

# On the Physical Meaning of Bond Indices from the Population Analysis of Higher Order Densities

Roberto C. Boicchio<sup>†</sup>

*Departamento de Física, Facultad de Ciencias Exactas y Naturales, Universidad de Buenos Aires, Ciudad Universitaria 1428, Buenos Aires, Argentina*

Robert Ponec\*

*Institute of Chemical Process Fundamentals, Czech Academy of Sciences, Prague 6-Suchdol, Czech Republic*

Luis Lain and Alicia Torre

*Departamento de Química Física, Facultad de Ciencias, Universidad del País Vasco, Apdo.644, Bilbao, Spain*

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In this study, the physical meaning and mutual relations of multicenter bond indices arising from various population analysis schemes is analyzed and discussed. The reported relations were numerically tested at ab initio SCF level on a series of molecules involving the representatives of systems with classical two-center two-electron (2c-2e) bonds as well as three-center two-electron (3c-2e) and three-center four-electron (3c-4e) bonds. The results show that the generalized population analyses are very suitable tools for detecting the presence and localization of multicenter bonding in molecules.

## Introduction

Quantum chemical calculations are rapidly becoming a routine tool for obtaining the energies and the structures of both stable and transient molecular species. Unfortunately, the increased sophistication necessary to obtain sufficient accuracy leads to the loss of transparency of corresponding wave functions. For this reason, the introduction of new sophisticated computational methods is accompanied by the parallel design of the auxiliary procedures, allowing us to extract the structural information hidden in the wave function and to visualize it in terms close to classical chemical concepts of bonds, bond orders, VB structures, etc.<sup>1–13</sup> One of the most widely used such procedures is the so-called population analysis and, in the years following its first introduction by Mulliken,<sup>14</sup> this idea was frequently generalized and extended.<sup>15–20</sup> One such extension concerns the generalization toward the visualization of bonding in molecules exceeding the ordinary scheme of well localized two-center two-electron (2c-2e) bonds and containing such more complex bonding patterns like three-center bonding, hypervalence, etc. In recent years, it has been shown that appropriately generalized population analyses leading to the introduction of the so-called multicenter bond indices can be designed<sup>21–28</sup> and, in terms of these indices, the structure of a number of complex molecules could indeed be understood.<sup>29–32</sup> The common feature of all versions of population analyses is that a certain molecular property, usually related to density matrixes, is being decomposed into contributions, usually associated with atoms or their combinations. The question thus naturally can arise as to what is the physical meaning and mutual relation of populations resulting from various alternative procedures. The aim in this study is just to address this question in detail.

## Theoretical

As already mentioned, the idea of population analysis is based on the partitioning of a certain molecular property into contributions usually associated with atoms or their combinations. Depending on what quantity is subjected to such partitioning, various types of population analysis can be introduced and, accordingly, various types of information can be extracted from it. The simplest quantity that was subjected to the partitioning of population analysis is the molecular electron density  $\rho(r)$ . Such analysis, first proposed by Mulliken,<sup>14</sup> was closely related to usual quantum chemical representation of the density function in terms of an AO expansion.

$$\rho(r) = \sum_{\mu} \sum_{\nu} P_{\mu\nu} \chi_{\mu}(r) \chi_{\nu}(r) \quad (1)$$

This density satisfies the natural normalization shown in eq 2

$$\int \rho(r) dr = N \quad (2)$$

Because each of the AO basis functions is usually localized on a certain atom, the total number of electrons  $N$  can be decomposed into contributions according to on which center the AO basis functions are localized. In this way, the concept of atomic electron density  $P_A$  as a contribution of the atom  $A$  to the total number of electrons  $N$  could be introduced

$$N = \sum_{\mu} \sum_{\nu} P_{\mu\nu} \int \chi_{\mu}(r) \chi_{\nu}(r) dr = \sum_A \sum_{\mu} (PS)_{\mu\mu} = \sum_A P_A \quad (3)$$

where

$$S_{\mu\nu} = \int \chi_{\mu}(r) \chi_{\nu}(r) dr \quad (4)$$

\* Corresponding author.

<sup>†</sup> Member of Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET), República Argentina.

and

$$P_A = \sum_{\mu}^A (PS)_{\mu\mu} \quad (5)$$

Another quantity that can be subjected to the partitioning of the population analysis is the so-called exchange part of the pair density defined at the SCF level, which is of our concern here, by eq 6

$$\gamma_{\text{exch}}(r_1, r_2) = \frac{1}{4} \rho_1(r_1, r_2) \rho_1(r_2, r_1) \quad (6)$$

where  $\rho_1(r_1, r_2)$  is the nondiagonal element of the first-order density matrix. This exchange density satisfies the normalization (7)

$$2 \int \gamma_{\text{exch}}(r_1, r_2) dr_1 dr_2 = N \quad (7)$$

and quite parallel to partitioning of orbital based expansion of  $\rho(r)$ , the individual contributions can be introduced in this case as well. This type of analysis is in fact equivalent to the analysis originally introduced by Wiberg<sup>3</sup> and subsequently generalized by Giambiagi et al. and by Mayer<sup>11,12</sup> and the pair population analysis recently proposed by one of us.<sup>33,34</sup> The typical feature of this analysis is that in contrast to the decomposition of the electron density  $\rho(r)$ , where only monoatomic terms (atomic densities  $P_A$ ) were possible, the partitioning of the exchange density leads to mono- and biatomic contributions.

$$N = \frac{1}{2} \sum_{\mu} \sum_{\nu} (PS)_{\mu\nu} (PS)_{\nu\mu} = \frac{1}{2} \sum_A W_A + \frac{1}{2} \sum_{A \neq B} W_{AB} \quad (8)$$

The physical meaning of biatomic terms is quite clear; they provide the information about between which atoms the bonding electron pairs are predominantly shared and therefore represent the theoretical equivalent of the classical concept of bond order.<sup>3,11,12</sup> A little bit more complex situation is, however, with monoatomic terms. To get monoatomic terms with clear physical meaning, it is useful to rewrite first the normalization in eq 8 in the form of eq 9.

$$\sum_A \frac{1}{2} (W_A - \sum_{B \neq A} W_{AB}) + \sum_{B \neq A} W_{AB} = N \quad (9)$$

Denoting now the whole complex monoatomic term as  $Q_A$  and taking into account that the total number of electrons  $N$  can also be expressed as a sum of atomic densities  $P_A$ , the physical meaning of the monoatomic term  $Q_A$  can straightforwardly be deduced from eq 10

$$Q_A = P_A - \sum_{B \neq A} W_{AB} \quad (10)$$

Referring to this equation and taking into account that the second term on its right-hand side represents the total number of pairs that the atom A is able to share with remaining atoms (which is equivalent to the classical concept of valence<sup>5</sup>), then the quantity  $Q_A$  can straightforwardly be interpreted as the unshared charge on atom A. These values thus provide the information about the eventual presence of free and core electron pairs on atom A.

The interpretation of the physical meaning of monoatomic terms from Mulliken and Wiberg population analysis just presented represents, however, only one particular step in the solution of the more general problem of mutual relation of bond

indices from the hierarchy of generalized population analyses.<sup>22,23,25,27</sup> The first step in such generalization represents the population analysis based on the partitioning of the functional  $D(r_1, r_2, r_3)$ , derived from the third-order density matrix

$$D(r_1, r_2, r_3) = \frac{1}{4} \rho_1(r_1, r_2) \rho_1(r_2, r_3) \rho_1(r_3, r_1) \quad (11)$$

which was shown to lead to the so-called three-center bond indices. This functional also satisfies the normalization to the total number of electrons.

$$3 \int D(r_1, r_2, r_3) dr_1 dr_2 dr_3 = N \quad (12)$$

Introducing again the usual orbital expansion for the individual terms  $\rho_1(r_i, r_j)$ , the normalization (eq 12) can be rewritten in the following form

$$N = \frac{1}{4} \sum_{\alpha} \sum_{\beta} \sum_{\gamma} (PS)_{\alpha\beta} (PS)_{\beta\gamma} (PS)_{\gamma\alpha} \quad (13)$$

Because of the three-index nature of this equation, the application of the population partitioning allows one to introduce mono-, bi-, and triatomic contributions.

$$N = \sum_A \Delta_A + \sum_{A < B} \Delta_{AB} + \sum_{A < B < C} \Delta_{ABC} \quad (14)$$

The physical meaning of three-center terms is again quite clear; they are identical with the so-called three-center bond indices<sup>24-28</sup> and, as such, they straightforwardly detect the eventual presence of three-center bonding in a molecule. A little bit more complex situation is noted, however, with mono- and biatomic terms because similar terms appeared already in the population analysis of exchange pair density (eq 8) and the question thus naturally arises about how they are related to the corresponding indices  $Q_A$  and  $W_{AB}$ .

To elucidate this relationship, let us start first with the monoatomic term  $\Delta_A$ . For this purpose, it is necessary to write down first the detailed expression for this term

$$\Delta_A = \frac{1}{4} \sum_{\alpha}^A \sum_{\beta}^A \sum_{\gamma}^A (PS)_{\alpha\beta} (PS)_{\beta\gamma} (PS)_{\gamma\alpha} \quad (15)$$

If we now take into account that the restricted summation in eq 15 can schematically be written as

$$\sum_{\alpha}^A = \sum_{\alpha}^{\text{all}} - \sum_{B \neq A} \sum_{\alpha}^B \quad (16)$$

then after inserting eq 16 into eq 15 and taking into account the idempotency of the matrix  $\mathbf{PS}$ , the original formula eq 15 can be rewritten in the alternative form.

$$\Delta_A = Q_A + \frac{1}{4} \sum_{B \neq A} \sum_{C \neq A} \sum_{\alpha}^A \sum_{\beta}^B \sum_{\gamma}^C (PS)_{\alpha\beta} (PS)_{\beta\gamma} (PS)_{\gamma\alpha} \quad (17)$$

Taking into account that the last term on the right-hand side of eq 17 is identical (up to a proportionality factor 1/4) with the original heuristic definition of three-center bond index  $I_{ABC}$ ,<sup>24-28</sup>

$$I_{ABC} = \sum_{\alpha}^A \sum_{\beta}^B \sum_{\gamma}^C (PS)_{\alpha\beta} (PS)_{\beta\gamma} (PS)_{\gamma\alpha} \quad (18)$$

then eq 17 can be rewritten in the form shown in eq 19

$$\Delta_A = Q_A + \frac{1}{4} \sum_{B \neq A} \sum_{C \neq A} I_{ABC} \quad (19)$$

which clearly shows the physical meaning of the monatomic term  $\Delta_A$ . It is equal to “unshared” charge on atom A corrected by an additional term containing, together with genuine three-center populations  $I_{ABC}$ , also some two-center terms of the type  $I_{ABB}$  resulting from  $B = C$  in summations (eq 19).

In a similar way it is also possible to look at the relation of biatomic bond index  $W_{AB}$  to the biatomic term  $\Delta_{AB}$  from the decomposition (eq 14). The algebraic manipulations are again similar to in the previous case so that it is not necessary to go into details and only the final formula will be given.

$$\Delta_{AB} = \frac{3}{2} W_{AB} - \frac{3}{4} \sum_{C \neq B} \sum_{A \neq C} I_{ABC} \quad (20)$$

As it is again possible to see, the relation between  $W_{AB}$  and  $\Delta_{AB}$  is also relatively simple and, in fact, they differ only by the correcting term that contains only genuine three-center terms  $I_{ABC}$ . There is, however, one interesting implication resulting from the eq 20. This implication concerns the already reported result that in molecules well represented by localized 2c-2e bonds, the three-center populations are negligible. From this result it follows that if three-center bonding is not present in the molecule, the relation between  $\Delta_{AB}$  and  $W_{AB}$  takes an especially simple form

$$\Delta_{AB} = \frac{3}{2} W_{AB} \quad (21)$$

so that both indices are in this case entirely equivalent. This equivalence thus also explains the existence of the approximate normalization (eq 22) frequently observed for molecules without three-center bonds

$$N \cong \sum_A \Delta_A + \sum_{A < B}^{\text{bonded}} \Delta_{AB} \quad (22)$$

On the other hand, when three-center bond contributions cannot be neglected, then neither of the populations, whether  $W_{AB}$  or  $\Delta_{AB}$ , can be regarded as “pure” two-center bond indices but some contaminating three-center bonding contributions are present in them as well.

In a similar way it would now be possible to analyze the mutual relation of individual populations resulting from the partitioning of higher than third-order densities. The simplest such case corresponds to the partitioning of the functional

$$D(r_1, r_2, r_3, r_4) = \frac{1}{8} \rho_1(r_1, r_2) \rho_1(r_2, r_3) \rho_1(r_3, r_4) \rho_1(r_4, r_1) \quad (23)$$

related to the fourth-order density matrix. This functional satisfies the normalization (24)

$$N = \frac{1}{8} \sum_{\alpha} \sum_{\beta} \sum_{\gamma} \sum_{\delta} (PS)_{\alpha\beta} (PS)_{\beta\gamma} (PS)_{\gamma\delta} (PS)_{\delta\alpha} \quad (24)$$

and in keeping with the idea of population analysis this equation can be decomposed to mono-, bi-, tri- and tetra-atomic populations (eq 25)

$$N = \sum_A \Delta_A^{(4)} + \sum_{A < B} \Delta_{AB}^{(4)} + \sum_{A < B < C} \Delta_{ABC}^{(4)} + \sum_{A < B < C < D} \Delta_{ABCD}^{(4)} \quad (25)$$

**TABLE 1: Calculated Values of Mono- and Biatomic Populations for Several Selected Molecules with Well-Localized 2c-2E Bonds**

| molecule         | fragment | $P_A$ | $Q_A$  | $W_{AB}$ | $\Delta_{AB}$ |
|------------------|----------|-------|--------|----------|---------------|
| H <sub>2</sub> O | O        | 8.660 | 6.884  |          |               |
|                  | H        | 0.670 | -0.216 |          |               |
|                  | OH       |       |        | 0.888    | 1.335         |
| NH <sub>3</sub>  | N        | 7.854 | 5.120  |          |               |
|                  | H        | 0.715 | -0.192 |          |               |
|                  | NH       |       |        | 0.911    | 1.381         |
| CH <sub>4</sub>  | C        | 6.400 | 2.615  |          |               |
|                  | H        | 0.900 | -0.076 |          |               |
|                  | CH       |       |        | 0.946    | 1.417         |

Without going into details of the necessary algebraic manipulations, we present here only the final formulas for the corresponding populations

$$\begin{aligned} \Delta_{ABCD}^{(4)} &= 3I_{ABCD} \\ \Delta_{ABC}^{(4)} &= 3I_{ABC} - \frac{3}{2} \sum_{D \neq A, B, C} \Delta_{ABCD}^{(4)} \\ \Delta_{AB}^{(4)} &= 7W_{AB} - \frac{7}{4} \left( \sum_{C \neq A} I_{ABC} + \sum_{C \neq B} I_{ABC} \right) - \frac{1}{2} \left( \sum_{C \neq A} I_{AABC} + \sum_{C \neq B} I_{ABBC} \right) - \frac{3}{8} \left( \sum_{C \neq A} I_{AABC} + \sum_{C \neq B} I_{ABBC} \right) \\ \Delta_A^{(4)} &= P_A - \frac{3}{8} \sum_{B \neq A} I_{AAAB} - \frac{3}{8} \sum_{B \neq A, C \neq A} I_{AABC} - \frac{1}{8} \sum_{B \neq A, C \neq A, D \neq A} I_{ABCD} \quad (26) \end{aligned}$$

The physical meaning of the tetra-atomic term is again completely clear; it just represents the contribution from eventual four-center bonding in the molecules. The physical meaning of remaining terms is, however, more complex and it is evident that these terms always contain contaminating contributions from higher order bond effects. Thus, for example, in the case of triatomic population  $\Delta_{ABC}^{(4)}$ , the leading three-center component is contaminated by the four-center terms and only if these terms can be neglected can this population be regarded as a “net” three-center bond index.

Having presented the necessary theoretical background, let us now test the aforementioned partitionings by some numerical calculations. The results of such calculations are summarized in Tables 1 and 2.

## Results and Discussion

The partitionings just presented were numerically tested on a series of simple molecules that involved the molecules of H<sub>2</sub>O, NH<sub>3</sub>, and CH<sub>4</sub> as the representatives of the systems well described by the Lewis model of localized two-center two-electron (2c-2e) bonds, and H<sub>3</sub><sup>+</sup>, B<sub>2</sub>H<sub>6</sub>, allylcation, and allyl-anion as the representatives of the systems with three-center bonding. The calculations were performed by the ab initio method using the program Gamess-US.<sup>35</sup> The basis set was 6-31G\*\* for neutral molecules and cations and 6-31G++ for the allyl anion. For all systems, the molecules were considered in completely optimized molecular geometries. Let us attempt now to discuss the results of our calculations and let us start first with the series of molecules with well-localized 2c-2e bonds. In this case, because of absence of multicenter bonding

**TABLE 2: Calculated Values of Mono-, Bi-, and Triatomic Populations for Selected Molecules with 3-Center Bonds**

| molecule     | fragment                      | $Q_A$          | $\Delta_A$ | $W_{AB}$ | $\Delta_{AB}$ | $I_{ABC}$ |
|--------------|-------------------------------|----------------|------------|----------|---------------|-----------|
| $H_3^+$      | H                             | -0.222         | 0.074      |          |               |           |
|              | HH                            |                |            | 0.444    | 0.444         |           |
|              | HHH                           |                |            |          |               | 0.296     |
| $B_2H_6$     | B                             | 1.465          | 2.520      |          |               |           |
|              | H                             | 0.056          | 0.287      |          |               |           |
|              | BB                            |                |            | 0.506    | 0.415         |           |
|              | (BH) <sub>terminal</sub>      |                |            | 0.993    | 1.501         |           |
|              | (BH) <sub>bridging</sub>      |                |            | 0.483    | 0.558         | 0.238     |
| allyl cation | C <sub>1</sub>                | 2.232          | 3.405      |          |               |           |
|              | C <sub>2</sub>                | 2.560          | 3.157      |          |               |           |
|              | C <sub>1</sub> C <sub>2</sub> |                |            | 1.484    | 2.056         |           |
|              | C <sub>1</sub> C <sub>3</sub> |                |            | 0.245    | 0.179         |           |
|              | C <sub>1</sub> H              |                |            | 0.922    | 1.388         |           |
|              | C <sub>2</sub> H              |                |            | 0.914    | 1.387         | 0.252     |
|              | CCC                           |                |            |          |               |           |
|              | allyl anion                   | C <sub>1</sub> | 1.852      | 2.956    |               |           |
|              | C <sub>2</sub>                | 3.145          | 3.867      |          |               |           |
|              | C <sub>1</sub> C <sub>2</sub> |                |            | 1.582    | 2.546         |           |
|              | C <sub>1</sub> C <sub>3</sub> |                |            | 0.002    | 0.191         |           |
|              | C <sub>1</sub> H              |                |            | 0.981    | 1.506         |           |
|              | C <sub>2</sub> H              |                |            | 0.967    | 1.468         | -0.231    |
|              | CCC                           |                |            |          |               |           |

interactions, the interpretation of monoatomic populations  $Q_A$  and  $\Delta_A$ , as well as biatomic populations  $W_{AB}$  and  $\Delta_{AB}$  is especially simple. This interpretation can be best demonstrated by comparison of the values of biatomic populations that can be expected to satisfy the simplified relation in eq 21 and is evident that the simple proportionality is indeed satisfied with remarkable accuracy. Also relatively simple to interpret are the values of unshared charge  $Q_A$ , whose values qualitatively correspond with the classically expected values 6, 4, and 2, respectively. The actual values are always slightly higher than these idealized limits, which can be explained by greater electronegativity of the central atom X compared with hydrogen.

A little bit more complex, but also more interesting, situation is with molecules containing three-center bonding. The most interesting situation is again with biatomic terms  $W_{AB}$  and  $\Delta_{AB}$ , which in some cases satisfy the simplified relation in eq 21, whereas in others, the three-center terms has to be taken into account. The factor discriminating between these two possibilities is the character of the bond. The bonds well represented by the Lewis model of well-localized 2c-2e bonds (e.g., the terminal BH bonds in  $B_2H_6$  or CH bonds in allyl cation or anion), satisfy the simple relation in eq 21. On the other hand, where the biatomic fragment AB includes the atoms involved in three-center bonding, the general relation in eq 20 has to be applied. However, the fact that three-center bonds are usually localized only in certain parts of the molecules makes it possible to simplify the eq 20 even further. Thus, for example, the fragment BH involving the bridging bonds in  $B_2H_6$  is a part of three-center BHB bond and the three-center term  $I_{BHB}$  thus represents the only one, dominant, correcting term. The general eq 20 thus reduces in this case to the simplified form shown in eq 27

$$\Delta_{BH} \cong \frac{3}{2}W_{AB} - \frac{3}{4}I_{BHB}$$

$$\Delta_{BB} \cong \frac{3}{2}W_{BB} - 2\frac{3}{4}I_{BHB} \quad (27)$$

Similar simplified relations then hold also for remaining systems,  $H_3^+$ , allylcation, and allylanion

$$\Delta_{HH} \cong \frac{3}{2}W_{HH} - \frac{3}{4}I_{HHH}$$

$$\Delta_{CC} \cong \frac{3}{2}W_{CC} - \frac{3}{4}I_{CCC} \quad (28)$$

and because it is possible to check, the values calculated from simplified relations in eqs 27 and 28 are indeed very close to the exact ones. This result is very interesting because it confirms the findings of our previous studies that three-center bonding, if present in a molecule, is always quite strictly localized to only certain regions in the molecule, whereas the rest of the molecule is generally well described by classical 2c-2e bonds. Another interesting conclusion that can be deduced from the presented results concerns the difference in sign between three-center terms  $I_{CCC}$  for allyl cation and allyl anion. The interpretation of this difference was recently proposed<sup>22</sup> in a sense that positive three-center bond indices are to be expected for (3c-2e) bonds, whereas negative contributions are characteristic of (3c-4e) bonds. Based on this interpretation, the three-center CCC bond in allyl cation is of the (3c-2e) type and that in allylanion is of the (3c-4e) type.

Here it is also fair to mention that another criterion for distinguishing between the (3c-2e) and (3c-4e) bonding was recently proposed by Giambiagi et al.<sup>26</sup> However, even if the authors' claim that the predictions of both criteria may differ, there is no such conflict in our case.

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