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Pair Population Analysis within AIM Theory

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The pair population analysis developed some time ago as a straightforward link between quantum chemical and classical picture of bonding was generalized by incorporating its formalism into the framework of AIM theory. A detailed numerical comparison between the results derived from the original pair population analysis and those from AIM generalization is reported. On the basis of this comparison, the reliability of both approaches is evaluated. In addition to this a numerical test of the accuracy of the Lewis electron pair model is also reported.

Introduction

The empirically known fact that atoms in molecules are held together by forces displaying both high directionality and saturation culminated in the last century by the formulation of the classical structural theory. This theory, based on the concepts of valence and chemical bond, has proved to be extremely fruitful and stimulated the development of both organic and inorganic chemistry for more than 150 years. 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 postulates of chemistry. The intuitively discovered relation of the phenomenon of chemical bonding with the electronic structure of molecules was placed on safe theoretical basis with the advent of quantum theory, and it is interesting that the first method of solving the Schrödinger equation, the so-called VB method,[2,3] was also straightforwardly based on the idea of electron pairing. Since that time, the newly established field of quantum chemistry has undergone an enormous progress and there is now no problem to generate reliable wave functions even for sizable molecules. Unfortunately, the increased sophistication of wave functions brings one unpleasant side effect. This effect is that these functions become more and more complex and, consequently, it is more and more difficult to trace in them anything reminiscent of the classical chemical bonds of the Lewis model.

Nevertheless, the immense debt which chemistry owes to this model stimulated and still stimulates the attempts to reconcile both alternative pictures of bonding.[4−21] If we disregard earlier studies based on the idea of localized orbitals,[4−6] the first attempt to substantiate the electron pair nature of chemical bonding theoretically is represented by the so-called loge theory.[7,8] Closely related to this theory are also more recent studies by Mel-Levy and Julg,[14,15] who proposed to identify chemical bonds with the regions of small fluctuation of electron pair. Unfortunately, these early attempts were not entirely convincing and it was even proposed to abandon the idea of chemical bonds as the basic building block of molecules.[16]

Despite these discouraging results, the intuitive belief in deeper physical meaning of the Lewis structural formulas survived and still stimulates the attempts at the elucidation of the role of electron pairing in chemical bonding.[17−22] Into the framework of these efforts can be included the formalism of so-called pair population analysis[23] in terms of which the direct link between rigorous quantum mechanics and the Lewis classical model was straightforwardly established.[24−26] This analysis, originally based on the Mulliken-like partitioning of the pair density matrix, was subsequently generalized[27] by reformulating the whole approach within the framework of AIM theory.[28] Unfortunately, at the time ref 27 was written, we were not able to perform the calculations at the corresponding level of the theory and so the tests of the accuracy of the Lewis model reported therein were only approximate. The first to fully explore the potential of the AIM generalized pair population analysis was thus Fradera et al. in a recent study,[29] in which the approximate nature of our calculations was repeatedly emphasized. In the meantime, the formalism of AIM theory was implemented in our laboratories so that the test of the accuracy of the Lewis model suggested in ref 27 can now be reconsidered. Our aim in this study is to report the detailed numerical comparison of the original pair population analysis with the exact AIM generalization and to evaluate thus the reliability and eventual shortcomings of previous approximate analyses.

Theoretical

Although the formalism of the pair population analysis is sufficiently described in the original studies,[23−26] we consider

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it worthwhile to review briefly the basic principles of the approach to the extent necessary for the purpose of this study. The basic idea of this analysis is the straightforward application of the Mulliken-like partitioning of the spin-free pair density $\rho(r_1,r_2)$

$$\rho(r_1,r_2) = \sum_{\alpha}\sum_{\beta}\Gamma_{\alpha\beta}\lambda_{\alpha}(r_1,r_2)\lambda_{\beta}(r_1,r_2) \tag{1}$$

where $\Gamma_{\alpha\beta}$ are the elements of the matrix representing the pair density in the basis of two-electron functions $\lambda_{\alpha},\lambda_{\beta}$, the so-called geminals.

As is well-known, the matrix Γ can be factorized into two blocks which correspond to the singlet and triplet states of electron pairs.

$$\Gamma = \Gamma^{(s)} \oplus \Gamma^{(t)} \tag{2}$$

and their respective traces are[30,31]

$$\mathrm{Tr}\,\Gamma = N(N-1)/2 \tag{3}$$

$$\mathrm{Tr}\,\Gamma^{(s)} = N(N+2)/8 - S(S+1)/2 \tag{4}$$

$$\mathrm{Tr}\,\Gamma^{(t)} = 3N(N-2)/8 + S(S+1)/2 \tag{5}$$

In these equations N denotes the number of electrons in the system and S its spin quantum number.

In the case of singlet states of N-electron systems $S = 0$ and, consequently, the following holds:

$$\mathrm{Tr}\,\Gamma^{(s)} - \frac{1}{3}\mathrm{Tr}\,\Gamma^{(t)} = N/2 \tag{6}$$

Based on this equation, it is useful to introduce the so-called effective pair populations as mono- and biatomic contributions from the Mulliken-like partitioning of eq 6

$$\Pi^{(s)}_{AA} - \frac{1}{3}\Pi^{(t)}_{AA} = \Pi^{(eff)}_{AA} \tag{7}$$

$$\Pi^{(s)}_{AB} - \frac{1}{3}\Pi^{(t)}_{AB} = \Pi^{(eff)}_{AB} \tag{8}$$

As has been shown in the studies,[23−25] the values of these effective pair populations are closely related to the Lewis electron pair model and, based on their values, the classical Lewis structures can be straightforwardly reproduced. In this connection it is also worth reminding that at the SCF level the effective pair populations are equivalent to the well-known Wiberg or Wiberg−Mayer indices,[32,33] which are well-known to represent the theoretical counterpart of the classical concept of bond multiplicity. Due to this property, the biatomic effective pair populations characterize the connectivity between the atoms (including the multiplicity of the corresponding bonds) while monatomic populations provide the information about the eventual presence of free electron pairs on atoms.

The relation between the effective pair populations and chemical bonds is also underlined by the normalization derived from eq 6

$$\sum_{A}\Pi^{(eff)}_{AA} + \sum_{A<B}\Pi^{(eff)}_{AB} = N/2 \tag{9}$$

Another interesting property of effective pair populations is that the values of $\Pi^{(eff)}_{AB}$ are usually very small for the pairs of atoms not connected in the classical structural formula by a bond. As a consequence, the exact normalization (9) can often be rewritten in the form (10), which can be regarded as a simple numerical test of how well the molecular structure is described by a classical Lewis formula.

$$\sum_{A}\Pi^{(eff)}_{A} + \sum_{A<B}^{\text{bonded}}\Pi^{(eff)}_{AB} \approx N/2 \tag{10}$$

As demonstrated in the studies,[23−25,34] the approximate normalization is usually satisfied by molecules well represented by a classical model of localized two-center two-electron (2c−2e) bonds. On the other hand, the deviations from the approximate normalization are generally observed for molecules like electron-deficient boranes, metal clusters, etc. containing multicenter bonds.[34,35]

Although the pair population analysis was originally formulated only at semiempirical level of the theory, the extension to ab initio level is quite straightforward. As it was shown in the study,[36] the effective pair populations are usually much less sensitive to the quality of the basis set than the well-known Mulliken populations. Despite these favorable findings, it is true, however, that the dependence on the quality of the basis set cannot be completely disregarded. Moreover, some systematic bias of the populations resulting from the artificial Mulliken-like partitioning of the electron charge between individual atoms can also be expected. It is generally accepted that most of these shortcomings of the Mulliken-like partitioning can to a considerable extent be reduced within the AIM theory.[28] In view of this superiority, the extension of the pair population analysis was proposed some time ago.[27] In this study, based on the revival of the old idea of chemical bond as a region of small fluctuation of the electron pair,[14] it was shown that at SCF level, the effective pair populations can be regarded as an approximation to interloge correlation terms $F(X,Y)$ introduced many years ago by Bader and Stephens.[37] [The interloge correlation terms reduce to effective pair populations if the explicit integration over the atomic domains is replaced by the Mulliken-like approximation of the corresponding integrals.[27]]

$$F(X,Y) = 2\int_{\Omega_X}\mathrm{d}r_1\int_{\Omega_Y}\rho(r_1,r_2)\,\mathrm{d}r_2 - N(X)N(Y) \approx -\Pi^{(eff)}_{XY} \tag{11}$$

The close parallel with the effective pair populations is clearly seen also from the existence of the general normalization

$$\sum_{A}F(A,A) + \sum_{A<B}2F(A,B) = -N \tag{12}$$

that is a straightforward counterpart of the formula (9). Based on this parallel, the $F(X,Y)$ terms can be related to the Lewis formula in exactly the same way as the effective pair populations. Moreover, the above originally empirical interpretation of pair populations[24−26] was put on safer theoretical footing in the study[27] in which the interloge correlation terms $F(A,A)$, $F(A,B)$ were interpreted in terms of fluctuation. Thus, e.g., it was shown that the necessary condition for minimizing the fluctuation in a biatomic region Ω_{AB} formed as a union of individual atomic regions Ω_A and Ω_B is the sufficiently large value of the term $F(A,B)$. This term can be regarded as a measure of sharing the electrons between atoms A and B. Consistent with this interpretation is the identification of $F(A,B)$ (and, of course, also of $\Pi^{(eff)}_{AB}$) with bond order[27,38]

$$B_{AB} = -2F(A,B) \tag{13}$$

TABLE 1: Calculated Values of Geometrical Parameters of the Studied Molecules[a]

molecule	parameter	value	molecule	parameter	value
H_2	R_{HH}	0.733	C_2H_4	R_{CC}	1.325
F_2	R_{FF}	1.350		R_{CH}	1.077
N_2	R_{NN}	1.083		∠HCH	116.8
HF	R_{HF}	1.10	C_2H_2	R_{CC}	1.191
H_2O	R_{OH}	0.944		R_{CH}	1.060
	∠HOH	106.6	CO_2	R_{CO}	1.145
NH_3	R_{NH}	1.000	$N_3^{(-)}$	R_{NN}	1.160
	∠HNH	108.2	N_2O	R_{NN}	1.096
CH_4	R_{CH}	1.085		R_{NO}	1.187
	∠HCH	109.5	SO_2	R_{SO}	1.423
LiH	R_{LiH}	1.624		∠OSO	118.1
LiF	R_{LiF}	1.572	SO_3	R_{SO}	1.412
C_2H_6	R_{CC}	1.544		∠OSO	120.0
	R_{CH}	1.085			
	∠CCH	111.6			

[a] Bond lengths are in angströms, bond angles in degrees.

In addition, this interpretation can simply be put into a quantitative mathematical form which, for example, was recently used for the formulation of the localization procedure yielding the orbitals (chemical bonds) which satisfy the condition of the minimal fluctuation of electron pair.[39]

The close relation of interloge correlation terms $F(X,Y)$ to the effective pair populations and, consequently, to the classical Lewis model finds its reflection also in the existence of approximate normalization (14), which can be regarded as a counterpart of the formula (10)

$$\sum_{A} F(A,A) + \sum_{A<B}^{\text{bonded}} 2F(A,B) \approx -N \tag{14}$$

One of the aims of this study is to show that, contrary to what was claimed in ref 29, the approximate normalization retains its validity also if the original pair populations are replaced by their exact equivalents within AIM theory.

Computations

The above-reported formalism was applied to a series of simple molecules ranging from ideally nonpolar homoatomic systems to highly polar molecules (H_2. N_2, F_2, HF, H_2O, NH_3, CH_4, C_2H_6, C_2H_4, C_2H_2, LiH, LiF, CO_2, N_2O, $N_3^{(-)}$, SO_2, SO_3). The calculations at ab initio SCF level were performed using the Gaussian 94 series of programs.[40] The calculations were performed in most cases using the Dunning−Huzinaga DZVP basis set[41] implicitly incorporated in the Gaussian program. The only exception was the molecule of LiF for which it was not possible to perform the virial partitioning of the electron density in this basis. In this case, Bader's analysis was performed using a 6-31G basis set. Similar complications with the virial partitioning were observed also for the molecule of C_2H_2, where in addition to four nuclear attractors, coinciding with individual C and H atoms, another fifth nonnuclear attractor was localized in the middle of the CC bond. This of course complicates the interpretation of the AIM generalized pair population analysis and so the molecule of acetylene was not further considered.

The geometries of all the molecules were completely optimized at each particular level and the resulting geometrical parameters are summarized in Table 1.

The wave functions generated in the first step were subsequently subjected to the formalism of both Mulliken-like and AIM generalized pair population analysis using our own codes interfaced with the Gaussian. The results of the calculations are summarized in Tables 2 and 3.

TABLE 2: Calculated Values of Effective Pair Populations and Their AIM Generalized Counterparts for a Series of Nonpolar Molecules

molecule	type	$2\Pi^{(\mathrm{eff})}_{XX}$ $\Pi^{(\mathrm{eff})}_{XY}$	idealized limit	$-F(X,X)$ $-F(X,Y)$	idealized limit
H_2	H	0.50	0.50	0.50	0.50
	H−H	0.50	0.50	0.50	0.50
N_2	N	5.558	5.50	5.482	5.50
	N≡N	1.441	1.50	1.518	1.50
F_2	F	8.524	8.50	8.346	8.50
	F−F	0.474	0.50	0.635	0.50
CH_4	C	4.600	4.00	3.789	4.00
	HH	0.386	0.50	0.503	0.50
	C−H	0.486	0.50	0.490	0.50
C_2H_6	C	4.474	4.00	3.758	4.00
	H	0.414	0.50	0.517	0.50
	C−C	0.451	0.50	0.490	0.50
	C−H	0.493	0.50	0.484	0.50
C_2H_4	C	4.328	4.00	3.940	4.00
	H	0.388	0.50	0.477	0.50
	C═C	0.976	1.00	0.941	1.00
	C−H	0.499	0.50	0.492	0.50

TABLE 3: Calculated Values of SCF Effective Pair Populations and Their AIM Generalized Counterparts for a Series of Polar Molecules

molecule	type	$2\Pi^{(\mathrm{eff})}_{XX}$ $\Pi^{(\mathrm{eff})}_{XY}$	idealized limit	$-F(X,X)$ $-F(X,Y)$	idealized limit
CH_4	C	4.600	4.00	3.789	4.00
	H	0.386	0.50	0.503	0.50
	C−H	0.486	0.50	0.490	0.50
	H...H	−0.003	0.00	0.045	0.00
NH_3	N	6.330	5.50	6.898	5.50
	H	0.288	0.50	0.164	0.50
	N−H	0.469	0.50	0.426	0.50
	H...H	−0.002	0.00	0.001	0.00
H_2O	O	7.756	7.00	8.604	7.00
	H	0.218	0.50	0.066	0.50
	O−H	0.451	0.50	0.314	0.50
	H...H	0.000	0.00	0.007	0.00
HF	F	9.052	8.50	9.441	8.50
	H	0.144	0.50	0.042	0.50
	H−F	0.401	0.50	0.258	0.50
LiH	Li	2.368	2.50	1.988	2.00[a]
	HH	0.648	0.50	1.841	2.00[a]
	Li−H	0.490	0.50	0.086	0.00[a]
LiF	Li	2.012	2.50	1.972	2.00[a]
	F	9.500	8.50	9.818	10.00[a]
	LiF	0.245	0.50	0.104	0.00[a]

[a] The values correspond to the limit of complete ionization

Results and Discussion

Having reviewed the basic theoretical background, let us confront the results of the original Mulliken-like pair population analysis with the exact AIM based generalization and let us start first by comparing of both approaches at the HF level of the theory. The simplest situation is for ideally nonpolar homoatomic systems (H_2, N_2, etc.) where it is easy to understand not only the calculated values qualitatively, but also the values from both approaches are closely related quantitatively. The qualitative interpretation of the pair populations can be best demonstrated by the simplest case of H_2 molecule and arises from the well-known result of the expansion of MO wave function in terms of VB structures [In the ground state of H_2

only one singlet and no triplet pair can be formed so that the effective pair populations are identical to pure singlet populations.]

$$|\varphi_1\overline{\varphi_1}| = \frac{1}{2}|\chi_a\overline{\chi_a}| + \frac{1}{2}|\chi_b\overline{\chi_b}| + \frac{1}{\sqrt{2}}\left\{\frac{1}{\sqrt{2}}(|\chi_a\overline{\chi_b}| + |\chi_b\overline{\chi_a}|)\right\} \tag{15}$$

According to this expansion, the bonding electron pair is 1:1 distributed between ionic (monatomic) and covalent (biatomic) contributions. As a consequence, each of the monatomic pair populations attains the value 0.25 ($^1/_2 \times {}^1/_2$), while the biatomic pair population is equal to 0.5 which corresponds to the classical bond order $B_{AB} = 2\Pi_{AB}^{(eff)} = 1.0$. Assuming now that the same partitioning of bonding electron pair also applies to the case of multiple bonded systems, the values of 1.0 and 1.5 can be expected for biatomic pair populations of nonpolar double and triple bonds, respectively. As it is possible to see in Table 2, the actual values of biatomic pair populations of H−H, F−F, C−C, C═C, and N≡N bonds very closely approach these idealized limits. Similarly, it is also possible to interpret the values of monatomic pair populations. In this case, however, it is necessary to be aware of the fact that in addition to ionic contribution of 0.25 per each ideally shared electron pair, the eventual presence of core or free electron pairs on the atom contributes to the corresponding atomic term by one unit per pair. As a consequence, the monatomic pair population of nitrogen in N_2 and fluorine in F_2 can be expected to be equal to 2.75 ($2 \times 1 + 3 \times 0.25$) and 4.25 ($4 \times 1 + 1 \times 0.25$), respectively. As can be seen in the Table 2, the actual values of atomic pair populations are again very close to these idealized limits. The close parallel of idealized and actual pair populations is not restricted only to the case of ideally nonpolar systems, but as it is possible to see from the Table 2, the close coincidence is observed also for heteropolar bonds of low polarity. Consistent with the above-introduced interpretation, the values of biatomic pair populations of C−H bond in various hydrocarbons are again close to 0.5 while the atomic population on C is close to 2 ($1 \times 1 + 4 \times 0.25$).

The above-discussed nonpolar or low polar systems are also interesting because of the especially simple relation between effective pair populations and their exact AIM-based counterparts. This is due to the fact that the electron pairs in these systems are nearly ideally shared so that the artificial 1:1 Mulliken-like partitioning of electron or pair density, characteristic of the original pair population analysis, still represents a reasonable and realistic enough approximation to the exact virial partitioning. As a consequence, the values of effective pair populations and interloge correlation terms are related by a simple proportionality

$$\begin{aligned} -F(\mathrm{A,A}) &\approx 2\Pi^{(eff)}(\mathrm{A,A}) \\ -F(\mathrm{A,B}) &\approx \Pi^{(eff)}(\mathrm{A,B}) \end{aligned} \tag{16}$$

where the factor of 2 appears as a consequence of the differences in normalization between (9) and (12). As it is possible to see in Table 2, the actual values of AIM pair populations are not very different from the values expected on the basis of relation 16. We can thus see that the picture of bonding suggested for nonpolar systems by original pair population analysis is practically equivalent to the picture resulting from the exact AIM-based reformulation of the theory.

The only exception that apparently seems to contradict the simple proportionality (20) is the molecule of F_2, for which the AIM bond order slightly exceeds the idealized value of unity expected on the basis of the Lewis model. The reasons for this interesting discrepancy are not completely clear at this moment but it is likely that they are related to the specific nature of bonding in the F_2 molecule which, for example, differs from other single bonds by an exceptionally low bond energy.[42] In this connection it is also interesting to remark that the specific nature of F−F bond was discussed some time ago in a study.[43] It was proposed that in addition to the ordinary MO picture of bonding, an alternative model can also be proposed, according to which the increase of the F−F bond order can be admitted, although the corresponding mechanism of bonding apparently participates only marginally.

Having demonstrated the close parallel of effective pair populations and their exact AIM-based counterparts for nonpolar systems, let us confront, in a similar way, the results of both approaches for heteropolar systems. The calculated values of effective pair populations and interloge correlation terms F(A,A), F(A,B) for systems containing bonds of gradually increasing polarity are summarized in Table 3. As it is possible to see in the table, the situation here is slightly more complex and the deviations from the simple picture observed for nonpolar systems become apparent. The general feature straightforwardly evident from the table is that the deviations from the idealized values systematically increase with increasing polarity of the bonds and predominantly concern the values of F(A,A) and F(A,B) resulting from AIM-based generalization of the pair population analysis. The polarity of the bond can straightforwardly be measured by the values of the monatomic terms F(A,A) for which the exaltation over the idealized limits (Table 3) is observed for the most electronegative atom in the bond while for its electropositive partner the values are accordingly lower. As it is also possible to see in Table 3, the extent of these deviations systematically increases with increasing polarity of the bond and in the limiting case of LiF molecule, the values of F(Li,Li) and F(F,F) are close to the expectation for the limit of the completely ionic bond ($-F(X,X) = N(X)$).

Although the same general trend is also detectable in the values of pair populations $\Pi_{AA}^{(eff)}$, the variation is in this case much less pronounced. Moreover, the artificial 1:1 distribution of the bonding electron pair into covalent and ionic contributions resulting from the Mulliken-like partitioning of the pair density is still apparent. Consistent with this systematic bias, the values of biatomic pair populations $\Pi_{AB}^{(eff)}$ are in all cases not too much different from the idealized value of 0.5. This systematic bias of pair populations is again remedied within the AIM approach and consistent with the expectation, the increased ionicity of the bond is accompanied by a deep complementary decrease of the covalent bond order F(A,B) and in the limit of practically ionic bond (LiH, LiF), the values of AIM covalent bond orders F(Li,H) or F(Li,F) dramatically decrease.

Another interesting application of the pair population analysis concerns the evaluation of the accuracy of the classical Lewis structural formula. As already mentioned above, this accuracy can simply be evaluated by comparing the actual value of the approximate normalization sum (10) or (14) with the exact limit. This quantitative criterion was used in the study,[27] but as the actual values were obtained only for approximate pair populations based on Mulliken-like partitioning, we would like to show that the picture of bonding does not change qualitatively when upgrading from approximate to exact description. This can best be demonstrated by the series of simple molecules H_2O, NH_3, CH_4, C_2H_6, C_2H_4, whose structures can be expected to be well described by the single Lewis formula. The values of the

TABLE 4: Calculated Values of Approximate Normalization Sums (10) and (14) for a Series of Molecules Well Described by Lewis Structural Formula

molecule	sum (10) SCF	exact	sum (14) SCF	exact
CH_4	5.016	5.000	−9.725	−10.00
NH_3	5.004	5.000	−9.949	−10.00
H_2O	4.999	5.000	−9.992	−10.00
C_2H_6	9.125	9.000	−17.407	−18.00
C_2H_4	8.067	8.000	−15.610	−16.00

TABLE 5: Calculated Values of Pair Populations for Molecules Containing Multicenter Bonds

molecule	type	$\Pi_{AB}^{(eff)}$	$-F(A,B)$
N_2O	N···O	0.139	0.376
$N_3^{(-)}$	N···N	0.929	0.600
CO_2	O···O	0.109	0.386
SO_2	O···O	0.052	0.562
SO_3	O···O	0.024	0.438

approximate normalization sums (10) and (14) for all the above molecules are summarized in Table 4. From this table it is evident that although the deviations between the approximate normalization and the exact limit are less for the sum (10), the accuracy of the approximate sum (14) is also very satisfactory and even in the case of most deviating systems, the error does not exceed 3−4%.

Such a situation is not, however, absolutely general and as already observed by us in previous studies,[27,34,35] there are molecules for which the accuracy of the approximate normalization is indeed much less. Such is, for example, the case of electron-deficient boranes, metal clusters,[34,35,44] or some other molecules like N_2O, $N_3^{(-)}$ etc., whose common structural feature is the presence of multicenter bonds. This is also the case of CO_2, SO_2, and SO_3 molecules, discussed in ref 29 as an example questioning the approximate normalization. The origin of these deviations is evident—it is the existence of nonnegligible bonding interaction between classically nonbonded atoms in these molecules. This is clearly demonstrated by the data in Table 5. As it is possible to see in this table, the values of populations between nonbonded terminal atoms are indeed considerably greater than in the case of “normal” molecules like H_2O, NH_3, etc. (Table 3). According to our experience, the failure of the approximate normalization is typical for molecules containing multicenter bonding and the existence of these nonclassical bonds was indeed detected in many systems.[34,35,44,45] This detection is based on the values of the so-called multicenter bond indices[46−53] which are defined as mono-, bi-, and generally k-atomic contributions resulting from the Mulliken-like partitioning of the multiple product of the (**PS**) matrix where **P** is the charge density bond order matrix and **S** the overlap one.

$$\frac{1}{2^{k-1}}\mathrm{Tr}(\mathbf{PS})^k = N = \sum_{A}\Delta_{A}^{(k)} + \sum_{A<B}\Delta_{AB}^{(k)} + \cdots \sum_{A<B<\ldots<K}\Delta_{ABC\ldots K}^{(k)} \qquad (17)$$

In the particular case of the most common three-center bonding, the values of three-center bond index $\Delta_{ABC}^{(3)}$ are defined as

$$\Delta_{ABC}^{(3)} = \frac{3}{2}\sum_{\alpha}^{A}\sum_{\beta}^{B}\sum_{\gamma}^{C}(\mathbf{PS})_{\alpha\beta}(\mathbf{PS})_{\beta\gamma}(\mathbf{PS})_{\gamma\alpha} \qquad (18)$$

As repeatedly demonstrated by various authors,[44−53] the presence of three-center bond in a molecule can reliably be detected by the nonnegligible value of the above index for certain well-localized triads of atom. Such is just the case of CO_2, N_2O, $N_3^{(-)}$, SO_2, and SO_3 molecules whose values of multicenter bond indices resulting from the partitioning (17) for $k = 3$ are summarized in Table 6.

TABLE 6: Calculated Values of Three-Center Bond Indices from Mulliken-like Partitioning and the Corresponding AIM Generalization for Molecules Containing Three-Center Bonds

molecule	type	$\Delta_{ABC}^{(3)}$	AIM generalized index[a]
N_2O	NNO	−0.527	−0.208
$N_3^{(-)}$	NNN	−0.804[b]	−0.361
CO_2	OCO	−0.267	−0.048
SO_2	OSO	−0.311	−0.068
SO_3	OSO	−0.189	−0.023

[a] Similar to what was reported for biatomic indices $F(X,Y)$ and $\Pi_{XY}^{(eff)}$, also the AIM generalized three-cemter bond indices reduce to (18) if the explicit integration over atomic domains is replaced by the Mulliken-like approximation of the corresponding integrals. [b] Mulliken-like bond indices in this anionic system were found to be very sensitive to the quality of the basis set. The value presented in the table was obtained in 6-31G** basis. In the case of more flexible 6-31G++ basis the value is −1.079, which is still consistent, at least qualitatively, with the 3c−4e nature of the NNN bond. In the case of DH++ basis containing additional diffuse functions, the value is surprisingly positive (0.518). The fact that this is an artifact of the Mulliken-like partitioning is clearly demonstrated on the value of AIM generalized three-center bond index whose value in DH++ basis is −0.361 compared to −0.367 in 6-31G** and 6-31G++ bases.

In addition to allowing the detection of the presence of three-center bonding, another interesting information about the nature of these bonds can also be deduced from the sign of the corresponding indices. Thus, while the positive value of the three-center bond index is typical for three-center two-electron bonds (characteristic especially for electron-deficient boranes), the negative value of this index means a three-center four-electron (3c-4e) bond.[45] As it is possible to see in Table 6, the values of three-center indices are in all cases negative, which implies that three-center bonds in the corresponding molecules are of 3c-4e nature.

Although the existence of three-center bonds in these molecules is widely accepted, one can certainly ask whether or to what extent the values of multicenter indices are biased by the use of artificial Mulliken-like partitioning in (21). With this in mind, we have studied the possibilities of formulating the generalized population analysis within the AIM theory similar to previously reported generalization of Mulliken-like pair population analysis.[27] We have found that such a generalization is indeed possible and the detailed study of the phenomenon of multicenter bonding will be published elsewhere.[54] Without going into unnecessary details, we present in Table 6 the preliminary results of our calculations for the particular case of the N_2O, $N_3^{(-)}$, CO_2, SO_2, and SO_3 molecules. Although the values of AIM generalized three-center bond indices in CO_2, SO_2, and SO_3 are slightly lower than in remaining cases, the presence of 3c-4e bond is still strongly supported even in these molecules. Similar lowering of AIM generalized three-center bond index was observed also in the case of diborane.[54] As the existence of 3c−2e bonds is in this case beyond any doubts, the reasons for the reported lowering of three-center bond index have still to be clarified and additional studies are certainly required to elucidate the manifestations of the phenomenon of multicenter bonding within AIM theory.

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