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Studies of Population Analysis at the Correlated Level: Determination of Three-Center Bond Indices

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This paper constitutes an extension of our previous works on multicenter bondings and bond orders in order to determine three-center indices at the correlated level. A new manipulation of our algorithms allows us to establish suitable relationships between three-center bond indices, two-center bond ones, and the number of effectively unpaired electrons, at any level of theory. Several numerical calculations of population analysis, in selected molecules, are carried out, and the results are analyzed and discussed.

1. Introduction

During the past decades, new theoretical and computational techniques have appeared in the literature providing a spectacular advance of the quantum chemistry and other related areas. This progress has allowed one to know much better the nature and features of chemical bondings but quite often the used methodologies have turned out to be too sophisticated for the ordinary chemical language. Classical concepts as atomic charges, bond indices, valences, free valence indices, etc. are still extremely useful for chemists in the understanding and description of molecular structures as well as in the study of reactivity of molecules, radicals, and other species. Within the methods which enable us to describe these quantities, avoiding the explicit use of the cumbersome *N*-electron wave functions, the studies of electronic population analysis have revealed to be very useful tools.

As is well-known, the techniques of population analysis carry out partitionings of a determined molecular property into different contributions which are usually expressed by the elements of the reduced density matrices and the elements of the overlap matrices.[1−4] These partitionings are performed in the Hilbert space spanned by the basis function set (Mulliken scheme) or alternatively over the physical space (topological scheme). In particular, bond indices related with the classical two-center two-electron scheme of bonding have extensively been studied, at any level of theory, through the partitioning of the *N* electrons in the system.[5−18] However, there are a significant number of systems in which this model turns out to be too simple to get an appropriate description of the molecular features. Examples of such systems are the electron deficient molecules such as boranes, carboranes, or hypervalent molecules for which the existence of three-center two-electron or three-center four-electron bondings has been proposed.[19−25] In a previous study, we have described the physical meaning and mutual relationships between multicenter bond indices which arise from various population analysis schemes, testing numerically our equations at the Hartree−Fock level of theory.[24] The first purpose of this paper is to go beyond reporting a rigorous theoretical framework which is valid at any level of theory as well as results of three-center bond indices obtained at correlated level.

On the other hand, the effectively unpaired electron density matrix has proved to be an appropriate tool to describe the radical and diradical character in molecules of any spin symmetry as well as other aspects related with valences.[26−32] Recently, we have reported the connection between the elements of this matrix and two-center two-electron bond indices at the correlated level using population analysis techniques.[33,34] Another aim of this report is to extend this study so that we can describe a partitioning of the *N* electrons in the system which allows to relate three-center indices, two-center ones, and the matrix of effectively unpaired electrons.

We have organized this paper as follows. The second section describes the basic theoretical concepts which will be used in this work. The third section reports the algorithms and formulas of population analysis proposed for describing three-center indices. In the fourth section, some results for several systems and the corresponding discussion are presented. Finally, some remarks and conclusions are presented in the last section

2. Theoretical Background

Let us consider a set of orthonormal orbitals $\{i, j, k, l,...\}$ and the corresponding spin−orbital set $\{i^\alpha, i^\beta, j^\alpha, j^\beta, k^\alpha, k^\beta, l^\alpha, l^\beta...\}$. As is well-known, the operator number of electrons is $\hat{N} = \sum_\sigma \sum_{i,j} \delta_{ij}\, c^\dagger_{i\sigma} c_{j\sigma}$ where $c^\dagger_{i\sigma}$, $c_{j\sigma}$, etc. are the creation and annihilation fermion operators used in the second quantized formalism[35] and σ is the spin coordinate (α or β). The spin-free first-order replacement operators of partices and holes are, respectively[36]

$$E^i_j = \sum_\sigma c^\dagger_{i\sigma} c_{j\sigma} \tag{1}$$

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$$\bar{E}^i_j = \sum_\sigma c_{i\sigma} c^\dagger_{j\sigma} \qquad (2)$$

The expectation values of these operators for a determined N-electron state $|\mathscr{L}\rangle$ define the matrix elements of the spin-free first-order density matrix of particles and holes

$$^1D^i_j = \langle \mathscr{L} | E^i_j | \mathscr{L} \rangle \qquad (3)$$

$$^1\bar{D}^i_j = \langle \mathscr{L} | \bar{E}^i_j | \mathscr{L} \rangle \qquad (4)$$

Using the spin-free replacement operators one can express $\hat{N}$ as

$$\hat{N} = \sum_{i,j} \delta_{ij}\, E^i_j \qquad (5)$$

and the substitution of the Kronecker delta by the well-known relation $\delta_{ij} = {}^1\!/_2({}^1D^i_j + {}^1\bar{D}^i_j)$ allows us to write eq 5 as

$$\hat{N} = \frac{1}{2}\sum_{i,j} {}^1D^i_j\, E^i_j + \frac{1}{2}\sum_{i,j} {}^1\bar{D}^i_j\, E^i_j \qquad (6)$$

or, alternatively

$$\hat{N} = \sum_{i,j} \frac{1}{2}({}^1D^i_j - {}^1\bar{D}^i_j)\, E^i_j + \sum_{i,j} {}^1\bar{D}^i_j\, E^i_j \qquad (7)$$

Closing both sides of eq 7 by the N-electron state $|\mathscr{L}\rangle$, one obtains the number of electrons of the system, N. In this way, the second term of the right-hand side (rhs) in this eq, that is, $\sum_{i,j} {}^1\bar{D}^i_j\, E^i_j$, produces

$$N_\mathrm{u} = \sum_{i,j} {}^1\bar{D}^i_j\, {}^1D^j_i = \sum_i u^i_i = \sum_i (2\, {}^1D^i_i - \sum_j {}^1D^i_j\, {}^1D^j_i) \qquad (8)$$

in which N_u is the number of effectively unpaired electrons, which is the trace of the density matrix of effectively unpaired electrons[26−28]

$$u^i_j = \sum_k {}^1\bar{D}^i_k\, {}^1D^k_j = 2\, {}^1D^i_j - \sum_k {}^1D^i_k\, {}^1D^k_j \qquad (9)$$

The density matrix of effectively unpaired electrons is a one-electron matrix initially proposed by Takatsuka et al.[26] and Takatsuka and Fueno[27] to characterize the occupancy of different portions of space by spin-up and spin-down electrons. According to these authors, the density of effectively unpaired electrons represents the spatial distribution of odd electrons in open shell molecules but it also accounts for the partial split of electron pairs that appears, even in closed shell systems, when the electronic correlation is taken into account. More recently Staroverov and Davidson have studied the properties of this matrix in connection with the extent of the radical and diradical character in molecules and transition states of any spin multiplicity.[29,30] Likewise, we have described the relationships between cumulant matrices[31,37] and the effectively unpaired electron density matrix carrying out preliminary studies of topological population analyses[33] with this tool. Other alternatives to describe the effectively unpaired electron density have also been proposed;[38] however, in this paper, the most "classical" formulation of this matrix will be used since it appears in this form in the quantum framework.

The matrix elements ${}^1\bar{D}^i_j$ and ${}^1\!/_2({}^1D^i_j - {}^1\bar{D}^i_j)$ are the coefficients of the first-order operator E^i_j of the rhs in eq 7. Hence, these quantities can be regarded as the one-electron integrals used in the second quantized formalism. The unpaired electron number integrals are just the ${}^1\bar{D}^i_j$ matrix elements since they provide the calculation of the "unpaired electron number", $N_\mathrm{u} = tr({}^1\bar{D}\ {}^1D)$ (see eq 8). Similarly, according to this approach, the matrix elements ${}^1\!/_2({}^1D^i_j - {}^1\bar{D}^i_j)$, that is the first term of the rhs in eq 7 are the paired electron number integrals and consequently the number of paired electrons, N_p, must be calculated as $N_\mathrm{p} = \sum_{i,j} {}^1\!/_2({}^1D^i_j - {}^1\bar{D}^i_j){}^1D^j_i$ which is equivalent to

$$N_\mathrm{p} = \sum_{i,j,k} \frac{1}{2}({}^1D^i_j - {}^1\bar{D}^i_j)\, {}^1D^j_k\, \delta_{ki} \qquad (10)$$

The substitution in eq 10 of the Kronecker delta by $\delta_{ki} = {}^1\!/_2({}^1D^k_i + {}^1\bar{D}^k_i)$ taking into account eq 9, allows us to express

$$N_\mathrm{p} = \frac{1}{4}\sum_{i,j,k} {}^1D^i_j\, {}^1D^j_k\, {}^1D^k_i - \frac{1}{4}\sum_{i,j} u^i_j\, {}^1\bar{D}^j_i \qquad (11)$$

Consequently, the total number of electrons of the system is

$$N = \frac{1}{4}[\sum_{i,j,k} {}^1D^i_j\, {}^1D^j_k\, {}^1D^k_i - \sum_{i,j} u^i_j\, {}^1\bar{D}^j_i] + N_\mathrm{u} \qquad (12)$$

which can also be expressed only in terms of the first-order reduced density matrix elements as

$$N = \frac{1}{4}[tr({}^1D)^3 + tr(u\ {}^1D) - 2\, N_\mathrm{u}] + N_\mathrm{u} \qquad (13)$$

Equation 13 accounts for the total number of electrons (paired and unpaired) of the system at any level of theory. A similar equation, in terms of the trace of the square of the ${}^1D$ matrix that is, $N = {}^1\!/_2[tr({}^1D)^2 - N_\mathrm{u}] + N_\mathrm{u}$, has recently been reported in ref 33 providing a suitable determination of classical two-center bond indices through studies of population analysis. As eq 13 is expressed in terms of the cube of the ${}^1D$ matrix, it provides the appropriate tools to detect and evaluate three-center bond indices, which is performed in the next sections.

3. Population Analysis

A partitioning of N electrons in eq 13 according to Mulliken[1,2] scheme leads to

$$N = \sum_A \Delta^{(3)}_A + \sum_{A<B} \Delta^{(3)}_{AB} + \sum_{A<B<C} \Delta^{(3)}_{ABC} + \sum_A u_A \qquad (14)$$

where

$$\Delta^{(3)}_A = \frac{1}{4}\sum_i^A \sum_j^A \sum_k^A {}^1D^i_j\, {}^1D^j_k\, {}^1D^k_i + \frac{1}{4}\sum_i^A \sum_j^A u^i_j\, {}^1D^j_i - \frac{1}{2}\sum_i^A u^i_i \qquad (15)$$

$$\Delta^{(3)}_{AB} = \frac{1}{4}\left[\frac{3!}{2}(\sum_i^A \sum_j^A \sum_k^B {}^1D^i_j\, {}^1D^j_k\, {}^1D^k_i + \sum_i^A \sum_j^B \sum_k^B {}^1D^i_j\, {}^1D^j_k\, {}^1D^k_i)\right] + \frac{1}{2}\sum_i^A \sum_j^B u^i_j\, {}^1D^j_i \qquad (A < B) \quad (16)$$

$$\Delta^{(3)}_{ABC} = \frac{1}{4}\sum_{P(ABC)} \sum_i^A \sum_j^B \sum_k^C {}^1D^i_j\, {}^1D^j_k\, {}^1D^k_i \qquad (A < B < C) \quad (17)$$

$$u_A = \sum_i^A u_i^i \tag{18}$$

A, B, C, etc. stand for different nuclei of the system, the superscript (3) means that the corresponding quantities $\Delta^{(3)}$ derive from the partitioning of a cubic equation and $P(ABC)$ are the permutations ABC, ACB, etc. The last term in eq 14 constitutes the partitioning of the unpaired electrons; the populations u_A coincide with Mayer's free valence on the nucleus A for singlet wave functions.[8] The three first terms in eq 14 represent the partitioning of the paired electrons according to they belong to one, two or three nuclei so that $\Delta^{(3)}_{ABC}$ is an appropriate quantity to describe a three-center bonding.

Heuristic exchange type two-center bond indices, I_{AB}, and three-center bond indices, I_{ABC}, have been defined as[8,19−22]

$$I_{AB} = \sum_i^A \sum_j^B {}^1D_j^i \, {}^1D_i^j \tag{19}$$

$$I_{ABC} = \sum_i^A \sum_j^B \sum_k^C {}^1D_j^i \, {}^1D_k^j \, {}^1D_i^k \tag{20}$$

A simple algebra allows us to establish the relationships between the above bond indices and the quantities resulting from the partitioning of N electrons expressed by formula 14

$$I_{AB} = \frac{2}{3} \Delta^{(3)}_{AB} + \frac{1}{3} \sum_{C \neq A C \neq B} \Delta^{(3)}_{ABC} + \frac{1}{6} \sum_i^A \sum_j^B {}^1D_j^i \, u_i^j \tag{21}$$

$$\sum_{P(ABC)} I_{ABC} = 4\, \Delta^{(3)}_{ABC} \tag{22}$$

A rigorous derivation of eq 19 has recently been proposed and tested, at the correlated level, in systems with conventional bonding patterns.[33] However, eq 21 shows that in systems possessing three-center bondings the three-center contribution is hidden in an average way in the I_{AB} indices. Moreover, as the products ${}^1D_j^i \, u_i^j$ only produce exchange type terms, the "exchange type" representation of bond indices is kept in this scheme.

Other definitions of bond indices[14,22] are based on the covariance or correlation of fluctuations of the charge operators $\hat{q}_A$, $\hat{q}_B$, and $\hat{q}_C$, that is $-2\, \langle(\hat{q}_A - \langle\hat{q}_A\rangle)(\hat{q}_B - \langle\hat{q}_B\rangle)\rangle$ (two centers) and $2\langle(\hat{q}_A - \langle\hat{q}_A\rangle)(\hat{q}_B - \langle\hat{q}_B\rangle)(\hat{q}_C - \langle\hat{q}_C\rangle)\rangle$ (three centers) where $\hat{q}_A = \sum_i^A E_i^i$ and similarly for $\hat{q}_B$ and $\hat{q}_C$. Both definitions of bond indices, exchange, and fluctuation, are coincident at the Hartree−Fock level but lead to different numerical values when correlated wave functions are used. A determination of fluctuation type bond indices requires to handle second-order and third-order reduced density matrices, which arise from the products $\hat{q}_A\hat{q}_B$ and $\hat{q}_A\hat{q}_B\hat{q}_C$, respectively. However, the exchange type definitions only need the elements of the first-order reduced density matrix which provides a simpler procedure in a computational point of view. Within the topological approach, the whole real space is partitioned according to the Bader's atomic regions,[3] Ω_A. Taking into account that this partitioning holds $\Omega = \cup_A \Omega_A$ and $\Omega_A \cap \Omega_B = \Phi$ $(\forall A, B; A \neq B)$, eq 13 can be written in the form

$$N = \sum_{\Omega_A} \Delta^{(3)}_{\Omega_A} + \sum_{\Omega A < \Omega B} \Delta^{(3)}_{\Omega_A \Omega_B} + \sum_{\Omega_A < \Omega_B < \Omega_C} \Delta^{(3)}_{\Omega_A \Omega_B \Omega_C} + \sum_{\Omega_A} u_{\Omega_A} \tag{23}$$

which is the counterpart of eq 14 in the topological approach and where

$$\Delta^{(3)}_{\Omega_A} = \frac{1}{4} [\sum_{i,j,k,l,m,n} {}^1D_j^i \, {}^1D_l^k \, {}^1D_n^m \, S_{in}(\Omega_A)\, S_{kj}(\Omega_A)\, S_{ml}(\Omega_A) + \sum_{i,j,k,l} u_j^i \, {}^1D_l^k \, S_{il}(\Omega_A)\, S_{kj}(\Omega_A) - 2 \sum_{i,j} u_j^i \, S_{ij}(\Omega_A)] \tag{24}$$

$$\Delta^{(3)}_{\Omega_A \Omega_B} = \frac{1}{4} \left[\frac{3!}{2} (\sum_{i,j,k,l,m,n} {}^1D_j^i \, {}^1D_l^k \, {}^1D_n^m \, S_{in}(\Omega_A)\, S_{kj}(\Omega_A)\, S_{ml}(\Omega_B) + \sum_{i,j,k,l,m,n} {}^1D_j^i \, {}^1D_l^k \, {}^1D_n^m \, S_{in}(\Omega_A)\, S_{kj}(\Omega_B)\, S_{ml}(\Omega_B)) \right] + \frac{1}{2} \sum_{i,j,k,l} u_j^i \, D_l^{1k} \, S_{il}(\Omega_A)\, S_{kj}(\Omega_B) \quad (\Omega_A < \Omega_B) \tag{25}$$

$$\Delta^{(3)}_{\Omega_A \Omega_B \Omega_C} = \frac{1}{4} \sum_{P(\Omega_A \Omega_B \Omega_C)} \sum_{i,j,k,l,m,n} \times {}^1D_j^i \, {}^1D_l^k \, {}^1D_n^m \, S_{in}(\Omega_A)\, S_{kj}(\Omega_B)\, S_{ml}(\Omega_C) \quad (\Omega_A < \Omega_B < \Omega_C) \tag{26}$$

$$u_{\Omega A} = \sum_{i,j} u_j^i \, S_{ij}(\Omega_A) \tag{27}$$

in which $S_{ij}(\Omega_A)$, $S_{kl}(\Omega_B)$, etc. are the elements of the overlap matrices calculated over the regions Ω_A, Ω_B, etc. and $P(\Omega_A \Omega_B \Omega_C)$ are the permutations $\Omega_A \Omega_B \Omega_C$, $\Omega_A \Omega_C \Omega_B$, etc. Equations 24−27 are the counterparts of eqs 15−18, respectively, in the topological version.

Two-center indices in a topological sheme have been calculated for a number of systems at uncorrelated and correlated level.[4,12,15,33] However, only uncorrelated topological exchange type three-center indices have been reported so far for a few number of systems.[39] Topological exchange type two-center indices $I_{\Omega_A \Omega_B}$ and three-center indices $I_{\Omega_A \Omega_B \Omega_C}$ have been defined as

$$I_{\Omega_A \Omega_B} = \sum_{i,j,k,l} {}^1D_j^i \, {}^1D_l^k \, S_{il}(\Omega_A)\, S_{kj}(\Omega_B) \tag{28}$$

$$I_{\Omega_A \Omega_B \Omega_C} = \sum_{i,j,k,l,m,n} {}^1D_j^i \, {}^1D_l^k \, {}^1D_n^m \, S_{in}(\Omega_A)\, S_{kj}(\Omega_B)\, S_{ml}(\Omega_C) \tag{29}$$

Obviously, the above proposed $\Delta^{(3)}_{\Omega_A \Omega_B \Omega_C}$ indices are equivalent to

$$\Delta^{(3)}_{\Omega_A \Omega_B \Omega_C} = \frac{1}{4} \sum_{P(\Omega_A \Omega_B \Omega_C)} I_{\Omega_A \Omega_B \Omega_C} \tag{30}$$

4. Results and Discussion

The quantities reported in the previous section have been tested on numerical determinations in order to check their possibilities to describe and to detect simultaneously three-center bondings, two-center ones, and unpaired electrons at correlated level. The calculations were carried out using a modified Gaussian 94[40] program, which generated the first-order reduced density matrix elements as well as the elements of the overlap matrices $S_{ij}(\Omega_A)$ which appear in the topological approach. In a subsequent step, these matrices were subject to population analysis by our own computational implementation. The reported results have been obtained with the basis sets 6-31G. For all systems, the geometries were optimized for these basis sets within configuration interaction (CI) wave functions with single

TABLE 1: Calculated Values of Bond Indices I_{AB} and Populations $\Delta^{(3)}_{AB}$, $\Delta^{(3)}_{ABC}$, u_A (Mulliken-Type) and Bond Indices $I_{\Omega_A\Omega_B}$ and Populations $\Delta^{(3)}_{\Omega_A\Omega_B}$, $\Delta^{(3)}_{\Omega_A\Omega_B\Omega_C}$, u_{Ω_A} (Topological) for Systems with Three-Center Bondings in the SDCI Approximation

system	fragment	I_{AB}	$\Delta^{(3)}_{AB}$	$\Delta^{(3)}_{ABC}$	u_A	$I_{\Omega_A\Omega_B}$	$\Delta^{(3)}_{\Omega_A\Omega_B}$	$\Delta^{(3)}_{\Omega_A\Omega_B\Omega_C}$	u_{Ω_A}
H_3^+	H				0.039				0.039
	HH	0.425	0.428			0.427	0.429		
	HHH			0.416				0.418	
B_2H_6	B				0.162				0.095
	$H_{terminal}$				0.044				0.065
	$H_{bridging}$				0.048				0.071
	BB	0.465	0.418			0.146	0.064		
	$(BH)_{terminal}$	0.947	1.441			0.673	0.936		
	$(BH)_{bridging}$	0.434	0.519			0.383	0.426		
	BHB			0.303				0.136	
CO_2	C				0.216				0.168
	O				0.253				0.277
	CO	1.784	2.947			1.518	2.387		
	OO	0.254	0.650			0.370	0.666		
	OCO			−0.537				−0.224	
allyl cation	C_1				0.205				0.194
	C_2				0.212				0.198
	H_1				0.033				0.039
	H_2				0.032				0.040
	C_1C_2	1.351	1.929			1.395	1.851		
	C_1H_1	0.894	1.369			0.909	1.321		
	C_2H_2	0.882	1.339			0.903	1.307		
	CCC			0.291				0.342	
allyl anion	C_1				0.213				0.201
	C_2				0.199				0.192
	H_1				0.040				0.046
	H_2				0.042				0.049
	C_1C_2	1.430	2.358			1.430	2.132		
	C_1H_1	0.928	1.427			0.980	1.409		
	C_2H_2	0.933	1.429			0.926	1.326		
	CCC			−0.352				−0.141	
Li_4O	Li				0.111				0.066
	O				0.296				0.475
	LiO	0.366	0.500			0.373	0.409		
	LiLi	0.251	0.184			0.091	0.046		
	LiOLi			0.031				0.097	
	LiLiLi			0.171				0.040	
SO_3	S				0.232				0.210
	O				0.260				0.268
	SO	1.199	2.080			1.311	2.111		
	OO	0.189	0.453			0.266	0.501		
	OSO			−0.277				−0.143	
	OOO			−0.062				−0.060	

and double excitations (SDCI). As is well-known, these basis sets are nonorthogonal and consequently, in the Mulliken-type calculations, the matrix elements ${}^1D^i_j$ have systematically been replaced by $({}^1PS)^i_j$ where ${}^1P$ and S are the usual charge density and overlap matrices, respectively.

Table 1 reports the results obtained in the SDCI approximation for systems in which the existence of three-center bondings is commonly accepted (H_3^+, B_2H_6, CO_2, allyl cation, allyl anion) as well as in hypervalent molecules (Li_4O and SO_3) whose description needs nonclassical patterns. This table provides the possibility to perform a direct comparison between the results arising from the two population analysis procedures which have been described in the previous section according to the partitionings (14) and (23). The unpaired electron populations found for these systems are due to the partial splitting which arise from the dispersal of the occupation numbers of the orbitals in the expansion on several Slater determinants. Apart from the B_2H_6 molecule which possesses special features, the first conclusion that can be drawn is that the monatomic populations of unpaired electrons are similar in the Mulliken (u_A) and the topological ($u_{\Omega A}$) versions except in the case of the CO_2 molecule ($u_O = 0.253$, $u_{\Omega_O} = 0.277$, $u_C = 0.216$, $u_{\Omega_C} = 0.168$) and in the Li_4O one ($u_O = 0.296$, $u_{\Omega_O} = 0.475$, $u_{Li} = 0.111$, $u_{\Omega_{Li}} = 0.066$). Our interpretation is that these large differences are due to the stronger electronegative character of the oxygen atom which is better described in the topological method than in the Mulliken-type one.[41] A wider discussion of u_A and $u_{\Omega A}$ populations and their relationships with atomic valences has recently been reported in ref 42. Except in the Li_4O case, the values found for the three-center populations are nonnegligible and the corresponding fragments coincide with the regions where the three-center bondings are expected. The positive values for these populations have been interpreted as three-center two-electron bonds, whereas the negatives ones describe three-center four-electron bonds.[19,21,43] The two above proposed partitionings provide identical sign for the three-center populations in all studied systems but the topological method produces lower values except in the case of allyl cation which has already been pointed out in previous works.[39] The major differences between the shared electron populations arising from both methods are found in the B_2H_6 molecule where the topological approach clearly predicts lower values. Although these differences are in agreement with the results reported by other authors,[4,13] the value found for $\Delta^{(3)}_{\Omega_B\Omega_H\Omega_B} = 0.136$ allows us to confirm that even the topological method predicts the existence of the three-center bonding.

Table 2 shows the results corresponding to identical systems calculated in the closed-shell HF approach in order to carry out

TABLE 2: Calculated Values of Bond Indices I_{AB} and Populations $\Delta^{(3)}_{AB}$, $\Delta^{(3)}_{ABC}$ (Mulliken-Type) and Bond Indices $I_{\Omega_A\Omega_B}$ and Populations $\Delta^{(3)}_{\Omega_A\Omega_B}$, $\Delta^{(3)}_{\Omega_A\Omega_B\Omega_C}$ (Topological) for Systems with Three-Center Bondings in the HF Approximation

system	fragment	I_{AB}	$\Delta^{(3)}_{AB}$	$\Delta^{(3)}_{ABC}$	$I_{\Omega_A\Omega_B}$	$\Delta^{(3)}_{\Omega_A\Omega_B}$	$\Delta^{(3)}_{\Omega_A\Omega_B\Omega_C}$
H_3^+	HH	0.444	0.444		0.444	0.444	
	HHH			0.444			0.444
B_2H_6	BB	0.443	0.384		0.125	0.049	
	$(BH)_{terminal}$	0.992	1.513		0.662	0.920	
	$(BH)_{bridging}$	0.445	0.538		0.371	0.413	
	BHB			0.313			0.123
CO_2	CO	1.810	2.972		1.515	2.378	
	OO	0.233	0.606		0.362	0.648	
	OCO			−0.515			−0.211
allyl cation	C_1C_2	1.408	2.025		1.454	1.932	
	C_1H_1	0.917	1.406		0.937	1.365	
	C_2H_2	0.903	1.373		0.934	1.350	
	CCC			0.291			0.363
allyl anion	C_1C_2	1.469	2.433		1.482	2.205	
	C_1H_1	0.976	1.504		1.017	1.460	
	C_2H_2	0.975	1.496		0.958	1.374	
	CCC			−0.361			−0.143
Li_4O	LiO	0.332	0.454		0.381	0.402	
	LiLi	0.274	0.195		0.110	0.055	
	LiOLi			0.029			0.112
	LiLiLi			0.202			0.054
SO_3	SO	1.243	2.112		1.375	2.190	
	OO	0.162	0.390		0.234	0.437	
	OSO			−0.247			−0.126
	OOO			−0.046			−0.046

TABLE 3: Calculated Values of Bond Indices I_{AB} and Populations $\Delta^{(3)}_{AB}$, $\Delta^{(3)}_{ABC}$, u_A (Mulliken-Type) and Bond Indices $I_{\Omega_A\Omega_B}$ and Populations $\Delta^{(3)}_{\Omega_A\Omega_B}$, $\Delta^{(3)}_{\Omega_A\Omega_B\Omega_C}$, u_{Ω_A} (Topological) for Systems Not Containing Three-Center Bondings in the SDCI Approximation

system	fragment	I_{AB}	$\Delta^{(3)}_{AB}$	$\Delta^{(3)}_{ABC}$	u_A	$I_{\Omega_A\Omega_B}$	$\Delta^{(3)}_{\Omega_A\Omega_B}$	$\Delta^{(3)}_{\Omega_A\Omega_B\Omega_C}$	u_{Ω_A}
H_2O	O				0.234				0.242
	H				0.040				0.036
	OH	0.777	1.167			0.748	1.107		
	HH	0.004	0.009			0.013	0.008		
	HOH			−0.006				0.024	
NH_3	N				0.231				0.230
	H				0.039				0.039
	NH	0.845	1.285			0.878	1.282		
	HH	−0.002	0.005			0.020	0.015		
	HNH			−0.018				0.032	
CH_4	C				0.213				0.189
	H				0.044				0.050
	CH	0.927	1.420			0.946	1.350		
	HH	−0.009	−0.004			0.036	0.028		
	HCH			−0.021				0.044	
C_2H_6	C				0.197				0.177
	H				0.040				0.047
	CH	0.932	1.435			0.937	1.335		
	CC	0.885	1.410			0.953	1.308		
	CCH			−0.028				0.040	
	HCH			−0.024				0.045	

a checkup over the influence of the correlation. Within this model, all matrix elements u^i_j, described in eq 9, are zero,[30,31] and consequently, this kind of wave funtions cannot predict unpaired electron populations (they have not been included in this table). This fact shows itself the inadequacy of this model for which the partitionings described in eqs 14 and 23 turn out to be identical to those obtained from the idempotency of the HF first-order reduced density matrix, that is $N = {}^1/_4 \sum_{i,j,k} {}^1D^i_j\, {}^1D^j_k\, {}^1D^k_i$. In other words, the HF treatment provides a simplified picture of perfect pairing which only corresponds to the well-known Lewis model. Apart from the impossibility for describing monatomic populations of unpaired electrons the results of the two-center and three-center populations are not too different from those reported in Table 1. The sign of the three-center populations is identical to the correlated case for all of the systems and the differences between the Mulliken and topological procedures for the B_2H_6 molecule are similar. It is worthwhile to point out that in systems reported in Tables 1 and 2 the second term of the right-hand side in eq 21 is nonnegligible, due to the presence of three-center bondings (some $\Delta^{(3)}_{ABC}$ indices have significant values). Positive $\Delta^{(3)}_{ABC}$ indices (like in H_3^+ and B_2H_6 systems) make that the corresponding I_{AB} and $\Delta^{(3)}_{AB}$ values are close or even $\Delta^{(3)}_{AB} < I_{AB}$. However, negative $\Delta^{(3)}_{ABC}$ indices increase the differences between $\Delta^{(3)}_{AB}$ and I_{AB} (like in CO_2, allylanion and SO_3 molecules). A similar behavior can be observed for the $\Delta^{(3)}_{\Omega_A\Omega_B}$ and $I_{\Omega_A\Omega_B}$ indices in the topological treatment.

Tables 3 and 4 describe the results for systems which present conventional patterns of bondings (H_2O, NH_3, CH_4, and C_2H_6), that is, with absence of three-center bondings. As can be seen in the correlated calculations as well as in the HF ones, very

TABLE 4: Calculated Values of Bond Indices I_{AB} and Populations $\Delta^{(3)}_{AB}$, $\Delta^{(3)}_{ABC}$ (Mulliken-Type) and Bond Indices $I_{\Omega_A\Omega_B}$ and Populations $\Delta^{(3)}_{\Omega_A\Omega_B}$, $\Delta^{(3)}_{\Omega_A\Omega_B\Omega_C}$ (Topological) for Systems Not Containing Three-Center Bondings in the HF Approximation

system	fragment	I_{AB}	$\Delta^{(3)}_{AB}$	$\Delta^{(3)}_{ABC}$	$I_{\Omega_A\Omega_B}$	$\Delta^{(3)}_{\Omega_A\Omega_B}$	$\Delta^{(3)}_{\Omega_A\Omega_B\Omega_C}$
H_2O	OH	0.794	1.192		0.748	1.109	
	HH	0.006	0.010		0.013	0.007	
	HOH			−0.003			0.024
NH_3	NH	0.865	1.314		0.890	1.313	
	HH	0.001	0.006		0.021	0.014	
	HNH			−0.015			0.033
CH_4	CH	0.960	1.472		0.983	1.402	
	HH	−0.008	−0.003		0.038	0.031	
	HCH			−0.021			0.048
C_2H_6	CH	0.964	1.486		0.970	1.381	
	CC	0.904	1.451		0.989	1.356	
	CCH			−0.032			0.042
	HCH			−0.024			0.049

small values have been obtained for the quantities related with multicenter bondings and nonnegligible values have only been observed for two-center contributions corresponding to pairs of classically bonded atoms. According to eq 21, these small values justify the approximation

$$I_{AB} \approx \frac{2}{3}\Delta^{(3)}_{AB} \qquad (31)$$

which also holds for the topological procedure

$$I_{\Omega_A\Omega_B} \approx \frac{2}{3}\Delta^{(3)}_{\Omega_A\Omega_B} \qquad (32)$$

as were proposed by us[24,39] at Hartree−Fock level for systems which lack three-center bondings.

5. Concluding Remarks

In conclusion, in this paper, we have proposed a partitioning of N electrons in molecules and ions which provides the numerical determination of unpaired electron populations as well as electron populations related with three-center and two-center bondings within the same framework. Our algorithms, which yield reasonable results, constitute the extension at correlated level of our previous studies on three-center bondings and on the relationships between bond indices and the unpaired electron density matrix. The reported calculations have been obtained with first-order reduced density matrices and overlap matrices which require a low computational cost. We are currently studying in our laboratories the basis dependence of our results which will also be compared with results obtained from higher-order reduced density matrices.

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