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Multicenter bonding within the AIM theory

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Abstract. This study reports the incorporation of recently proposed formalism for the detection and localization of multicenter bonding in molecules, the so-called generalized population analysis, into the framework of the atoms in molecules (AIM) theory. The reliability of this new approach is tested by direct numerical comparison of the values of multicenter bond indices derived from both the original and the AIM-generalized forms of the population analysis.

Key words: Chemical bonding – Multicenter bonds – AIM theory

Introduction

One of the most fundamental chemical concepts is the tenet of the chemical bond. The first to correctly recognize the electronic nature of the phenomenon of chemical bonding was G. N. Lewis [1] and his idea that chemical bonds are formed by shared electron pairs has become one of the basic chemical postulates. The Lewis theory assumed this sharing to take place between a pair of atoms and, as a consequence, it was inherently able to rationalize only the structure of molecules containing the so-called 2-center 2-electron (2c-2e) bonds. Although these bonds are certainly able to describe the structure of the vast majority of molecules, there are nevertheless some other systems whose bonding patterns are apparently more complex. Typical examples in this respect are the electron-deficient boranes and, in order to understand their structure, the concept of 3-center bonding has been invoked [2, 3]. The phenomenon of 3-center (or generally multicenter) bonding is not, however, restricted only to electron-deficient boranes, but this type of bonding is also present in other non-classical systems like metal clusters, distorted lithiocarbons, etc. [4, 5]. Moreover, the same concept was applied some time ago to the elucidation of the phenomenon of hypervalence [6–11]. Although in some cases the presence of multicenter bonding can be predicted on the basis of simple qualitative considerations (Lipscomb's rules [12, 13]), there are also other more complex systems where such an approach is neither simple nor unique [14]. It was therefore of special importance that a systematic theoretical procedure was proposed some time ago in terms of which the eventual presence of multicenter bonding could straightforwardly be detected. The formalism is known under the name "generalized" or "non-linear population analysis" [15–22] and using this approach the structures of various non-trivial systems could be explained [23, 24].

Despite the undeniable success of this new methodology in describing the phenomenon of multicenter bonding, one has to be aware of the fact that in its original form the whole formalism has some important inherent limitations. These limitations arise from the use of a Mulliken-like approximation [25] in calculating the values of multicenter bond indices. As a consequence, the generalized population analysis can be expected to suffer from the same limitations as the well-known Mulliken population analysis [26, 27]. Most of these limitations can be reduced to a considerable extent within Bader's AIM theory [28]. In view of this superiority one should ask whether it would not be possible to avoid the limitations of the original formalism of generalized population analysis by incorporating it into the framework of the AIM theory.

Our aim in this study is to report such a generalization. The paper is organized as follows. In the next section the theoretical background underlying the incorporation of the whole hierarchy of generalized population analyses [21] into the framework of the AIM theory is introduced. Some computational details related to the application of the resulting approach to systems with both classical and non-classical bonding patterns are subsequently reported. Finally, the values of

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Contribution to the Proceedings of the 2000 Symposium on Chemical Bonding: State of the Art in Conceptual Quantum Chemistry multicenter bond indices derived from both the original Mulliken-like and the AIM-generalized population analysis are discussed and compared.

Theoretical

The generalized population analysis [15–22] is based on the idempotency property of SCF density matrix expressed by the identity of Eq. (1)

$$\frac{1}{2^{k-1}}Tr(PS)^k = N \ , \tag{1}$$

where P is the usual charge density-bond order matrix and S the overlap one. Depending now on the actual value of the exponent k, the identity [Eq. (1)] can be partitioned into mono-, bi- and generally k-center contributions [Eq. (2)] which can be attributed some clear physical or chemical meaning.

$$N = \sum_A \Delta_A^{(k)} + \sum_{A<B} \Delta_{AB}^{(k)} + \sum_{A<B<C} \Delta_{ABC}^{(k)} + \cdots \sum_{A<B<C\ldots<K} \Delta_{ABC\ldots K}^{(k)} \tag{2}$$

The simplest situation is for $k = 1$, where the partitioning yields only monoatomic contributions whose physical meaning is the Mulliken charge of the atom [Eq. (3)].

$$N = \sum_A \sum_\mu^A (PS)_{\mu\mu} = \sum_A P_A \tag{3}$$

This definition of atomic charge can be generalized using Bader's virial partitioning [28] of one-electron density function $\rho(r)$ and within this approach Eq. (3) can be expressed in the form of Eq. (4):

$$N = \sum_A \int_A \rho(r)dr = \sum_A N(A) \ , \tag{4}$$

where the integration is performed over the atomic region Ω_A of the atom A, and N(A) is the corresponding Bader's charge of the atom A.

Another often used partitioning of the identity, Eq. (1), is for $k = 2$ which, in the case of the Mulliken-like approach, yields mono- and biatomic contributions [Eq. (5)] that are identical with the well-known Wiberg or Wiberg-Mayer indices [29, 30].

$$N = \frac{1}{2}\sum_\mu \sum_\nu (PS)_{\mu\nu}(PS)_{\nu\mu} = \frac{1}{2}\left\{\sum_A W_{AA} + \sum_{A\neq B} W_{AB}\right\} \tag{5}$$

The usefulness of these indices consists in that their values often approach classical bond multiplicities and, as such, they are sometimes called 2-center bond indices. Although originally introduced rather heuristically [29], these indices were shown to be related to the pair density [20], and in fact they are equivalent to mono- and biatomic contributions resulting from the Mulliken-like partitioning of the so-called exchange part of the pair density, Eq. (6) [31].

$$\rho_{exch}(r_1,r_2) = \frac{1}{2}\rho(r_1)\rho(r_2) - \rho(r_1,r_2) \tag{6}$$

In this formula $\rho(r_1,r_2)$ denotes the pair density and $\rho(r_1)$ the ordinary first-order density. This general formulation is interesting because it opens up the possibility of incorporating the definition of the bond index into the framework of Bader's AIM theory. Such an incorporation was recently proposed by several independent groups [32–35].[1] Within this approach, the general definition of the correlated bond indices is defined by Eq. (7):

$$1/2W_{AB} \approx -F(A,B) = N(A)N(B) - 2\int_A dr_1 \int_B \rho(r_1,r_2)dr_2 \tag{7}$$

These quantities, introduced originally by Bader [38], satisfy the normalization, Eq. (8), which can be regarded as the generalized form of the identity, Eq, (2).

$$-\sum_A \sum_B F(A,B) = N \tag{8}$$

This identity can be alternatively transformed to the form, Eq. (9), analogous to Eq. (2):

$$N = \sum_A \Omega_A^{(2)} + \sum_{A<B} \Omega_{AB}^{(2)} \tag{9}$$

where the corresponding terms are straightforwardly related to the above introduced F(A,B) quantities, Eq. (10).

$$\Omega_{AB}^{(2)} = -2F(A,B) \tag{10}$$

In the case of the SCF approximation the above approach leads to the partitioning of the identity, Eq. (11),

$$2\sum_A \sum_B \sum_i^{occ} \sum_j^{occ} \langle i \mid j\rangle_A \langle i \mid j\rangle_B = N \tag{11}$$

where $\langle i \mid j\rangle_A$ denotes the overlap integral of occupied molecular orbitals i and j over the atomic region of the atom A.

Having summarized the philosophy underlying the incorporation of the hierarchy of generalized population analyses into the framework of the AIM theory, let us now extend the whole approach to the analogous generalization of the 3-center bond indices. For this purpose it is useful to introduce the quantity F(A,B,C), Eq. (12),

$$\begin{aligned} F(A,B,C) &\\ = 6\int_A dr_1 \int_B dr_2 \int_C \rho(r_1,r_2,r_3)dr_3 - N(A)N(B)N(C) &\\ + N(A)N(B) + N(A)N(C) + N(B)N(C) & \end{aligned} \tag{12}$$

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[1] Another AIM based definition of bond index was proposed some time ago by Cioslowski [36, 37]. This definition is not, however, based on the exact correlated pair density but on natural orbitals and their occupation numbers

where $\rho(r_1,r_2,r_3)$ is the spinless third-order density, Eq. (13):

$$\rho(r_1,r_2,r_3)=\frac{N(N-1)(N-2)}{6}\int\Psi^2(r_1,r_2,.....r_N)\,d\sigma_1 d\sigma_2 d\sigma_3 dx_4....dx_N \tag{13}$$

and N(X) has identical meaning as in Eqs. (4) and (7).

The above introduction of the 3-center bond index straightforwardly follows from previous theoretical studies [39, 40], in which the index was defined as the expectation value of the operator, Eq. (14),

$$I_{ABC}\approx\left\langle\left(\widehat{q}_A-\left\langle\widehat{q}_A\right\rangle\right)\left(\widehat{q}_B-\left\langle\widehat{q}_B\right\rangle\right)\left(\widehat{q}_C-\left\langle\widehat{q}_C\right\rangle\right)\right\rangle \tag{14}$$

where $\widehat{q}_X$ denotes the operator of the number of particles on the atom X.

Similarly, the 3-center bond index was independently introduced also in the study [20], and Eq. (12) is in fact nothing but the straightforward transcription of the approach [20] into the framework of the AIM theory.

The quantities F(A,B,C) satisfy the normalization, Eq. (15),

$$\frac{1}{2}\sum_A\sum_B\sum_C F(A,B,C)=N \tag{15}$$

and parallel to Eq. (9), the AIM-generalized partitioning into mono-, bi-, and triatomic contributions can be straightforwardly introduced, Eq (16).

$$N=\sum_A\Omega_A^{(3)}+\sum_{A<B}\Omega_{AB}^{(3)}+\sum_{A<B<C}\Omega_{ABC}^{(3)} \tag{16}$$

In the closed shell SCF case this equation is transformed into Eq. (17):

$$2\sum_A\sum_B\sum_C\sum_i^{occ}\sum_j^{occ}\sum_k^{occ}\langle i\mid j\rangle_A\langle j\mid k\rangle_B\langle k\mid i\rangle_C=N\ . \tag{17}$$

Eq. (17) has also been derived by Bochicchio et al. using the second quantization formalism and field operators and this derivation will be published elsewhere [41]. Obviously Eq. (17) is the AIM counterpart of Eq. (18):

$$\frac{1}{4}\sum_A\sum_B\sum_C\sum_\mu^A\sum_\nu^B\sum_\lambda^C(PS)_{\mu\nu}(PS)_{\nu\lambda}(PS)_{\lambda\mu}=N \tag{18}$$

which defines the 3-center bond indices within the ordinary Mulliken-like form of the generalized population analysis. The partitioning of these equations then allows the straightforward comparison of multicenter bond indices within both approaches. Although 3-center bonding certainly represents the most common type of multicenter bonding, the above reported methodology can straightforwardly be generalized also to other types of non-classical bonds. Thus, for example, the eventual existence of *p*-center bonding could be described within the AIM theory by the function, Eq. (19)

$$\begin{aligned}F(A_1,A_2,\ldots A_p)&=p!\int_{A_1}dr_1\int_{A_2}dr_2\ldots\int_{A_p}\rho(r_1,r_2,\ldots r_p)dr_p\\&\quad-N(A_1)\ldots N(A_p)+N(A_1)\ldots N(A_{p-1})\\&\quad+N(A_1)\ldots N(A_{p-2})N(A_p)+\ldots.\end{aligned} \tag{19}$$

which satisfies the normalization, Eq. (20)

$$(-1)^{p-1}\frac{1}{(p-1)!}\sum_{A_1}\ldots.\sum_{A_p}F(A_1,A_2,\ldots A_p)=N \tag{20}$$

This formula reduces again in the closed shell SCF case to Eq. (21):

$$2\sum_{A_1}\ldots.\sum_{A_p}\sum_{i_1}^{occ}\ldots\sum_{i_p}^{occ}\langle i_1\mid i_2\rangle_{A_1}\ldots.\langle i_p\mid i_1\rangle_{A_p}=N\ , \tag{21}$$

which can be regarded as the AIM counterpart of the Mulliken-like expression, Eq. (22):

$$\frac{1}{2^{p-1}}\sum_A\sum_B\ldots\sum_P\sum_\mu^A\sum_\nu^B\ldots\sum_\pi^P(PS)_{\mu\nu}(PS)_{\nu\lambda}\ldots(PS)_{\pi\mu}=N \tag{22}$$

The above reported generalized methodology was implemented in our laboratories and one of the basic aims of this study is to compare the AIM-generalized multicenter bond indices with their original Mulliken-like counterparts. As the most common type of multicenter bonding are 3-center bonds, the numerical tests have been specifically performed for this particular case.

Computations

Two types of calculations have been performed in this study. In the first step the geometry of the studied molecules was completely optimized within the *ab initio* SCF approach in the Dunning-Huzinaga SDZVP basis set [42]. The calculations were performed using the Gaussian 94 series of programs [43]. These calculations primarily served to generate the density matrices and integrals involved in Eq. (17) required for the above reported analysis. The above methodologies were implemented in our laboratories using our own codes, which can be obtained upon request. The results of our calculations are summarized in Tables 1–3 and in the next section the conclusion from our analysis will be reported. Prior to presenting these results, it is perhaps necessary to emphasize that our results have been obtained within a closed shell SCF approximation which at present represents the only level at which the above approach is practically feasible. The generalization beyond the SCF approximation, although possible in principle, is quite difficult since it would require the knowledge of correlated higher-order densities, which are not at easily available from contemporary quantum chemical programs. This is especially true of the correlated third-order density, which, for obvious reasons, is not at present available in any such program. A slightly better situation is with the pair density, which is recently available from within Gamess [32, 44] and in the near future could hopefully be available also from pair-density functional theory [45, 46].

Table 1. Calculated values of ordinary and AIM generalized 3-center bond indices for a series of molecules containing three center bonds

Molecule	ABC (AB)	$\Delta^{(3)}_{ABC}$, $\Delta^{(3)}_{AC}$	$\Omega^{(3)}_{ABC}$, $\Omega^{(3)}_{AC}$	Type	Basis
H_3^+	HHH	0.444 (0.444)[a]	0.444	3c-2e	6–31G[b}
	HH	0.444	0.444		
Allyl cation	CCC	0.305 (0.375)	0.409	3c-2e	D95(p,d)
	CC	0.138	0.284		
B_2H_6	BHB	0.372 (0.375)	0.049	3c-2e	D95(p,d)
	BB	0.404	0.010		
Allyl anion	CCC	−0.351 (–0.375)	−0.111	3c-4e	D95(p,d)
	CC	0.283	0.275		
CO_2	OCO	−0.267 (−0.75)	−0.048	3c-4e	D95(p,d)
	OO	0.461	0.604		
N_2O	NNO	−0.526 (−0.75)	−0.208	3c-4e	D95(p,d)
	NO	0.682	0.668		
N_3^-	NNN	−0.945 (−0.75)	−0.363	3c-4e	D95(p,d)
	NN	1.174	1.081		

[a] Numbers in parentheses correspond to idealized values from the analytical model of 3-center bonds
[b] In this case the virial partitioning was impossible in D95(d,p) basis

Table 2. Calculated values of bond indices for molecules not containing multicenter bonds[a]

Molecule	Type	$\Delta^{(3)}_{ABC}$, $\Delta^{(3)}_{AC}$	W_{AB}	$\Omega^{(3)}_{ABC}$, $\Omega^{(3)}_{AB}$	$\Omega^{(2)}_{AB}$
H_2O	O-H	1.354 (1.353)[b]	0.902	0.936 (0.942)	0.628
	H...H	+0.014	0.000	0.028	0.007
	HOH	−0.014	–	0.016	–
NH_3	N-H	1.420 (1.407)	0.938	1.252 (1.279)	0.853
	H...H	0.000	−0.002	0.008	0.015
	NHN	−0.013	–	0.028	–
	HHH	0.002	–	0.000	–
CH_4	C-H	1.481 (1.458)	0.972	1.388 (1.471)	0.981
	H...H	−0.003	−0.006	0.034	0.037
	HCH	−0.015	–	0.055	–
	HHH	0.012	–	0.004	–

[a] All the data were calculated using D95(p,d) basis
[b] Numbers in parentheses were calculated from the approximate proportionality, Eqs. (23) and (24)

Table 3. Calculated values of 3-center bond indices of negatively charged species in several basis sets

Molecule	Basis	Type	$\Delta^{(3)}_{ABC}$	$\Omega^{(3)}_{ABC}$
Allyl anion	6-31G	CCC	−0.363	−0.142
	6-31G**		−0.322	−0.118
	6-31G++		−0.410	−0.097
	D95(p,d)		−0.351	−0.111
	D95++		−0.472	−0.010
N_3^-	6-31G	NNN	−0.965	−0.513
	6-31G**		−0.804	−0.367
	6-31G++		−1.079	−0.367
	D95(p,d)		−0.945	−0.363
	D95++		0.518	−0.361

Results and discussion

The importance of generalized population analysis for the detection of multicenter bonding arises from the empirical observation that among the vast number of three- or higher-center contributions resulting from the partitioning, Eq. (2), for $k \geq 3$, only a relatively very small proportion of the terms attains non-negligible values. Moreover, these non-negligible contributions are localized only between certain groups of atoms which, interestingly, coincide with the regions where multicenter bonds are expected in the molecule. The typical example in this respect is the molecule of diborane, where in keeping with the presence of two 3-center bonds in BHB fragments [12, 13], only two non-negligible 3-center contributions exist in the partitioning, Eq. (2), for $k = 3$, and these contributions are indeed localized in two BHB fragments. This empirical finding opened the way to the systematic investigation of molecules in which the presence of multicenter bonds was expected and, using this approach, the structure of numerous complex molecules could indeed be rationalized [23, 24]. The interpretation of multicenter bond indices was subsequently put on a safer theoretical basis by introducing a simple analytical model of 3-center bond [21, 47]. In terms of this model it was not only possible to understand the numerical values of 3-center bond indices but also to use them for the characterization of the nature of these bonds. Thus, for example, the positive value of the 3-center bond index indicates a three-center two-electron (3c-2e) bond, while the three-center four-electron (3c-4e) bonds are characterized by the negative value of the index. Despite the undeniable usefulness of these indices for structural elucidation of non-classical systems, it is true that because of being based on Mulliken-like partitioning, this approach can be expected to suffer from similar deficiencies that are known to affect the ordinary Mulliken population analysis [26, 27]. These deficiencies are to a considerable extent reduced within Bader's AIM theory and the primary aim of this study is to report the extension of the original formalism into the framework of this theory. Starting from this extension, the second aim of this study is to report a detailed numerical comparison of both approaches and to evaluate thus the reliability of AIM-generalized analysis for the detection of multicenter bonding in molecules.

For this purpose we have chosen a series of simple molecules (H_3^+, allyl cation, B_2H_6, allyl anion, CO_2, N_2O, N_3^-), for which the presence of 3-center bonds is widely accepted and was also detected by the original Mulliken-like 3-center bond indices. The results of our calculations are summarized in Table 1, in which both original and AIM generalized bond indices are included. Consistent with what was said above, only the non-vanishing values of 3-center indices are given and, as it is possible to see, these contributions are in all cases localized in regions where the 3-center bonds are expected.

The first conclusion that can be deduced from This table is that there is no qualitative difference in the predictions of both alternative approaches so that the regions detected to contain 3-center bonds within one approximation are similarly identified also using the other approach. In addition to this first qualitative conclusion, one can also appreciate the close correspondence of both approaches in characterizing the nature of 3-center bonds. Thus, for example, the 3c-2e bonds in H_3^+, allyl cation, and B_2H_6 are in all cases correctly characterized by the positive value of the index, while the negative sign of the index in the remaining cases is clearly consistent with the 3c-4e nature of the bonds.

Despite close parallel of both approaches at a qualitative level, there are, nevertheless, some quantitative differences that need to be discussed. These differences concern, above all, the comparison of actual numerical values with the expectation resulting from the analytical model of the 3-center bond [21, 47]. The idealized values from this model are also included into Table 1 and, as it is possible to see, the actual values from Mulliken-like partitioning do not differ too much from these limits in most cases. This result is not very surprising since the analytical model is also based on the idea of Mulliken-like partitioning. On the other hand, the situation with the AIM-generalized indices is slightly more complex, as no simple analytical model can evidently be formulated for virial partitioning. The only exception is the case of the highly symmetrical H_3^+ ion for which both original and AIM generalized indices are evidently identical. Although it is true that the AIM-generalized indices cannot be quantitatively related to any analytical model, it is nevertheless the case that some AIM generalized values in Table 1 are relatively low compared to others. This concerns above all the case of B_2H_6. This huge reduction is indeed very interesting since nothing similar is observed for the ordinary Mulliken-like analysis and, moreover, the existence of 3-center BHB bonds in this molecule is beyond any doubt. For this reason we hesitate to accept the interpretation offered in [32], in which the existence of 3-center bond in this molecule was questioned and we rather prefer to seek a possible explanation of this puzzling failure. Such an explanation requires us to scrutinize the results of the generalized population analysis in more detail and to concentrate also on the values of other bond indices. Thus, for example, the existence of a 3-center bond in some fragment ABC necessarily requires the existence of non-negligible bonding interactions between terminal atoms [21, 33]. The values of the corresponding 2-center bond indices in systems like H_3^+, allyl anion, allyl cation, etc., for which no reduction of the AIM 3-center index was observed, are indeed consistent with this expectation. These results contrast, however, with the value of the AIM index between non-bonded boron atoms, which displays a dramatic decrease. A possible explanation of this strong reduction of B···B bonding interactions can be offered in terms of the approach proposed some time ago by Mayer [48]. The central idea of this approach is the concept of the so-called "effective AO's within the AIM theory". In terms of this approach, the reduction of the B···B bond index can be attributed to low or negligible population of effective AO's on either bridging hydrogens or borons. Such a situation would manifest itself in the AIM charges on the bridging hydrogens, which would be close to -1. The actual AIM charge is -0.72. This clearly suggests that the bonding situation corresponds in this case to the low population of the effective AO's on boron and the observed reduction of the AIM 3-center BHB index can thus apparently be attributed just to this low population. This low population also affects the value of the total AIM charge on the boron, which is equal to $+2.14$. Moreover, if this charge is compared with the analogous charges on individual hydrogens (-0.72 for bridging H, -0.71 for terminal H), the electron distribution reflected by the AIM analysis suggests the BH bonds to be very polar. This, however, is quite different from the picture of bonding resulting from the ordinary Mulliken-population analysis and the question thus may naturally arise, which of the two analyses is the more realistic. Generally one would expect that AIM analysis should be superior but as the bond indices from this analysis so dramatically contradict the generally accepted model of two 3c-2e BHB bonds, we rather believe that the failure of AIM theory to detect 3c-2e BHB bonds is due to an insufficiently realistic density function on which the analysis is based. This belief is also supported by the analysis of the topology of electron distribution where the existence of a bond path and the bond critical point was detected between bridging hydrogens together with two ring critical points situated inside of the bridging HBH fragments. This type of bonding topology seems rather consistent with the existence of HBH 3c-2e bonds and the value of the corresponding 3c index, albeit still rather low, is indeed higher than for BHB fragments (0.052 vs. 0.049). As, however, the existence of a bond between two negatively charged hydrogens is very unlikely, it is probable that the above found topology is not sufficiently realistic and we believe that further improvement of the quality of the calculations will result in the correction of this probable bias. A systematic study of the basis set dependence of bonding topology in diborane and B_2H_6 and other boranes is being pursued in our laboratory and the results will be published elsewhere.

Summarizing the above results we can conclude that although the above introduced AIM generalization is apparently able to detect the presence of multicenter bonds in molecules, some questions concerning the manifestations of multicenter bonding within the AIM theory, especially in electron-deficient boranes, still remain to be clarified.

Having demonstrated the relatively close parallel of the original Mulliken-like and the AIM generalized formalism, let us scrutinize now another important aspect of both approaches. This aspect concerns the above-mentioned empirical fact that in the case of absence of multicenter bonding, the values of all the corresponding multicenter indices are very small. In order to demonstrate this particular aspect, we report the values of bond indices for several simple molecules for which no 3-center bonding is expected (H_2O, NH_3, CH_4) in Table 2. Consistent with the above expectation, the values of all 3-center bond indices are in these cases really very small and the only non-vanishing values are observed for 2-center contributions corresponding to pairs of classically bonded atoms. These contributions thus express the connectivity between the atoms in the same way as the well-known Wiberg indices (or their AIM generalized counterparts). The detailed relation between these two types of indices was recently discussed in our study [49] where we showed that in the case of the absence of 3-center bonding, the $\Delta^{(3)}_{AB}$ are related to W_{AB} by simple proportionality, Eq. (23).

$$\Delta^{(3)}_{AB} \approx \frac{3}{2} W_{AB} \ , \tag{23}$$

As it is possible to see from Table 2, this simple relation is indeed satisfied with surprising accuracy. But, as can also be seen from this Table, the same proportionality holds also in the case of AIM generalized indices, Eq. (24):

$$\Omega^{(3)}_{AB} \approx \frac{3}{2} \Omega^{(2)}_{AB} \tag{24}$$

This result is very interesting since it demonstrates that the AIM generalized bond indices can be interpreted quite similarly as the original Mulliken-like ones. This also concerns the molecules containing 3-center bonds, where the original formulas of Eqs. (23) and (24) have to be modified by taking into account the interfering effect of multicenter contributions [49].

The final aspect of original Mulliken-like and AIM generalized population analyses which we are going to discuss concerns the basis set dependence of multicenter bond indices. As we have already said above, such a dependence can generally be expected for any kind of Mulliken-like population analysis and this was in fact one of the reasons for introducing the reported generalization. The problem of the basis set sensitivity of the original multicenter bond indices was addressed in previous studies [50, 51] where it was shown that it is not serious enough to question the qualitative picture of bonding suggested by the corresponding indices. This, however, is true only for neutral molecules or cations, where the increasing flexibility of the basis sets causes the values of indices to more or less steadily converge to some limits. As will be shown, however, in this study, the deficiencies of Mulliken-like partitioning may become very serious for negatively charged ions for which the extended basis sets with additional diffuse functions are generally required. This can clearly be demonstrated by the data in Table 3 in which the 3-center bond indices for allyl anion, and N_3^-, in several basis sets are summarized.

The deficiency of Mulliken-like indices, especially for extended basis sets, can clearly be demonstrated by the value of the 3-center bond index in the azide ion where one can observe the complete reversal of the sign. The fact that this reversal is to be regarded as an artifact of the Mulliken-like partitioning can clearly be demonstrated by comparing with the analogous AIM generalized indices. As expected, the basis set dependence of the index is in this case less dramatic. The indices steadily converge to some limiting value whose sign, quite in keeping with the expected 3c-4e nature of NNN bond, is negative in all cases.

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