeny and Mulliken [1,2], the idea of population analysis has been extended and generalized by various authors [3–14] providing information not only about classical two-center and two-electron (2c–2e) bonds [15,16] but also about the eventual presence of multicenter bondings in which the electrons are shared among more than two centers [17,20].

Despite the undeniable success of generalized population analyses for describing and rationalizing the structure of various nontrivial molecular systems (metal clusters, hypervalent molecules [21], electron deficient compounds [22]), it is true, however, that all these procedures are not free from inherent limitations and restrictions [23–25]. Thus,

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e.g., these procedures can be applied only to wavefunctions obtained by ordinary LCAO expansions in which the basis functions are centered in individual atoms. In addition to this, another conceptual limitation of this approach concerns the arbitrary 1 : 1 partitioning of the electronic charge between different basis functions, which can lead, especially in the case of polar systems, to systematic bias in the values of bond indices and populations. Most of these shortcomings can be avoided by performing a partitioning of the electronic charge in the physical space. Such a partitioning can, for example, be carried out within the Atoms in Molecules (AIM) theory, in which an atom is regarded as a region of space bounded by a surface of zero flux in the gradient vector field of the electron density [26–28]. Within this theory a partition of the real space is carried out according to these atomic domains. In studies reported by several independent groups [29,30], a generalization of population analysis within AIM theory was performed and it was shown that this approach allows one to characterize the extent of electron sharing between two atomic regions  $A$  and  $B$  by the so-called delocalization index  $\delta(A, B)$ . However, these quantities can straightforwardly be applied only to the elucidation of the structures of molecules well described by Lewis model of localized (2c–2e) bond, but there are other molecules whose bonding patterns are much more complex. Our aim in this paper is to go beyond the classically bonded systems so that more complex bonding patterns can be considered. We report appropriate mathematical tools to describe bondings involving a number of centers higher than two (multicenter bondings), within a topological population analysis.

The paper is organized as follows. In the next section the basic concepts of population analysis within the atomic region scheme are formulated in the second quantized formalism. Section 3 carries out a generalization of those concepts constructing the appropriate tools for describing three- and higher center bondings, which is the main aim of this paper. Finally, in the last section we report the values of bond indices obtained with these tools for some selected molecules at a Hartree–Fock level which prove the reliability of the described approach.

## 2. Basic bonding concepts within second quantization formalism

Let us consider the well-known annihilation,  $\psi(\lambda)$ , and creation,  $\psi^\dagger(\lambda)$ , field operators [31]

$$\begin{aligned}\psi(\lambda) &= \sum_i \phi_i(\lambda)c_i, \\ \psi^\dagger(\lambda) &= \sum_i \phi_i^*(\lambda)c_i^\dagger,\end{aligned}\tag{1}$$

where  $c_i$  and  $c_i^\dagger$  are the usual annihilation and creation fermion operators [31,32],  $\{\phi_i(\lambda)\}$  is a set of orthogonal spin-orbitals and  $\lambda$  stands for the spatial  $r$  and spin  $\sigma$  coordinates of a fermion.

Closing both sides of the product  $\psi^\dagger(\lambda)\psi(\lambda)$  by an  $N$ -electron state  $|\mathcal{L}\rangle$  we obtain the first-order reduced density function  $\rho_1(\lambda) = \langle \mathcal{L} | \psi^\dagger(\lambda)\psi(\lambda) | \mathcal{L} \rangle$  and integrating over the whole space  $\Omega$  we have

$$\int_{\Omega} \langle \mathcal{L} | \psi^\dagger(\lambda)\psi(\lambda) | \mathcal{L} \rangle d\lambda = \sum_{i,j} \langle \mathcal{L} | c_i^\dagger c_j | \mathcal{L} \rangle \int_{\Omega} \phi_i^*(\lambda)\phi_j(\lambda) d\lambda = N. \quad (2)$$

We can now consider the partitioning of the whole space  $\Omega$  according to the Bader's atomic regions  $\Omega_A$  which, as is well known, are defined by surfaces having zero flux in the gradient vector field of the electron density [26]. Taking into account that this partitioning holds  $\Omega = \bigcup_A \Omega_A$  and  $\Omega_A \cap \Omega_B = \emptyset$  ( $\forall A, B, A \neq B$ ), equation (2) can be written

$$N = \sum_A \sum_{i,j} {}^1D_j^i \langle \phi_i(\lambda) | \phi_j(\lambda) \rangle_{\Omega_A} = \sum_A N_A, \quad (3)$$

where  ${}^1D_j^i = \langle \mathcal{L} | c_i^\dagger c_j | \mathcal{L} \rangle$  are the matrix elements of the first-order reduced density matrix (1-RDM) and  $\langle \phi_i(\lambda) | \phi_j(\lambda) \rangle_{\Omega_A}$  are the overlap integrals calculated over those regions.  $N_A$  is the corresponding charge of the atomic region  $A$ .

The product of two pairs of operators  $\psi^\dagger(\lambda_1)\psi^\dagger(\lambda_2)\psi(\lambda_2)\psi(\lambda_1)$  leads to the second-order reduced density function  $\rho_2(\lambda_1, \lambda_2) = (1/2)\langle \mathcal{L} | \psi^\dagger(\lambda_1)\psi^\dagger(\lambda_2)\psi(\lambda_2)\psi(\lambda_1) | \mathcal{L} \rangle$  and following an identical procedure it holds

$$\begin{aligned} & \int_{\Omega} \langle \mathcal{L} | \psi^\dagger(\lambda_1)\psi^\dagger(\lambda_2)\psi(\lambda_2)\psi(\lambda_1) | \mathcal{L} \rangle d\lambda_1 d\lambda_2 \\ &= \sum_{i,j,k,l} \langle \mathcal{L} | c_i^\dagger c_k^\dagger c_l c_j | \mathcal{L} \rangle \int_{\Omega} \phi_i^*(\lambda_1)\phi_k^*(\lambda_2)\phi_l(\lambda_2)\phi_j(\lambda_1) d\lambda_1 d\lambda_2 = N(N-1), \quad (4) \end{aligned}$$

which in terms of the atomic regions can be written

$$\binom{N}{2} = \sum_{i,j,k,l} {}^2D_{jl}^{ik} \sum_{A,B} \langle \phi_i(\lambda_1) | \phi_j(\lambda_1) \rangle_{\Omega_A} \langle \phi_k(\lambda_2) | \phi_l(\lambda_2) \rangle_{\Omega_B}, \quad (5)$$

where  ${}^2D_{jl}^{ik} = (1/2)\langle \mathcal{L} | c_i^\dagger c_k^\dagger c_l c_j | \mathcal{L} \rangle$  are the matrix elements of the second-order reduced density matrix (2-RDM).

The next step is to extract from equation (5) the structural information related to the chemical bondings. Let us consider the Hartree–Fock level where the  $N$ -electron state  $|\mathcal{L}\rangle$  is a Slater determinant, the matrix elements of the 1-RDM and 2-RDM are related by the expression [33]

$${}^2D_{jl}^{ik} = \frac{1}{2}({}^1D_j^i {}^1D_l^k - {}^1D_l^i {}^1D_j^k) \quad (6)$$

and the matrix elements  ${}^1D_j^i$  (HF) =  $n_i \delta_{ij}$  ( $n_i$  is the occupation number of the Hartree–Fock spin-orbitals in the HF determinant). In this situation equation (5) provides two independent terms. The first one,  $N^2 = (\sum_A N_A)(\sum_B N_B)$ , comes from the first term in equation (6); it is given by the product of two independent factors and, consequently,

does not provide information about bonding. The second one, coming from the second term (the exchange term) in equation (6), provides the information suitable for bonding description and can be written as

$$N = \sum_{A,B} \sum_i^{\text{occ}} \sum_j^{\text{occ}} \langle \varphi_i(\lambda_1) | \varphi_j(\lambda_1) \rangle_{\Omega_A} \langle \varphi_j(\lambda_2) | \varphi_i(\lambda_2) \rangle_{\Omega_B}, \quad (7)$$

in which the set  $\{\varphi_i(\lambda)\}$  means the Hartree–Fock spin-orbitals. Alternatively, this equation can be written

$$N = \sum_A \Omega_A^{(2)} + \sum_{A < B} \Omega_{AB}^{(2)}, \quad (8)$$

where  $\Omega_A^{(2)} = \sum_i^{\text{occ}} \sum_j^{\text{occ}} \langle \varphi_i(\lambda_1) | \varphi_j(\lambda_1) \rangle_{\Omega_A} \langle \varphi_j(\lambda_2) | \varphi_i(\lambda_2) \rangle_{\Omega_A}$  and  $\Omega_{AB}^{(2)} = 2 \sum_i^{\text{occ}} \sum_j^{\text{occ}} \langle \varphi_i(\lambda_1) | \varphi_j(\lambda_1) \rangle_{\Omega_A} \langle \varphi_j(\lambda_2) | \varphi_i(\lambda_2) \rangle_{\Omega_B}$ .

Equations (7) and (8) represent a partitioning of the  $N$  electrons of the system according to AIM theory, at the Hartree–Fock level. The contribution  $\Omega_A^{(2)}$  means the electronic localization into the region  $A$ , while the  $\Omega_{AB}^{(2)}$  provides a quantitative measure of the sharing of electrons between the atoms  $A$  and  $B$ . Hence, these  $\Omega_{AB}^{(2)}$  quantities, which are equivalent to the previously reported delocalization indices [30], describe conventional two-center bondings and can be related with the bond order [29,30,34]. Similar equations also have been reported using fluctuation criteria [29,34]. However, we will go beyond extending this treatment to the study of electronic delocalization within three or more atomic regions, which is performed in the next section.

### 3. The extension to multicenter bondings

According to the above outlined procedure we can now start with the product of three creation and annihilation field operators  $\psi^\dagger(\lambda_1)\psi^\dagger(\lambda_2)\psi^\dagger(\lambda_3)\psi(\lambda_3)\psi(\lambda_2)\psi(\lambda_1)$  which produces the third-order reduced density function  $\rho_3(\lambda_1, \lambda_2, \lambda_3)$ . In this way we obtain

$$\begin{aligned} & \int_{\Omega} \langle \mathcal{L} | \psi^\dagger(\lambda_1)\psi^\dagger(\lambda_2)\psi^\dagger(\lambda_3)\psi(\lambda_3)\psi(\lambda_2)\psi(\lambda_1) | \mathcal{L} \rangle d\lambda_1 d\lambda_2 d\lambda_3 \\ &= \sum_{i,j,k,l,m,n} \langle \mathcal{L} | c_i^\dagger c_k^\dagger c_m^\dagger c_n c_l c_j | \mathcal{L} \rangle \int_{\Omega} \phi_i^*(\lambda_1)\phi_k^*(\lambda_2)\phi_m^*(\lambda_3)\phi_n(\lambda_3)\phi_l(\lambda_2)\phi_j(\lambda_1) d\lambda_1 d\lambda_2 d\lambda_3 \\ &= N(N-1)(N-2), \end{aligned} \quad (9)$$

or

$$\sum_{i,j,k,l,m,n} {}^3D_{jln}^{ikm} \sum_{A,B,C} \langle \phi_i(\lambda_1) | \phi_j(\lambda_1) \rangle_{\Omega_A} \langle \phi_k(\lambda_2) | \phi_l(\lambda_2) \rangle_{\Omega_B} \langle \phi_m(\lambda_3) | \phi_n(\lambda_3) \rangle_{\Omega_C} = \binom{N}{3}, \quad (10)$$

where  ${}^3D_{jln}^{ikm} = (1/6)\langle \mathcal{L} | c_i^\dagger c_k^\dagger c_m^\dagger c_n c_l c_j | \mathcal{L} \rangle$  are the matrix elements of the third-order reduced density matrix (3-RDM).

Equation (10) contains the information about any possible bondings involving two and three centers as well as about the atomic charge in an atom. At the Hartree–Fock level the 3-RDM elements are expressed as

$${}^3D_{jln}^{ikm} = \frac{1}{6} ({}^1D_j^i {}^1D_l^k {}^1D_n^m - {}^1D_l^i {}^1D_j^k {}^1D_n^m - {}^1D_n^i {}^1D_l^k {}^1D_j^m - {}^1D_j^i {}^1D_n^k {}^1D_l^m + {}^1D_n^i {}^1D_j^k {}^1D_l^m + {}^1D_l^i {}^1D_n^k {}^1D_j^m), \quad (11)$$

which is the counterpart version of formula (6) at the third order.

Taking into account equation (11) and  ${}^1D_j^i(\text{HF}) = n_i \delta_{ij}$ , formula (10) can be straightforwardly transformed into

$$N = \sum_{A,B,C} \sum_i^{\text{occ}} \sum_j^{\text{occ}} \sum_k^{\text{occ}} \langle \varphi_i(\lambda_1) | \varphi_j(\lambda_1) \rangle_{\Omega_A} \langle \varphi_j(\lambda_2) | \varphi_k(\lambda_2) \rangle_{\Omega_B} \langle \varphi_k(\lambda_3) | \varphi_i(\lambda_3) \rangle_{\Omega_C}. \quad (12)$$

Equation (12) allows us to perform the partitioning of  $N$  electrons into mono-, bi- and triatomic region contributions in the sense of Bader’s atomic regions, so that

$$N = \sum_A \Omega_A^{(3)} + \sum_{A<B} \Omega_{AB}^{(3)} + \sum_{A<B<C} \Omega_{ABC}^{(3)}. \quad (13)$$

Hence, the above proposed integration of the third-order reduced density function is the appropriate procedure for relating three atomic regions. In equation (13)  $\Omega_{ABC}^{(3)} = 4 \sum_i^{\text{occ}} \sum_j^{\text{occ}} \sum_k^{\text{occ}} \langle \varphi_i(\lambda_1) | \varphi_j(\lambda_1) \rangle_{\Omega_A} \langle \varphi_j(\lambda_2) | \varphi_k(\lambda_2) \rangle_{\Omega_B} \langle \varphi_k(\lambda_3) | \varphi_i(\lambda_3) \rangle_{\Omega_C}$  can be considered the appropriate tools for describing three-center bondings within the topological partitioning. They are the counterparts of the three-center indices described in the Mulliken-like partition schemes [14,19,35].

The generalization of this procedure is straightforward. The product of  $p$  pairs of field operators produces the  $p$ -order reduced density function  $\rho_p(\lambda_1, \dots, \lambda_p)$ . Its integration makes it possible to relate  $p$  atomic regions and enables one to introduce indices for describing  $p$ -center bondings which have been detected by some authors [19]. The counterpart of formula (10) at  $p$ -order is

$$\sum_{i_1, \dots, i_p} \sum_{j_1, \dots, j_p} {}^pD_{j_1, \dots, j_p}^{i_1, \dots, i_p} \sum_{A_1, \dots, A_p} \langle \phi_{i_1}(\lambda_1) | \phi_{j_1}(\lambda_1) \rangle_{\Omega_{A_1}} \cdots \langle \phi_{i_p}(\lambda_p) | \phi_{j_p}(\lambda_p) \rangle_{\Omega_{A_p}} = \binom{N}{p}, \quad (14)$$

which at the Hartree–Fock level leads to

$$N = \sum_{A_1, \dots, A_p} \sum_{i_1, \dots, i_p}^{\text{occ}} \langle \varphi_{i_1}(\lambda_1) | \varphi_{i_2}(\lambda_1) \rangle_{\Omega_{A_1}} \cdots \langle \varphi_{i_p}(\lambda_p) | \varphi_{i_1}(\lambda_p) \rangle_{\Omega_{A_p}}, \quad (15)$$

from which the corresponding  $p$ -center bond indices  $\Omega_{A_1, \dots, A_p}^{(p)}$  can be directly derived.

#### 4. Results and discussion

In this section we report calculations performed in molecules in which the presence of three-center bondings is generally accepted as well as in molecules possessing only classical ( $2c-2e$ ) bondings. The purpose of these calculations is to demonstrate the ability of the  $\Omega_{ABC}^{(3)}$  indices for detecting and localizing the presence of three-center bondings within the AIM theory. In principle, this population analysis can be carried out at any level of the theory. However, correlated 3-RDM are not available in the usual quantum chemical codes. This fact has led us to work at a first step at the Hartree–Fock level, which is the only feasible approach in practice at present. In a subsequent study, correlated density matrices will be used for the calculation of three-center bond indices and the results will be published elsewhere [36].

The geometries of the studied molecules were optimized within the HF approach in Dunning Huzinaga SDZVP basis set [37] except in the case of the  $H_3^+$  system in which the partitioning was not achieved in this particular basis. The calculations were performed using the Gaussian 94 programs [38] which generated the integrals involved in equations (7) and (12). The above methodology was implemented in our laboratories using our own codes which are available upon request. The results are summarized in tables 1 and 2.

The results in table 1 refer to molecules in which the presence of three-center bondings is generally accepted and they have been previously studied in a Mulliken-like population analysis scheme [13]. In this table only the non-negligible  $\Omega_{ABC}^{(3)}$  values have been included. Among all possible three-center contributions resulting from the partitioning (13) for these systems, the only significant values are localized in the regions where multicenter bondings are expected. Another interesting aspect is related to the sign of the reported indices. In Mulliken-like population analyses, according to analytical models [39], the positive values of their corresponding three-center bond indices have been interpreted as characteristic of ( $3c-2e$ ) bonds and the negative ones as corresponding to ( $3c-4e$ ) bonds [40]. In this sense, the first conclusion that can be drawn is that there is no qualitative difference in the prediction of the nature of the three-center bondings in the Mulliken-like [13] and the present population analysis approaches.

Table 2 reports the results of partitionings (8) and (13) for several molecules in which no three-center bondings have been described. In these systems, the values of

Table 1  
Calculated values of AIM three-center indices in molecules possessing three-center bonds.

System	Fragment	$\Omega_{ABC}^{(3)}$	Type	Basis
$H_3^+$	HHH	0.444	( $3c-2e$ )	6-31G
allylcation	CCC	0.409	( $3c-2e$ )	D95( $p, d$ )
allylanion	CCC	-0.111	( $3c-4e$ )	D95( $p, d$ )
$N_2O$	NNO	-0.208	( $3c-4e$ )	D95( $p, d$ )
$N_3^-$	NNN	-0.363	( $3c-4e$ )	D95( $p, d$ )

Table 2  
Calculated values of AIM bond indices in molecules possessing classical (2c–2e) bonds in D95(*p, d*) basis.

System	Fragment	$\Omega_{ABC}^{(3)}, \Omega_{AB}^{(3)}$	$\Omega_{AB}^{(2)}$
H <sub>2</sub> O	O–H	0.936	0.628
	H–H	0.028	0.007
	HOH	0.016	–
NH <sub>3</sub>	N–H	1.252	0.853
	N–H	0.008	0.015
	NHN	0.028	–
	HHH	0.000	–
CH <sub>4</sub>	C–H	1.388	0.981
	H–H	0.034	0.037
	HCH	0.055	–
	HHH	0.000	–

all possible multicenter indices are very small and the only nonvanishing values are observed for two-center indices  $\Omega_{AB}^{(2)}$  and  $\Omega_{AB}^{(3)}$  which correspond to classically bonded atoms. Moreover, both two-center indices fulfill the proportionality relation

$$\Omega_{AB}^{(3)} \approx \frac{3}{2} \Omega_{AB}^{(2)}, \quad (16)$$

which has also been observed within the corresponding indices defined in Mulliken-like schemes when no multicenter bondings are to be found [13].

In conclusion, this paper has presented a simple and systematic procedure to derive classical and multicenter bond indices within a topological partitioning technique. The preliminary results, calculated at the HF level, show that this treatment for localizing three-center bondings in molecules is efficient. For the studied systems no qualitative differences are to be found when our results are compared with those from Mulliken-like treatments. However, the reported partitioning is free of the inherent basis dependency of those treatments and opens up a new way for a straightforward investigation of molecules in which the presence of multicenter (three and higher) bonds is to be expected.

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