Topological population analysis from higher order densities II. The correlated case

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This work describes the mathematical aspects of the generalization of our earlier study of topological population analysis [J. Math. Chem. 28 (2000) 83] beyond the scope of HF approximation. The paper shows the relation of this general approach to earlier, heuristically introduced, procedures of population analysis, exemplified by the Mulliken population analysis and its subsequent extensions which are straightforwardly derived from this framework as particular cases.

KEY WORDS: population analysis, bond orders, multicenter bond indices

1. Introduction

According to quantum mechanics, the most complete information about the properties of microscopic systems like atoms, molecules and clusters is contained in the N-electron wavefunction resulting from the solution of the corresponding Schrödinger equation. Although there is nowdays no problem to generate reliable wavefunctions even for sizeable systems, the complexity of these wavefunctions makes it more difficult to retrieve from them anything reminiscent of intuitive concepts of bonds, bond orders, valences etc., in terms of which chemists are used to think about molecules and their structures. The reason is that the vast amount of information contained in the wavefunction is, for chemical purposes, superflous. One important task of the chemical theory is therefore to design new auxilary methods and procedures allowing to eliminate this superflous information from the wavefuntions, so that the classical concepts could again be recovered from them. One of the most general and fruitful of such procedures is based on the transformation of the wavefunctions into simpler reduced density matrices and, during years, a wealth of studies dealing with the application of these matrices to structural elucidation was carried out.

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Among the well-known examples of such studies is the Mulliken population analysis [1] but, more recently, other related techniques were proposed in which the idea of the partitioning of the Hilbert space spanned by the basis functions between the atomic nuclei was systematically explored [2–10]. In addition to these earlier approaches, an alternative population analysis scheme was also formulated [11–17] within the AIM theory [18–21], in terms of which the real space is partitioned into atomic domains bounded by a surface of zero flux in the gradient vector field of the electron density. Into the framework of these efforts can also be included our recent study [17] in which the topological AIM generalized population analysis was formulated. In this study, however, the formalism was introduced only at the level of simple Hartree–Fock approximation. Nevertheless, the distribution of electrons in molecules is undoubtedly influenced by the electron correlation and, consequently, the values of bond indices and populations have also to be correspondingly affected. Our aim in this study is to address this question and to generalize the previously introduced formalism to correlated post-Hartree–Fock level of theory. In addition to this primary aim, another important achievement of this study is to demostrate the relation of the above most general formulation of the population analysis to the earlier, often heuristically introduced, procedures.

The paper is organized as follows: section 2 develops the mathematical treatment of the second-order correlation function, which provides the rigorous definition of correlated bond order or two-center bond index. This definition is based on the idea of an appropriate partitioning of the integrated correlation function, so that the corresponding bond orders are defined as two-center terms arising from such a partitioning. In the 3rd section, a similar treatment is applied to the third-order correlation function, which lead to the post-Hartree–Fock generalization of the concept of three-center bond index as the quantity allowing to detect and to localize the eventual presence of three-center bondings in molecules.

2. The second-order correlation function

In spite of its potencial importance, the generalization of the idea of bond order or two-center bond index beyond the scope of the Hartree–Fock approximation has so far received scarce attention and only a few studies addressing this problem can be found in the literature [11–15,22–24]. Moreover, the common problem to the majority of these studies is that, in addition to using different mathematical languages, they often use different terminology to denote the same quantity so that the close relation or equivalence of the corresponding approaches is not evident. In order to clarify this confusing situation, we are going to propose a general mathematical framework for the formulation of the post-Hartree–Fock population analysis in terms of the second quantized formalism. The fundamental role in this generalization belong to the concept of correlation function.

Let us define the second-order correlation function corresponding to an N-electron state $|\mathcal{L}\rangle$ as

$$^2\gamma = \frac{1}{2}\big[\langle\mathcal{L}|\psi^\dagger(\lambda)\psi(\lambda)|\mathcal{L}\rangle^2 - \langle\mathcal{L}|\psi^\dagger(\lambda_1)\psi^\dagger(\lambda_2)\psi(\lambda_2)\psi(\lambda_1)|\mathcal{L}\rangle\big] \tag{1}$$

where

$$\psi(\lambda) = \sum_i \phi_i(\lambda)\, c_i, \qquad \psi^\dagger(\lambda) = \sum_i \phi_i^*(\lambda)\, c_i^\dagger \qquad (2)$$

are the annihilation and creation field operators [25], c_i and $c_i^\dagger$ are the annihilation and creation fermion operators [25,26], $\{\phi_i(\lambda)\}$ is a set of orthogonal spin-orbitals and λ stands for the space r and spin σ coordinates of a fermion.

The integration of equation (1) over the whole space Ω leads to

$$\int_\Omega {}^2\gamma\, d\lambda_1 d\lambda_2 = \sum_{i,j,k,l} \left(\frac{1}{2}{}^1D_j^i\, {}^1D_l^k - {}^2D_{jl}^{ik}\right) \int_\Omega \phi_i^*(\lambda_1)\phi_k^*(\lambda_2)\phi_l(\lambda_2)\phi_j(\lambda_1)\, d\lambda_1\, d\lambda_2 \qquad (3)$$

where ${}^1D_j^i = \langle \mathcal{L}|c_i^\dagger c_j|\mathcal{L}\rangle$ are matrix elements of the first-order reduced density matrix and ${}^2D_{jl}^{ik} = \frac{1}{2}\langle \mathcal{L}|c_i^\dagger c_k^\dagger c_l c_j|\mathcal{L}\rangle$ are matrix elements of the second-order reduced density matrix. (Note that the trace of the matrix ${}^2D$ is $\binom{N}{2}$.) At the Hartree–Fock level, where $|\mathcal{L}\rangle$ is a Slater determinant, ${}^2D_{jl}^{ik} = \frac{1}{2}({}^1D_j^i\, {}^1D_l^k - {}^1D_l^i\, {}^1D_j^k)$ and, consequently, the function ${}^2\gamma$ is described only by the *exchange terms* ${}^1D_l^i\, {}^1D_j^k$. In equation (3), the integration over the whole space Ω can be performed in two different ways, as is described in the two following subsections.

2.1. Topological treatment

Within this approach let us consider, in equation (3), the partitioning of the whole space Ω into the Bader's atomic regions Ω_A [18]. Taking into account that it holds $\Omega = \bigcup_A \Omega_A$ and $\Omega_A \cap \Omega_B = \emptyset$ ($\forall A, B; A \neq B$), equation (3) can be written in the form

$$\sum_{\Omega_A}\sum_{\Omega_B}\sum_{i,j,k,l} \left(\frac{1}{2}{}^1D_j^i\, {}^1D_l^k - {}^2D_{jl}^{ik}\right) \int_{\Omega_A} \phi_i^*(\lambda_1)\phi_j(\lambda_1)\, d\lambda_1 \int_{\Omega_B} \phi_k^*(\lambda_2)\phi_l(\lambda_2)\, d\lambda_2 = \frac{N}{2} \qquad (4)$$

from which the following partitioning can be performed

$$N = \sum_{\Omega_A} \Delta_{\Omega_A}^{(2)} + \sum_{\Omega_A < \Omega_B} \Delta_{\Omega_A \Omega_B}^{(2)} \qquad (5)$$

where

$$\Delta_{\Omega_A}^{(2)} = \sum_{i,j,k,l} \left({}^1D_j^i\, {}^1D_l^k - 2{}^2D_{jl}^{ik}\right) S_{ij}(\Omega_A) S_{kl}(\Omega_A), \qquad (6)$$

$$\Delta_{\Omega_A \Omega_B}^{(2)} = 2\sum_{i,j,k,l} \left({}^1D_j^i\, {}^1D_l^k - 2{}^2D_{jl}^{ik}\right) S_{ij}(\Omega_A)\, S_{kl}(\Omega_B) \quad (\Omega_A < \Omega_B) \qquad (7)$$

and $S_{ij}(\Omega_A)$, $S_{ij}(\Omega_B)$ etc. are the matrix elements of the overlap matrices calculated over the regions Ω_A, Ω_B etc.

Consistent with the philosophy of the population analysis, the correlated bond order is given by the biatomic term $\Delta^{(2)}_{\Omega_A\Omega_B}$ in equation (5). It is interesting to remark that basically the same quantity was proposed as a measure of the correlated bond order in the study by Ponec and Uhlik [13]. Similarly, $\Delta^{(2)}_{\Omega_A\Omega_B}$ corresponds to the *delocalization index* described by Fradera et al. [14] as the sum $-(F(\Omega_A, \Omega_B) + F(\Omega_B, \Omega_A))$, where

$$F(\Omega_A, \Omega_B) = \sum_{i,j,k,l} \left(2^2 D^{ik}_{jl} - {}^1D^i_j \, {}^1D^k_l\right) S_{ij}(\Omega_A) S_{kl}(\Omega_B). \tag{8}$$

The same quantity was also reported by Angyan et al. [15] who denote it as the fluctuation bond order. All these concepts can straightforwardly be derived from equation (3).

2.2. Mulliken-type treatment

An alternative treatment of equation (3) leads to quantities that are significant in Mulliken population analysis procedures. From the direct integration of this equation we obtain

$$\text{tr}\left({}^2\gamma\right) = \sum_{i,k} \gamma^{ik}_{ik} = \sum_{i,k} \left(\frac{1}{2}{}^1D^i_i \, {}^1D^k_k - {}^2D^{ik}_{ik}\right) = \frac{N}{2} \tag{9}$$

which can be regarded as a partitioning of the N electrons in the molecule according to the diagonal elements γ^{ik}_{ik} of the matrix ${}^2\gamma$. Obviously, if the basis set is non-orthogonal equation (9) must be substituted by $\sum_{i,k}(\frac{1}{2}({}^1PS)^i_i({}^1PS)^k_k - ({}^2PSS)^{ik}_{ik}) = N/2$, where ${}^1P, {}^2P$ and S are the usual charge density, pair density and overlap matrices, respectively.

Equation (9) suggests the partitioning

$$N = \sum_A \Delta^{(2)}_A + \sum_{A<B} \Delta^{(2)}_{AB} \tag{10}$$

where

$$\Delta^{(2)}_A = \sum_i^A \sum_k^A \left({}^1D^i_i \, {}^1D^k_k - 2^2D^{ik}_{ik}\right), \tag{11}$$

$$\Delta^{(2)}_{AB} = 2\sum_i^A \sum_k^B \left({}^1D^i_i \, {}^1D^k_k - 2^2D^{ik}_{ik}\right) \quad (A < B) \tag{12}$$

and A, B, etc. stand for different nuclei of the molecule.

Expression (12) constitutes the definition of *bond order*, $\Delta^{(2)}_{AB}$, between two nuclei A and B at any level of theory and it turns out to be equivalent to the definition of bond order proposed by Giambiagi et al. [27] which has widely been used by Yamasaki and Goddard [28] and Yamasaki et al. [29] in terms of covariance (correlation of fluctuations) of the charge operators $\hat{q}_A$ and $\hat{q}_B$, that is, $\Delta^{(2)}_{AB} = -2\langle(\hat{q}_A - \langle\hat{q}_A\rangle)(\hat{q}_B - \langle\hat{q}_B\rangle)\rangle$. At the Hartree–Fock level, equation (12) leads to $\Delta^{(2)}_{AB} = 2\sum_i^A \sum_k^B {}^1D^i_k \, {}^1D^k_i$, which

corresponds, in the spin-orbital notation, to the bond index originally introduced by Wiberg [2] and subsequently generalized by Giambiagi et al. [30] and Mayer [31] and to the so called effective pair populations [8]. More recently, the terms $({}^1D_i^i \, {}^1D_k^k - 2\,{}^2D_{ik}^{ik})$ have been studied by Karafiloglou [22] in order to discuss the role of Coulomb and Fermi correlations in chemical bondings. Within our derivation all these concepts are easily obtained from the partitioning of the trace of the correlation density matrix ${}^2\gamma$.

3. The third-order correlation function

At the third-order level, the most appropiate definition for the correlation function turns out to be

$$
\begin{aligned}
{}^3\gamma = \frac{1}{6}\big[& 2\langle\mathcal{L}|\psi^\dagger(\lambda)\psi(\lambda)|\mathcal{L}\rangle^3 \\
& - \langle\mathcal{L}|\psi^\dagger(\lambda_1)\psi^\dagger(\lambda_2)\psi(\lambda_2)\psi(\lambda_1)|\mathcal{L}\rangle\langle\mathcal{L}|\psi^\dagger(\lambda_3)\psi(\lambda_3)|\mathcal{L}\rangle \\
& - \langle\mathcal{L}|\psi^\dagger(\lambda_1)\psi^\dagger(\lambda_3)\psi(\lambda_3)\psi(\lambda_1)|\mathcal{L}\rangle\langle\mathcal{L}|\psi^\dagger(\lambda_2)\psi(\lambda_2)|\mathcal{L}\rangle \\
& - \langle\mathcal{L}|\psi^\dagger(\lambda_2)\psi^\dagger(\lambda_3)\psi(\lambda_3)\psi(\lambda_2)|\mathcal{L}\rangle\langle\mathcal{L}|\psi^\dagger(\lambda_1)\psi(\lambda_1)|\mathcal{L}\rangle \\
& + \langle\mathcal{L}|\psi^\dagger(\lambda_1)\psi^\dagger(\lambda_2)\psi^\dagger(\lambda_3)\psi(\lambda_3)\psi(\lambda_2)\psi(\lambda_1)|\mathcal{L}\rangle\big]
\end{aligned}
\tag{13}
$$

which is equivalent to the functional suggested by one of us in [24].

The integration of the function ${}^3\gamma$ over the whole space Ω leads to

$$
\begin{aligned}
\int_\Omega {}^3\gamma \, \mathrm{d}\lambda_1 \, \mathrm{d}\lambda_2 \, \mathrm{d}\lambda_3 \\
= \sum_{i,j,k,l,m,n} \Bigg(& \frac{1}{3}{}^1D_j^i \, {}^1D_l^k \, {}^1D_n^m - \frac{1}{3}{}^1D_j^i \, {}^2D_{ln}^{km} - \frac{1}{3}{}^1D_l^k \, {}^2D_{jn}^{im} - \frac{1}{3}{}^1D_n^m \, {}^2D_{jl}^{ik} + {}^3D_{jln}^{ikm} \Bigg) \\
& \times \int_\Omega \phi_i^*(\lambda_1)\phi_k^*(\lambda_2)\phi_m^*(\lambda_3)\phi_n(\lambda_3)\phi_l(\lambda_2)\phi_j(\lambda_1) \, \mathrm{d}\lambda_1 \, \mathrm{d}\lambda_2 \, \mathrm{d}\lambda_3
\end{aligned}
\tag{14}
$$

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

3.1. Topological treatment

A topological treatment can be obtained when the whole space Ω, in equation (14), is regarded as a disjoint union of Bader atomic regions. In that case, the following partitioning can be performed:

$$
N = \sum_{\Omega_A} \Delta_{\Omega_A}^{(3)} + \sum_{\Omega_A < \Omega_B} \Delta_{\Omega_A \Omega_B}^{(3)} + \sum_{\Omega_A < \Omega_B < \Omega_C} \Delta_{\Omega_A \Omega_B \Omega_C}^{(3)}
\tag{15}
$$

and the three-center bond index can be identified with the triatomic component of the partitioning (15)

$$
\Delta^{(3)}_{\Omega_A \Omega_B \Omega_C} = 6 \sum_{i,j,k,l,m,n} \left({}^1D^i_j \, {}^1D^k_l \, {}^1D^m_n - {}^1D^i_j \, {}^2D^{km}_{ln} - {}^1D^k_l \, {}^2D^{im}_{jn} - {}^1D^m_n \, {}^2D^{ik}_{jl} + 3 \, {}^3D^{ikm}_{ikm} \right)
$$
$$
\times \, S_{ij}(\Omega_A) S_{kl}(\Omega_B) S_{mn}(\Omega_C) \quad (\Omega_A < \Omega_B < \Omega_C). \tag{16}
$$

The three-center bond index can also be formulated in terms of the function $F(\Omega_A, \Omega_B, \Omega_C)$:

$$
F(\Omega_A, \Omega_B, \Omega_C) = \sum_{i,j,k,l,m,n} \left({}^1D^i_j \, {}^1D^k_l \, {}^1D^m_n - {}^1D^i_j \, {}^2D^{km}_{ln} - {}^1D^k_l \, {}^2D^{im}_{jn} - {}^1D^m_n \, {}^2D^{ik}_{jl} + 3 \, {}^3D^{ikm}_{ikm} \right)
$$
$$
\times \, S_{ij}(\Omega_A) S_{kl}(\Omega_B) S_{mn}(\Omega_C) \tag{17}
$$

which is equivalent to

$$
F(\Omega_A, \Omega_B, \Omega_C) = \frac{1}{2} \Bigg[\sum_{i,j,k,l,m,n} \left(6 \, {}^3D^{ikm}_{ikm} - {}^1D^i_j \, {}^1D^k_l \, {}^1D^m_n \right) S_{ij}(\Omega_A) S_{kl}(\Omega_B) S_{mn}(\Omega_C)
$$
$$
- F(\Omega_B, \Omega_C) \sum_{i,j} {}^1D^i_j \, S_{ij}(\Omega_A)
$$
$$
- F(\Omega_A, \Omega_C) \sum_{k,l} {}^1D^k_l \, S_{kl}(\Omega_B)
$$
$$
- F(\Omega_A, \Omega_B) \sum_{m,n} {}^1D^m_n \, S_{mn}(\Omega_C) \Bigg]. \tag{18}
$$

This function is normalized to N and the sum of its different permutations is the three-center bond index $\Delta^{(3)}_{\Omega_A \Omega_B \Omega_C}$ that represents the sharing of electrons between three topological regions $(\Omega_A, \Omega_B, \Omega_C)$. A preliminary version of this function (normalized to $2N$) has previously been reported by us in [32] which is only valid at the Hartree–Fock level. However, the current formulation is quite general at any level of theory.

3.2. Mulliken-type treatment

In the Mulliken-type approach we integrate the ${}^3\gamma$ function over the whole space Ω, which leads to

$$
\mathrm{tr}\left({}^3\gamma \right) = \sum_{i,k,m} \gamma^{ikm}_{ikm} = \sum_{i,k,m} \Bigg(\frac{1}{3} {}^1D^i_i \, {}^1D^k_k \, {}^1D^m_m - \frac{1}{3} {}^1D^i_i \, {}^2D^{km}_{km} - \frac{1}{3} {}^1D^k_k \, {}^2D^{im}_{im}
$$
$$
- \frac{1}{3} {}^1D^m_m \, {}^2D^{ik}_{ik} + {}^3D^{ikm}_{ikm} \Bigg) = \frac{N}{3} \tag{19}
$$

which allows one to perform the partitioning of N electrons according to terms involving spin-orbitals centered on one-, two- or three nuclei.

The concept of three-center index has found a broad use as an appropriate tool to detect and to localize the presence of three-center bondings in molecules [33–37]. However, these indices have only been used at semiempirical and Hartree–Fock levels. The partitioning given in equation (19) provides the rigorous definition of *three-center bond index*, $\Delta_{ABC}^{(3)}$, at any level of theory. Following identical procedure as for second-order we have

$$\Delta_{ABC}^{(3)} = 6 \sum_i^A \sum_k^B \sum_m^C \left({}^1D_i^i \, {}^1D_k^k \, {}^1D_m^m - {}^1D_i^i \, {}^2D_{km}^{km} - {}^1D_k^k \, {}^2D_{im}^{im} - {}^1D_m^m \, {}^2D_{ik}^{ik} + 3{}^3D_{ikm}^{ikm} \right)$$

$$(A < B < C) \tag{20}$$

which can also be expressed in terms of the correlations between the fluctuations of the charge operators for nuclei A, B and C, that is $\Delta_{ABC}^{(3)} = 3\langle (\hat{q}_A - \langle \hat{q}_A \rangle)(\hat{q}_B - \langle \hat{q}_B \rangle)(\hat{q}_C - \langle \hat{q}_C \rangle) \rangle$. At the Hartree–Fock level equation (20) leads to the three-center index $\Delta_{ABC}^{(3)} = 6 \sum_i^A \sum_k^B \sum_m^C \, {}^1D_k^i \, {}^1D_m^k \, {}^1D_i^m$ which is the spin-orbital version of the formula previously reported by us [37] and it is proportional to the I_{ABC} index reported by other authors [6, 33–36].

Although the three-center bonds certainly represents the simplest form of multicenter bondings, the application of bond indices of higher than third-order was also recently reported by Giambiagi et al., who used, for example, six-center bond indices to discuss the aromaticity of benzenoid hydrocarbons [38]. It is, however, necessary to stress that the practical experience with the use of these indices for the interpretation of the molecular structures has so far been obtained only at semiempirical or Hartree–Fock levels of theory. The reason is that the calculations of multicenter indices at post-Hartree–Fock level rely on the knowledge of correlated higher order densities which are not available from standard quantum chemistry codes and, consequently, these calculations are not straightforward at present. We nevertheless belive that the systematic study of the effects of electron correlation on the phenomenon of multicenter bondings is worthwhile and first such studies are being performed in our laboratories.

Acknowledgements

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