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Determination of Three-Center Bond Indices from Population Analyses: A Fuzzy Atom Treatment

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This work proposes the use of the treatment referred to as *fuzzy atoms* to describe three-center bond indices within studies of electron population analysis. A simple manipulation of our algorithms reported previously for describing multicenter bondings enables us to introduce this methodology in our mathematical framework, providing suitable numerical determinations of three-center bond indices, two-center bond ones, and electron atomic populations. The results, obtained in selected systems, are discussed and compared to those arising from other procedures of population analysis.

1. Introduction

The studies of population analysis have proven to be powerful procedures for describing chemical bondings in molecules, avoiding the use of the N-electron wave functions that are always cumbersome. Classical concepts such as atomic charges, bond order indices (multiplicity), valences, free-valence indices, and so forth, which are of paramount importance for chemists, have been evaluated according to these methods, and the results show a good agreement with the genuine chemical knowledge. As is well-known, the studies of population analysis carry out a partitioning of the N electrons of the system into different contributions that are assigned to atoms, atomic regions, or groups of atoms (bonding regions), allowing one to describe conventional two-center bondings and more complex bonding patterns featured in determined molecules (multicenter bondings). The techniques of population analysis are classified within two different approaches according to the space where the analyses are performed (Hilbert space or physical space). Besides the most widely used Mulliken-type treatments, which deal with atomic functions centered at various sites in the molecule,[1,2] there are also other avenues of the Hilbert space analyses, for example, the Weinhold's natural population analyses, which deal with natural (in the Löwdin sense) orbitals.[3] In the alternative approach, the analyses are performed in the 3D space where the molecule is situated. The most important treatment in the 3D space analysis is the topological theory of atoms in molecules (AIM) of Bader, in which the N electrons are assigned to disjunct regions (or domains) of the physical space bounded by surfaces of zero flux in the gradient vector field of the electron density.[4−7]

The applicability of Mulliken-type procedures is limited to the use of basis sets whose functions have an atomic character, otherwise the understanding of their results is quite difficult.[8,9] The AIM theory is regarded as more realistic in describing chemical features by virtue of its physical grounds. However, it also presents some disadvantages related with its high computational cost. Another minor drawback is the fact that in some systems the surfaces of zero flux define nonnuclear attractor regions that cannot be directly related to any meaningful atomic region.[10−12] An alternative scheme of physical space decomposition is based on the use of fuzzy atoms, that is, a division of the 3D space into atomic regions that have no sharp boundaries but show a continuous transition from one to another.[13−16] This approach might be appropriate for describing atomic spatial regions with shared electrons, in agreement with the concept of chemical bonding.[17] Recently, the fuzzy atom procedure has been applied successfully to describe two-center bond orders and other related quantities from population analysis.[18,19] The aim of this paper is to extend the applications of the fuzzy atom treatment by studying its ability to describe multicenter bond indices, particularly the three-center ones. To achieve this goal, we have introduced the formalism of the fuzzy atom scheme into the mathematical framework of our previous reported studies on multicenter bondings,[20] which have been limited to Mulliken-type and topological approaches so far.

The article is organized as follows. The second section describes the theoretical aspects of the population analysis and their relationships with the fuzzy atom formulation. In the third section, we report the computational details and the results obtained in selected systems as well as a comparison to those arising from other procedures. Finally, the last section summarizes the concluding remarks.

2. Theoretical Aspects

We will refer to an N-electron system described by a determined wave function, Ψ. As is well-known, the matrix elements of the spin-free first-order reduced density matrix corresponding to that state are

$$^1D^i_j = \langle\Psi|\sum_\sigma c^\dagger_{i\sigma}\, c_{j\sigma}\,|\Psi\rangle \qquad (1)$$

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and, similarly, the spin-free first-order hole reduced density matrix elements are

$$^1\bar{D}^i_j = \langle\Psi|\sum_\sigma c_{i\sigma}\, c^\dagger_{j\sigma}\,|\Psi\rangle \tag{2}$$

where $i, j, k, l,...$ constitute a set of orthonormal orbitals, $c^\dagger_{i\sigma}/c_{j\sigma}$ are the standard creation/annihilation fermion operators, and σ is the spin coordinate (α or β).

The number of electrons of the system, N, can be expressed as

$$N = \sum_{i,j} {}^1D^i_j\, \delta_{ij} \tag{3}$$

The substitution of the Kronecker deltas by the well-known relation

$$\delta_{ij} = \frac{1}{2}\,({}^1D^i_j + {}^1\bar{D}^i_j) \tag{4}$$

which is a consequence of fermion operator anticommutation rules, leads to

$$N = \frac{1}{2}\sum_{i,j,k} {}^1D^i_j\, {}^1D^k_i\, \delta_{jk} + \frac{1}{2}\sum_i u^i_i \tag{5}$$

where the matrix elements u^i_j are defined as

$$u^i_j = \sum_k {}^1D^i_k\, {}^1\bar{D}^k_j \tag{6}$$

This matrix is known as the *effectively unpaired electron matrix* and its trace ($N_u = \sum_i u^i_i$) is the number of odd electrons in open shell systems plus the partial split of electron pairs that appears when correlation is taken into account (even in closed shell systems).[21−26]

Taking into account eq 6, another substitution of the Kronecker deltas in eq 5 leads to

$$N = \frac{1}{4}[\sum_{i,j,k} {}^1D^i_j\, {}^1D^j_k\, {}^1D^k_i + \sum_{i,j} {}^1D^i_j\, u^j_i - 2\sum_i u^i_i] + \sum_i u^i_i \tag{7}$$

This equation has been reported and used successfully in ref 20 as a starting point for developing algorithms for performing Mulliken-type and topological-type population analyses. The last term of this equation evaluates the number of effectively unpaired electrons,[23,24,26] whereas the terms in the brackets are related to the rest of electrons in the system. The third-order terms ${}^1D^i_j\, {}^1D^j_k\, {}^1D^k_i$ have proven to be useful particularly in detecting the presence of three-center bondings in systems that possess this feature.

Equation 7 can be reformulated in terms of new Kronecker deltas whose substitution according to eq 4 leads to a partitioning of quantity N in higher-order terms, as was reported in ref 27. However, as has been mentioned in the Introduction, the main aim of this paper is to study the capacity of the fuzzy atom procedure for describing three-center bond indices. Hence, to adapt eq 7 to physical space population analysis schemes, we propose to rewrite this equation as

$$N = \frac{1}{4}[\sum_{i,j,k,l,m,n} {}^1D^i_j\, {}^1D^k_l\, {}^1D^m_n\, \delta_{jk}\, \delta_{lm}\, \delta_{ni} + \sum_{i,j,k,l} {}^1D^i_j\, u^k_l\, \delta_{jk}\, \delta_{li} - 2\sum_{i,j} u^i_j\, \delta_{ji}] + \sum_{i,j} u^i_j\, \delta_{ji} \tag{8}$$

According to the fuzzy atom approach, a nonnegative continuous weight function, w_A, is introduced for each atom, A. These weight functions measure the degree in which a given point of space, $\boldsymbol{r}$, is considered to belong to atom A, fulfilling the conditions

$$w_A(\boldsymbol{r}) \geq 0 \tag{9}$$

$$\sum_A w_A(\boldsymbol{r}) \equiv 1 \tag{10}$$

Consequently, there are not any sharp boundaries between the atomic regions A, B, ... but a continuous transition from one to another. Obviously, the AIM formalism can be regarded as a particular case of the fuzzy atom approach in which all of the $w_A(\boldsymbol{r})$ values are zero or one.

Equation 10 lets us rewrite the Kronecker deltas as

$$\delta_{ij} = \langle i|\,j\rangle = \sum_A \langle i|w_A(\boldsymbol{r})|\,j\rangle = \sum_A S^i_j\,(A) \tag{11}$$

The substitution of these deltas in eq 8 allows one to perform the following partitioning based on the fuzzy atom approach

$$N = \sum_A \Delta_A + \sum_{A<B} \Delta_{AB} + \sum_{A<B<C} \Delta_{ABC} + \sum_A u_A \tag{12}$$

in which

$$\Delta_A = \frac{1}{4}[\sum_{i,j,k,l,m,n} {}^1D^i_j\, {}^1D^k_l\, {}^1D^m_n\, S^j_k(A)\, S^l_m(A)\, S^n_i\,(A) + \sum_{i,j,k,l} {}^1D^i_j\, u^k_l\, S^j_k(A)\, S^l_i\,(A) - 2\sum_{i,j} u^i_j\, S^j_i\,(A)] \tag{13}$$

$$\Delta_{AB} = \frac{1}{4}\left[\frac{3!}{2}(\sum_{i,j,k,l,m,n} {}^1D^i_j\, {}^1D^k_l\, {}^1D^m_n\, S^j_k(A)\, S^l_m(A)\, S^n_i\,(B) + \sum_{i,j,k,l,m,n} {}^1D^i_j\, {}^1D^k_l\, {}^1D^m_n\, S^j_k\,(B)\, S^l_m(B)\, S^n_i(A)\,)\right] + \frac{1}{2}\sum_{i,j,k,l} {}^1D^i_j\, u^k_l\, S^j_k\,(B)\, S^l_i\,(A) \quad (A < B) \tag{14}$$

$$\Delta_{ABC} = \frac{1}{4}\sum_{P(ABC)}\;\sum_{i,j,k,l,m,n} {}^1D^i_j\, {}^1D^k_l\, {}^1D^m_n\, S^j_k\,(A)\, S^l_m(B)\, S^n_i(C) \quad (A < B < C) \tag{15}$$

$$u_{\mathrm{A}} = \sum_{i,j} u^i_j\, S^j_i(A) \tag{16}$$

where $P(ABC)$ means the permutations ABC, ACB, and so forth.

Quantities Δ_A, Δ_{AB}, and Δ_{ABC} are the electronic populations associated to one center and the bonding populations related to two and three centers, respectively, within our fuzzy atom treatment, whereas the u_A one represents the population of the effectively unpaired electrons related with the atom, A, in that approach. According to the heuristic definitions of bond indices,[28,29] the expression for the two-center bond index, I_{AB}, in a fuzzy atom version has been reported in ref 18 as

$$I_{AB} = \sum_{i,j,k,l} {}^1D^i_j\, {}^1D^k_l\, S^j_k(A)\, S^l_i\,(B) \tag{17}$$

Similarly, the corresponding version of three-center index, I_{ABC}, can straightforwardly be formulated as

$$I_{ABC} = \sum_{i,j,k,l,m,n} {}^1D^i_j\,{}^1D^k_l\,{}^1D^m_n\,S^j_k(A)\,S^l_m(B)\,S^n_i(C) \qquad (18)$$

Equations 15 and 18 establish a simple relationship between three-center populations, Δ_{ABC}, and three-center bond indices, I_{ABC} ($\Delta_{ABC} = {}^1/_4 \sum_{P(ABC)} I_{ABC}$). Counterpart formulas of Δ_A, u_A, Δ_{AB}, and Δ_{ABC} quantities in the Mulliken-type and AIM versions as well as the results obtained from them were described in ref 20. In the following section, we report results arising from these three treatments in order to compare and discuss the ability of the fuzzy atom procedure for describing three-center bondings.

3. Results and Discussion

To perform test calculations within the above proposed fuzzy atom scheme, we chose two series of selected systems according to the expected presence (or absence) of three-center bondings. These calculations have been carried out using a modified Gaussian 94[30] program, which generated the first-order reduced density matrix elements. The values of the weight functions, w_A, and the numerical integration of the $S^i_j(A)$ expressions have been determined with a modified version of the code cited in ref 31, which follows a Becke integration scheme[15] on the basis of the weight functions originally proposed by this author. These weight functions, which satisfy eqs 9 and 10, depend on both the empirical Slater−Bragg atomic radii of the atoms composing the system under study and an iteration order, k, which defines the cutoff profiles of the functions. According to ref 17, we have chosen the value $k = 3$ and increased the radius of hydrogen to the value 0.35 Å. In a subsequent step, the above proposed population analysis has been performed by our own computational implementation. The obtained results are reported in Tables 1−4. Counterpart results for the studied systems within Mulliken and AIM population analysis schemes, taken from ref 20, have also been included in these Tables for the sake of comparison. All of the reported results have been obtained with the 6-31G basis sets. For all systems, the geometries have been optimized for these basis sets within configuration interaction (CI) wave functions with single and double excitations (SDCI).

TABLE 2: Calculated Values of Populations Δ_A, u_A from Fuzzy Atom, Mulliken-Type (in Parentheses) and AIM (in Brackets) Treatments for Systems with Three-Center Bondings in the SDCI Approximation

system	fragment	Δ_A	u_A
H_3^+	H	0.059 (0.061) [0.060]	0.039 (0.039) [0.039]
B_2H_6	B	2.697 (2.521) [2.032]	0.171 (0.162) [0.095]
	H_{terminal}	0.162 (0.264) [0.680]	0.043 (0.044) [0.065]
	H_{bridging}	0.081 (0.259) [0.521]	0.040 (0.048) [0.071]
allyl cation	C_1	2.978 (3.337) [3.040]	0.193 (0.205) [0.194]
	C_2	2.939 (3.210) [2.928]	0.201 (0.212) [0.198]
	H_1	0.121 (0.096) [0.128]	0.038 (0.033) [0.039]
	H_2	0.121 (0.086) [0.136]	0.039 (0.032) [0.040]
allyl anion	C_1	3.306 (3.599) [3.307]	0.199 (0.213) [0.201]
	C_2	2.900 (2.989) [2.894]	0.195 (0.199) [0.192]
	H_1	0.185 (0.249) [0.245]	0.044 (0.040) [0.046]
	H_2	0.181 (0.251) [0.260]	0.045 (0.042) [0.049]
CO_2	C	2.670 (2.523) [2.123]	0.232 (0.216) [0.168]
	O	5.723 (6.374) [6.969]	0.245 (0.253) [0.277]
N_3^-	N_1	5.029 (5.381) [5.059]	0.309 (0.310) [0.308]
	N_2	3.548 (4.194) [3.978]	0.260 (0.259) [0.263]

TABLE 1: Calculated Values of Bond Indices I_{AB} and Populations Δ_{AB}, Δ_{ABC} from Fuzzy Atom, Mulliken-Type (in Parentheses) and AIM (in Brackets) Treatments for Systems with Three-Center Bondings in the SDCI Approximation

system	bonding	I_{AB}	Δ_{AB}	Δ_{ABC}
H_3^+	HH	0.427 (0.425) [0.427]	0.429 (0.428) [0.429]	
	HHH			0.419 (0.416) [0.418]
B_2H_6	BB	0.819 (0.465) [0.146]	0.779 (0.418) [0.064]	
	$(BH)_{\text{terminal}}$	0.908 (0.947) [0.673]	1.320 (1.441) [0.936]	
	$(BH)_{\text{bridging}}$	0.443 (0.434) [0.383]	0.447 (0.519) [0.426]	
	BHB			0.376 (0.303) [0.136]
allyl cation	C_1C_2	1.454 (1.351) [1.395]	1.890 (1.929) [1.851]	
	C_1H_1	0.895 (0.894) [0.909]	1.282 (1.369) [1.321]	
	C_2H_2	0.887 (0.882) [0.903]	1.260 (1.339) [1.307]	
	CCC			0.366 (0.291) [0.342]
allyl anion	C_1C_2	1.556 (1.430) [1.430]	2.236 (2.358) [2.132]	
	C_1H_1	0.974 (0.928) [0.980]	1.380 (1.427) [1.409]	
	C_2H_2	0.895 (0.933) [0.926]	1.258 (1.429) [1.326]	
	CCC			−0.058 (−0.352) [−0.141]
CO_2	CO	2.190 (1.784) [1.518]	3.402 (2.947) [2.387]	
	OO	0.300 (0.254) [0.370]	0.572 (0.650) [0.666]	
	OCO			−0.242 (−0.537) [−0.224]
N_3^-	N_1N_2	2.123 (1.565) [1.930]	3.323 (2.780) [3.122]	
	N_1N_3	0.674 (0.687) [0.671]	1.150 (1.453) [1.231]	
	NNN			−0.280 (−0.849) [−0.451]

The results in Tables 1 and 2 refer to systems in the ground state, in which the existence of three-center bondings is well known (H_3^+, B_2H_6, allyl cation, allyl anion, CO_2, and N_3^-). The numerical determinations found in the H_3^+ cation turn out to be quite similar for all of the quantities in the three methods; this system is too simple to render any difference in the behavior of these treatments. However, in the B_2H_6 molecule, the Δ_{BHB}, Δ_{BB}, and Δ_B populations present higher values in the fuzzy method than in the Mulliken and AIM ones, which are compensated for by the lower values of the Δ_H populations. The diborane molecule has been considered as a typical example of a system possessing three-center two-electron bondings; the results arising from the fuzzy method clearly point to this feature ($\Delta_{BHB} = 0.366$) and also provide a suitable value for the conventional two-center bonding ($I_{BH} = 0.908$), which is in agreement with the genuine chemical behavior of this system. The allyl cation shows fewer differences between the AIM and fuzzy atom procedures, but the lightly higher value of $\Delta_{CCC} = 0.366$ (in fuzzy atoms) in comparison to $\Delta_{CCC} = 0.342$ (in AIM) confirms that the former method is appropriate to detect three-center bondings. In our opinion, the higher values found in the fuzzy atom treatment may be explained by the fact that in this approach there are no sharp boundaries between the different atomic domains, which favors the notion of shared electrons between the three nuclei. The negative character of the Δ_{ABC} populations has been interpreted as the presence of three-center four-electron bondings, whereas the positive ones describe three-center two-electron bondings.[29,32] This feature is also fulfilled

TABLE 3: Calculated Values of Bond Indices I_{AB} and Populations Δ_{AB}, Δ_{ABC} from Fuzzy Atom, Mulliken-Type (in Parentheses) and AIM (in Brackets) Treatments for Systems Not Containing Three-Center Bondings in the SDCI Approximation

system	bonding	I_{AB}	Δ_{AB}	Δ_{ABC}
H_2O	*OH*	1.089 (0.777) [0.748]	1.582 (1.167) [1.107]	
	HH	0.058 (0.004) [0.013]	0.036 (0.009) [0.008]	
	HOH			0.099 (−0.006) [0.024]
NH_3	*NH*	1.028 (0.845) [0.878]	1.464 (1.285) [1.282]	
	HH	0.049 (−0.002) [0.020]	0.034 (0.005) [0.015]	
	HNH			0.074 (−0.018) [0.032]
CH_4	*CH*	0.948 (0.927) [0.946]	1.337 (1.420) [1.350]	
	HH	0.040 (−0.009) [0.036]	0.030 (−0.004) [0.028]	
	HCH			0.055 (−0.021) [0.044]
C_2H_6	*CH*	0.922 (0.932) [0.937]	1.295 (1.435) [1.335]	
	CC	1.071 (0.885) [0.953]	1.416 (1.410) [1.308]	
	CCH			0.062 (−0.028) [0.040]
	HCH			0.052 (−0.024) [0.045]

TABLE 4: Calculated Values of Populations Δ_A, u_A from Fuzzy Atom, Mulliken-Type (in Parentheses) and AIM (in Brackets) Treatments for Systems Not Containing Three-Center Bondings in the SDCI Approximation

system	fragment	Δ_A	u_A
H_2O	*O*	6.200 (7.237) [7.406]	0.214 (0.234) [0.242]
	H	0.094 (0.056) [0.017]	0.050 (0.040) [0.036]
NH_3	*N*	4.568 (5.582) [5.511]	0.206 (0.231) [0.230]
	H	0.120 (0.085) [0.057]	0.047 (0.039) [0.039]
CH_4	*C*	3.091 (3.438) [2.968]	0.193 (0.213) [0.189]
	H	0.163 (0.159) [0.199]	0.049 (0.044) [0.050]
C_2H_6	*C*	3.010 (3.370) [2.913]	0.183 (0.197) [0.177]
	H	0.161 (0.162) [0.208]	0.045 (0.040) [0.047]

qualitatively in the fuzzy atom treatment as can be observed in the allyl anion, the CO_2 molecule, and the azide anion. The u_A quantities, which represent the free valences of the atoms, are detectable although they are low. Because all of the studied systems are singlets, these unpaired electron populations are due only to the partial splitting that arises from the dispersal of the occupation numbers of the orbitals in the expansion on several Slater determinants. The values obtained are similar in the fuzzy atom treatment and in the Mulliken and AIM methods in agreement with our previous determinations of this quantity.[24,33]

Tables 3 and 4 report the results for systems in the ground state that are appropriately described through conventional single bonds, that is, only possessing bondings fitted in with the classical two-center two-electron model (H_2O, NH_3, CH_4, and C_2H_6). The first conclusion that can be drawn out from these results is that the fuzzy atom procedure leads to bond indices I_{OH}, I_{NH}, I_{CH} (in both methane and ethane molecules), and I_{CC} close to unity, which is in good agreement with the classical chemical description of these systems. However, the three-center contributions are negligible in the three methods showing the lacking of this feature in these systems. Again, no significant differences have been found for the u_A quantity between the three procedures.

4. Concluding Remarks

In conclusion, in this paper we have explored the ability of the fuzzy atom scheme to describe three-center bondings. To carry out this purpose, we have adapted the mathematical framework of our previously reported studies of multicenter bond indices to the fuzzy atom approach. The obtained algorithms, which are valid at any level of theory, have been applied at correlated level. The results found show that this method also detects three-center two-electron bondings and provides similar or higher values than those obtained within the Mulliken and AIM procedures. Likewise, in qualitative agreement with the more traditional techniques, the fuzzy atom approach leads to negative values of three-center populations in systems that present three-center four-electron bondings. In systems that have only single bondings, the description of two-center bond indices also turns out to be satisfactory because this treatment provides indices closer to unity for the conventional bonded atoms in most of the systems studied and negligible values for three-center indices. These results and the lower computational cost of the fuzzy atom approach in comparion with the AIM treatment indicate that this methodology can be used as a reliable and cost-competitive technique within the studies of population analysis.

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