Investigation of Some Properties of Multicenter Bond Indices

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Various recently introduced multicenter bond indices were reviewed and their interrelations discussed. In addition to this analysis a simple three-center three-orbital model of three-center bonding was proposed and applied to several molecules with three-center bonds. The applicability of this model was tested by comparing with semiempirically and *ab-initio* calculated bond indices. It was shown that the simple model correctly describes the phenomenon of three-center bonding. Another interesting and useful application of this model concerns the interpretation of the indices as an indicator of the number of electrons involved in three-center bonding (3c-2e vs 3c-4e bonds).

1. Introduction

Although the majority of simple molecules are satisfactorily represented by a classical model of well-localized two-center two-electron (2c-2e) bonds, there are also a lot of examples where this simple model is inadequate. An example in this respect could be the electron deficient molecules like boranes or carboranes, metal atom clusters, etc., for which the existence of three-center two-electron (3c-2e) bonds was proposed.[1−6] Although the existence of three-center bonds can frequently be predicted on the basis of the so-called Lipscomb rules,[7,8] the problem frequently is that in some cases it may be quite difficult to decide where these bonds are to be localized in a molecule. Such a situation was encountered for example in several carboranes where the question was whether the three-center bonds involve BCB or CBC fragments.[9,10] Even if these problems can sometimes be solved using various localization schemes,[1] the need was felt still more urgently to have a procedure which could localize the three-center bonds in a molecule directly. These criteria seem to be satisfied by a recently proposed approach based on the use of the so-called multicenter bond indices.[12−20] These indices were independently proposed by several groups, and already the first examples have shown that by using this approach, the three-center bonds can be detected and localized.[9,21] Although the multicenter bond indices proposed by various groups were formally derived from quite different assumptions, a closer inspection of their properties demonstrates that they are in fact closely related. Our aim in this study is to report a detailed study of the properties of various types of multicenter bond indices and to propose a simple model allowing the evaluation of the strength of three-center bonds as well as to address an important problem of how many electrons are involved in three-center bonding (three-center two-electron (3c-2e) vs three-center four-electron (3c-4e) bonding).

2. Theory

2.1. Closed Shell Systems. The three-center bond indices were first proposed by Gaimbiagi[12] and independently also by Sannigrahi and Kar.[14] According to their proposal, the three-center bond indices were heuristically defined as a triatomic term,

$$I_{ABC} = \sum_{\alpha}^{A}\sum_{\beta}^{B}\sum_{\gamma}^{C}(PS)_{\alpha\beta}(PS)_{\beta\gamma}(PS)_{\gamma\alpha} \tag{1}$$

resulting from the partitioning of the expression

$$\sum_{\alpha}\sum_{\beta}\sum_{\gamma}(PS)_{\alpha\beta}(PS)_{\beta\gamma}(PS)_{\gamma\alpha} = 2^2 N \tag{2}$$

into mono-, bi-, and triatomic contributions. Analogously, z-center bond indices[14] were then related to the partitioning of the product

$$\sum_{\alpha}\sum_{\beta}...\sum_{\omega}(PS)_{\alpha\beta}(PS)_{\beta\gamma}...(PS)_{\omega\alpha} = 2^{z-1}N \tag{3}$$

Independently from this approach one of us (R.P.) has recently proposed a new alternative procedure of introducing the multicenter bond indices based on the formalism of the so-called pair population analysis.[22] Although the philosophy of this analysis is thoroughly described in the original study, we consider it worthwhile to recapitulate briefly the basic ideas of this approach to the extent necessary for the purpose of this study.

The (spinless) pair density, which is the basic quantity of this approach, is defined as a diagonal element of the second-order density matrix by

$$\rho(1,2) = N(N-1)/2\int\Psi^2(1, 2, ...N)\, d\sigma_1\, d\sigma_2\, d\mathbf{x}_3...d\mathbf{x}_N \tag{4}$$

in which the integration is over the spin coordinates of first two electrons and over the spin and space coordinates of remaining ($N-2$) electrons. This pair density can straightforwardly be expressed in the form of the expansion 5 in the basis

$$\rho(1,2) = \sum_{\alpha}\sum_{\beta}\sum_{\gamma}\sum_{\delta}\Omega_{\alpha\beta\gamma\delta}\chi_{\alpha}(1)\,\chi_{\beta}(1)\,\chi_{\gamma}(2)\,\chi_{\delta}(2) \tag{5}$$

of atomic orbitals and where the pair density itself is represented by the four-index matrix Ω. At the level of SCF approximation

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which is of our concern here, the matrix Ω can be expressed in terms of usual charge density bond order matrix P:

$$\Omega_{\alpha\beta\gamma\delta} = (1/2)P_{\alpha\beta}P_{\gamma\delta} - (1/4)P_{\alpha\gamma}P_{\beta\delta} \tag{6}$$

Although the population analysis schemes were proposed already for this orbital-based expansion (5),[23,24] we preferred in our approach to expand the pair density (4) in the basis of two-electron functions, the so-called geminals:

$$\rho(1,2) = \sum_i \sum_j \Gamma_{ij} \lambda_i(1,2)\, \lambda_j(1,2) \tag{7}$$

The advantage of this geminal expansion is that the pair density is now represented in terms of the normal two-index matrix Γ, which is much simpler to work with. The population analysis can thus be introduced in a direct analogy with normal Mulliken population analysis.[25] While the parallel with the Mulliken population analysis manifests itself in that only mono- and biatomic pair populations result from the expansion 7, there is also one important difference. This difference arises from the fact that the matrix Γ in expansion 7 is block diagonal, with one block corresponding to singlet and the other to triplet states of the electron pair.

$$\Gamma = \Gamma^{\mathrm{s}} \oplus \Gamma^{\mathrm{t}} \tag{8}$$

Because of this, it is possible to introduce the individual singlet and triplet pair populations, and the resulting formulas are given in eqs 9−12.

$$\Pi^{\mathrm{s}}_A = (1/4)\sum_{\mu}^{A}(PS)_{\mu\mu} + (1/4)\sum_{\mu<\nu}^{A}((PS)_{\mu\mu}(PS)_{\nu\nu} + (PS)_{\mu\nu}(PS)_{\nu\mu}) \tag{9}$$

$$\Pi^{\mathrm{s}}_{AB} = (1/4)\sum_{\mu}^{A}\sum_{\nu}^{B}((PS)_{\mu\mu}(PS)_{\nu\nu} + (PS)_{\mu\nu}(PS)_{\nu\mu}) \tag{10}$$

$$\Pi^{\mathrm{t}}_A = (3/4)\sum_{\mu<\nu}^{A}((PS)_{\mu\mu}(PS)_{\nu\nu} - (PS)_{\mu\nu}(PS)_{\nu\mu}) \tag{11}$$

$$\Pi^{\mathrm{t}}_{AB} = (3/4)\sum_{\mu}^{A}\sum_{\nu}^{B}((PS)_{\mu\mu}(PS)_{\nu\nu} - (PS)_{\mu\nu}(PS)_{\nu\mu}) \tag{12}$$

These populations in which P and S denote the normal first-order density matrix and the overlap matrix, respectively, satisfy the natural normalization condition

$$\sum_A(\Pi^{\mathrm{s}}_A + \Pi^{\mathrm{t}}_A) + \sum_{A<B}(\Pi^{\mathrm{s}}_{AB} + \Pi^{\mathrm{t}}_{AB}) = N(N-1)/2 \tag{13}$$

which requires the pair density to be normalized to the total number of pairs.

In a previous study[22] we have demonstrated that instead of these individual singlet and triplet pair populations, which are difficult to interpret, it is useful to introduce the so-called effective pair populations, which are defined as

$$\Pi^{\mathrm{eff}}_A = \Pi^{\mathrm{s}}_A - (1/3)\Pi^{\mathrm{t}}_A \tag{14}$$

$$\Pi^{\mathrm{eff}}_{AB} = \Pi^{\mathrm{s}}_{AB} - (1/3)\Pi^{\mathrm{t}}_{AB} \tag{15}$$

As can easily be demonstrated, these indices are in fact equivalent to the so-called Wiberg indices,[26] which are closely related to classical bond multiplicities.

$$\Pi^{\mathrm{eff}}_{AB} = (1/2)W_{AB} = (1/4)\sum_{\alpha}^{A}\sum_{\beta}^{B}(PS)_{\alpha\beta}(PS)_{\beta\alpha} \tag{16}$$

On the basis of this interpretation of effective pair populations, we attempted to generalize the formalism of the pair population analysis so as to be applicable also to more complex bonding situations with multicenter bonds, etc. The straightforward possibility of such a generalization is to analyze, instead of the pair density itself, its square since in this case also the three- and four-center terms can appear. Consistent with this philosophy, the so-called nonlinear pair population analysis was recently proposed.[15] In this analysis, the individual contributions were derived from the partitioning of the term 17 into mono-, bi-, tri-, and tetratomic contributions.

$$\sum_{\alpha}\sum_{\beta}\sum_{\gamma}\sum_{\delta}(\Gamma_{\alpha\gamma}\Sigma_{\gamma\beta})(\Gamma_{\beta\delta}\Sigma_{\delta\alpha}) = N(N-1)/2 \tag{17}$$

($\Sigma_{\alpha\beta}$ is the overlap integral in the geminal basis.)

$$\Sigma_{\alpha\beta} = \int \lambda_{\alpha}(1,2)\, \lambda_{\beta}(1,2)\, \mathrm{d}\tau_1\, \mathrm{d}\tau_2 \tag{18}$$

Parallel to what was observed for linear pair population analysis, we found it useful to introduce the effective pair populations also for nonlinear analysis.

$$\Delta^{\mathrm{eff}}_A = \Delta^{\mathrm{s}}_A - (1/3)\Delta^{\mathrm{t}}_A \tag{19}$$

$$\Delta^{\mathrm{eff}}_{AB} = \Delta^{\mathrm{s}}_{AB} - (1/3)\Delta^{\mathrm{t}}_{AB} \tag{20}$$

$$\Delta^{\mathrm{eff}}_{ABC} = \Delta^{\mathrm{s}}_{ABC} - (1/3)\Delta^{\mathrm{t}}_{ABC} \tag{21}$$

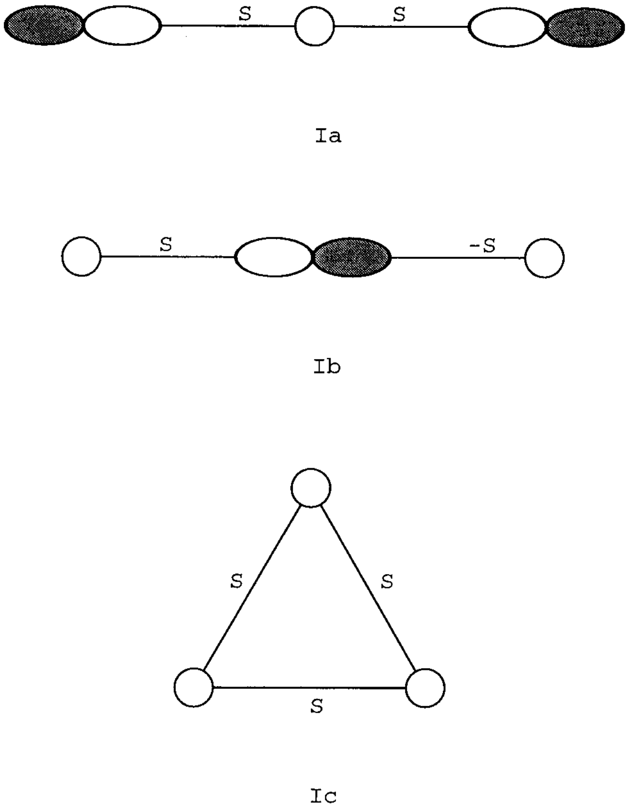
$$\Delta^{\mathrm{eff}}_{ABCD} = \Delta^{\mathrm{s}}_{ABCD} - (1/3)\Delta^{\mathrm{t}}_{ABCD} \tag{22}$$

In keeping with the expectations, the nonlinear effective pair populations Δ^{eff} are indeed able to detect the presence of multicenter bonding, and several examples of such a detection can be found in a recent study.[21] The three-center bonds were in all cases detected by the presence of a nonvanishing three-center term Δ_{ABC}. Although the above introduction of the nonlinear effective pair populations does not seem to exhibit any relation to previously introduced multicenter bond indices, such a relation does exist. As it is possible to show, the effective pair populations Δ^{eff} defined by eqs 19−22 are identical with mono-, bi-, tri-, and tetratomic components resulting from the decomposition of the term

$$(1/16)\sum_{\alpha}\sum_{\beta}\sum_{\gamma}\sum_{\delta}(PS)_{\alpha\beta}(PS)_{\beta\gamma}(PS)_{\gamma\delta}(PS)_{\delta\alpha} = N/2 \tag{23}$$

which is, except for the normalizing factor 1/16, equivalent to (3) for the specific case of the four-center bond index. This normalization which we propose to include in the original definition[12,14] of multicenter bond indices has the advantage of allowing the direct comparison of multicenter bond indices of different rank. This comparability arises from scaling the identity 3, from which the general z-center bond indices are derived, by a factor $1/2^z$, owing to which the identity 3 becomes normalized to the universal quantity $N/2$ irrespective of the value of z. Adopting this normalization, both types of multicenter bond indices are completely equivalent, irrespective of quite different underlying philosophies. In this connection it is worth noting the above mentioned relation of linear effective pair populations Π^{eff} to Wiberg indices. In view of this parallel, these indices can be regarded as two-center bond indices, and

SCHEME 1



as such, they straightforwardly describe the structure of molecules with well-localized 2c-2e bonds.[27,28]

Having demonstrated the close parallel between the multicenter bond indices and the effective pair populations Π^{eff} and Δ^{eff}, it is worth mentioning another useful property of these quantities as a simple measure of the relative strength of corresponding bonds. The simplest situation is with pair populations Π^{eff} which, as a good measure of the bond order, can be related via the so-called BEBO relationship[29−31] to the experimental bond energies. A bit more complex situation is, however, with genuine multicenter bonds, where the relationship analogous to the BEBO relation does not exist. To overcome this drawback, we propose here a simple model in terms of which it is possible to estimate the limiting value of three- or multicenter bond indices for ideal multicenter bonds. Because of the fact that in our previous studies we have never seen a case of a four-center bond, we confine our model to the simple case of a three-center bond only. For this purpose let us consider a simple three-center three-orbital model[32] proposed by one of us (I.M.) some time ago. This model, originally proposed for the description of 3c-2e bonds with the bonding topology Ia (Scheme 1) and 3c-4e bonds with bonding topology Ib, was further generalized to include also the case of 3c-4e bonds with topology Ia and 3c-2e bonds with topology Ib.

The advantage of these models is that they can be solved analytically, and such a solution straightforwardly demonstrates that irrespective of actual bonding topologies (Ia vs Ib) the 3c-2e bonds always give $I_{ABC} = 0.1875$, while the value $I_{ABC} = -0.1875$ results for 3c-4e bonds. Quite analogously, the bonding topology Ic, characteristic, for example, of the H_3^+ ion, leads to the idealized value $I_{ABC} = 0.2222$ for 3c-2e bonds. In connection with these models it is interesting to stress that the values of analytically derived indices do not depend on the actual values of overlap integrals between the interacting orbitals. This implies that the calculated idealized limits can be regarded as transferable from one case to another so that they can reasonably well be applied to various bonding situations.

This result is important for two reasons. The first of them is that it opens the possibility of estimating the relative strength of three-center bonding by comparing the actual value of I_{ABC} in a particular case with the limiting values derived from the above idealized models. The other important conclusion that can be deduced from the analysis of three-center bond indices concerns the evaluation of the number of electrons involved in such bonding. Such an evaluation is based on the fact that the three-center bond indices for 3c-2e and 3c-4e differ in sign. While the positive values of three-center bond indices imply the presence of a 3c-2e bond, the negative value can be regarded as an indication of the presence of 3c-4e bonding. In this connection is it fair to say that a similar interpretation of three-center bond indices was heuristically proposed by Kar and Marcos,[33] but their interpretation was subsequently questioned by Giambiagi.[34] The results of our analytical model thus provide independent support in favor of the original interpretation.

2.2. Open Shell Systems. Up to here all our considerations concerned the multicenter bond indices for closed shell molecules. Since, however, the phenomenon of multicenter bonding is not likely to be restricted to only closed shell species, it is of interest to extend the formalism of multicenter bond indices to the case of open shell species as well. The basis of this generalization is our previous study[16] in which we demonstrated that three-center bond indices are closely related to the decomposition of the quantity

$$\int \rho_1(1,2)\, \rho_1(2,3)\, \rho_1(3,1)\, \mathrm{d}\tau_1\, \mathrm{d}\tau_2\, \mathrm{d}\tau_3 \tag{24}$$

into mono-, bi-, and triatomic contributions. If, now, the closed shell expression for the nondiagonal element of first-order density matrix

$$\rho_1(i,j) = 2\sum_k \phi_k(i)\, \phi_k(j) \tag{25}$$

is replaced by an analogous open shell UHF equivalent

$$\rho_1(i,j) = \sum_k \phi_k(i)\, \phi_k(j) + \sum_l \overline{\psi_l}(i)\, \overline{\psi_l}(j) \tag{26}$$

then simple algebra straightforwardly leads to the identity

$$\sum_\alpha \sum_\beta \sum_\gamma ((PS)^\alpha_{\alpha\beta}(PS)^\alpha_{\beta\gamma}(PS)^\alpha_{\gamma\alpha} + (PS)^\beta_{\alpha\beta}(PS)^\beta_{\beta\gamma}(PS)^\beta_{\gamma\alpha}) = N_\alpha + N_\beta \tag{27}$$

whose decomposition into mono-, bi-, and triatomic contributions gives the desired three-center bond indices.

3. Results and Discussion

Having presented the theoretical background of our investigation of multicenter bond indices, let us proceed now to the quantitative confrontation of our simple model with the actual calculations. For this purpose we calculated the values of three-center bond indices for several simple molecules with both 3c-2e and 3c-4e bonds. The molecules studied involved the B_2H_6, allyl cation, allyl anion, H_3^+, $(FHF)^-$, and HNCO. In all cases the molecular geometries were completely optimized at each particular level. The calculations were performed both by the semiempirical AM1 method[35] and also at the *ab-initio* SCF level with basis sets ranging from minimal STO-3G to 6-31G* (for cations and neutrals) or the even more flexible 6-31+G** (for

TABLE 1: Comparison of AM1 and *ab-Initio* Calculated Values of Three-Center Bond Indices for Several Simple Molecules

molecule	population	AM1	STO-3G	6-31G*/6-31+G**
H_3^+	HHH	0.222	0.222	0.222
allyl cation	CCC	0.169	0.173	0.158
B_2H_6	BH_bB	0.175	0.174	0.178
allyl anion	CCC	−0.170	−0.173	−0.193
FHF^-	FHF	−0.119	−0.150	−0.025
HNCO	NCO	−0.240	−0.266	−0.176

anions). The *ab-initio* calculations were performed by Gaussian 92.[36] In all cases the molecular geometries were completely optimized at each particular level. The resulting values of three center bond indices are summarized in Table 1.

Before starting the discussion of these data it is useful to make a brief remark concerning the presumed basis set dependence of resulting populations. Although it is true that such a dependence can indeed be expected for any type of Mulliken-like population analysis, the tests which we recently performed for the closely related two-center bond indices[37] suggest that such a dependence is in fact smaller than might have been anticipated. We found, namely, that especially for better basis sets the values of populations are more or less converged to some final limiting values so that any further improvement in the quality of the basis brings only unimportant additional corrections. As a consequence, the negligible basis set dependence provides a certain guarantee that the discussion based on the values of multicenter bond indices will be meaningful.

After this preliminary remark, let us attempt now to discuss the values in Table 1. The simplest situation is for H_3^+, allyl cation, allyl anion, and B_2H_6, whose bonding topologies closely correspond to idealized analytical models (Ic and Ia respectively). As a consequence, the values of three-center bond indices closely approach the limits derived from analytical models irrespective of the method and basis set used. In this respect the most typical situation is for H_3^+ ion, where both semiempirical and *ab-initio* indices are exactly equal to the limiting value 0.222. This allows us to conclude that strong and completely developed 3c-2e bonds exist in H_3^+, allyl cation, and B_2H_6, while a strong 3c-4e bond can be expected to exist in allyl anion. A little bit more complex situation is the case of the remaining molecules HNCO and, especially, FHF^-, where the sensitivity of the indices to the quality of the method used starts to appear. This is especially true of FHF^-, where the values range from −0.150 for STO-3G basis set to −0.025 for 6-31+G** basis set. The reason for this enormous decrease is not so far completely clear to us, but it is probable that it can arise, at least in part, from the fact that the actual bonding topology is in this case much more complex than that for which the idealized limit was derived. Thus, for example, in addition to a simple 3c-4e σ bond for which the model applies, one also can imagine a counteracting π contribution to three-center bonding in this case. This could explain why the strong decrease is observed specifically for the high-quality 6-31+G** basis, where the polarization p orbitals on the hydrogen atom can be involved in π bonding, whereas for semiempirical or STO-3G *ab-initio* methods, where these polarization functions are not available, the resulting indices are quite close to idealized limits.

We can thus conclude that the multicenter bond indices can be regarded as a new efficient means of detection and localization of multicenter bonding in molecules, and we believe that their systematic use can substantially contribute to the visualization and better understanding of the structure of molecules with complex bonding patterns. In addition to this, the proposed simple three-center three-orbital model provides a good basis for the qualitative understanding of the factors responsible for the existence and the strength of three-center bonding in molecules.

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