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Pairing and unpairing electron densities in organic systems: Two-electron three center through space and through bonds interactions

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Two-electron three-center bonding interactions in organic ions like methonium (CH_5^+), ethonium ($C_2H_7^+$), and protonated alkanes $n - C_4H_{11}^+$ isomers (butonium cations) are described and characterized within the theoretical framework of the topological analysis of the electron density decomposition into its effectively paired and unpaired contributions. These interactions manifest in some of this type of systems as a concentration of unpaired electron cloud around the bond paths, in contrast to the well known paradigmatic boron hydrids in which it is not only concentrated close to the atomic nucleus and the bond paths but out of them and over the region defined by the involved atoms as a whole. This result permits to propose an attempt of classification for these interactions based in such manifestations. In the first type, it is called as interactions through bonds and in the second type as interactions through space type. © *2014 AIP Publishing LLC.* [http://dx.doi.org/10.1063/1.4873547]

INTRODUCTION

Electron deficient compounds like boron hydrids give rise to important complex patterns of bonding which has been associated to two-electron three-center interaction mechanisms.[1–5] These multi-center interactions are known to appear in a wide variety of molecular systems as organic ions,[6–8] metallic and non-metallic clusters among others.[9] Nevertheless, the different types of molecular systems, i.e., the boron hydrids and the carbonium ions show different patterns within this type of interactions characterizing the bonding interactions and thus constitute a landmark for comparative detailed studies about them.[10] The carbonium ions are important species formed by the protonation of alkanes in liquid super-acids transformations and constitute the evidence for formation of penta-coordinated carbon atoms states.[11–13] These species are considered as containing two-electron three-center bonds (2e-3c) and are obtained upon the insertion of a proton or carbenium ion in the CH or CC sequences. Their structures and energy have been studied by theoretical methods also including electron correlation effects and accurate predictions has been reached for methonium (CH_5^+),[13] ethonium ($C_2H_7^+$),[13] proponium, and isobutonium.[13] More complex structures within this type of compounds sharing these features are the isomeric forms of n-butonium cations, n-$C_4H_{11}^+$ which appear under the protonation of n-butane regarding this process is performed at the primary or secondary CH sequences or at two distinct types of CC sequences (external and internal).[6]

In previous works, we have studied two-electron three-center interactions on typical electron deficient systems like boron hydrides[5] and closo-boranes.[14] Consequently, a rule

based on the topological properties of the density of the effectively unpaired electrons collecting the conditions that a given distribution may follow to posses 2e-3c patterns of bonding has been established which also permitted to quantify these interactions, i.e., to define a measure of their "intensity." Nevertheless, these features seem to be manifested in electron distributions of organic compounds with own characteristics like in the above mentioned 2-C-n-butonium (where the protonation occurs at the internal CC sequence) and hence modifications on the rule's interpretation are induced to incorporate them into the 2c-3c patterns. The methodology introduced in the mentioned previous works[5,14] exhibits two complementary points of view, the so called non-local or integrated view based on the determination of magnitudes which are the result of the integration of the density. This vision can be applied as well as to single determinantal state functions as Hartree-Fock, DFT (Density Functional Theory), or correlated ones. The other view, the local one is supported by the topology of the electron distribution valid also for the two types of state functions.[25,26] Nevertheless, for a more detailed analysis of the correlation effects in the electron distribution description our approach decomposes the density into pairing and unpairing contributions according to the main idea of Lewis.[5,6,14–16,29] This scheme permits to analyze the role that the correlation effects play in bonding interaction phenomena.

The aim of this report is to describe the electronic distribution of the selected molecular systems by application of the topological analysis of the electron density and its decomposition into paired ($\rho^{(p)}(\mathbf{r})$) and unpaired ($\rho^{(u)}(\mathbf{r})$) contributions,[15,16] and to interpret the results from the mentioned quantum rule. This decomposition may be considered as the quantum Lewis conjecture regarding that both of the contributions have a different and definite physical character.[15,16] To this end, the information contained in the N-electron state function is transferred towards the fundamental

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chemical concepts[17–21] by means of the electron density which constitutes the central tool in the qualitative and quantitative description.[22–24] The two complementary methodologies mentioned above have the density and its contributions as the fundamental magnitudes for the present description. On one side, the *local formulation* relates the topological structure of the electron density $\rho(\mathbf{r})$ and its Laplacian field $\nabla^2\rho(\mathbf{r})$ to the localization and classification of their critical points (**cp**) which characterize these fields and therefore permits to extract and interpret the chemical information.[25,26] The classification of the cp's is performed considering the information featured as (r,s), where r is the *rank* (number of nonzero eigenvalues of the Hessian matrix of the density $\rho(\mathbf{r})$) and s the *signature* (sum of the signs of its eigenvalues). The points of interest are: $(3,-3)$, the nuclear critical point (**ncp**) which indicates a local maximum placed very close to the nuclear positions; the $(3,-1)$, bond critical point (**bcp**) where the concentration of the electron density shows a bonding interaction between two atoms.[25,26] The remaining cp's, *ring*, (**rcp**) and *cage*, (**ccp**) critical points, indicate the onset of more complex structures and are noted as $(3,+1)$ and $(3,+3)$, respectively.[25,26] The sign of the Laplacian field, i.e., the sum of the curvatures along the orthogonal coordinate axes which indicates locally depleted (positive) or locally concentrated (negative) electron density, is a valuable local descriptor for the behavior of the density around a point.[25,26] On the other side, the *nonlocal or integrated formulation*, is currently known as electronic population analysis and has several implementations[27,28] which permit to calculate and interpret the chemical fundamental quantities like covalent bond orders, valence and atomic populations among others.[17–21] Comparison of both contributions of the electron density with the total density itself, i.e., the main features that they share and those in which they differentiate has also been reported for systems with classical[15,16] and complex patterns of bonding in emblematic boron hydrids and closo-boranes.[5,14] Also a first approach to the understanding of the nature bonding in special organic systems has been carried out on the strained [1.1.1]propellane electron distribution describing the nature of the headbridge CC atoms bond and concluding the absence of 2e-3c complex patterns of bonding in this system.[29] The local point of view, examined here will allow us to define two types of interactions regarding the spatial domain of accumulation of the unpaired density. If it is close to the bond paths between atoms, the interaction will be called *through bond* (**TB**); if it "spillages" through the space beyond the bond path of interacting bondings and consequently strongly delocalizing in space, the interaction will be called *through space* (**TS**).

The organization of this article is as follows. The Theoretical Background section is devoted to a brief introduction to the theoretical methodology, i.e., the partitioning of the electron density, the relationships between the density gradients and the Laplacians of both fields, as well as the tools used to carry out the studies of topological population analysis. The Computational Details, Results, and Discussion section describes the computational details and the discussion of the results. The Concluding Remarks section is dedicated to the concluding remarks.

THEORETICAL BACKGROUND

The electron density, $\rho(\mathbf{r})$, in an N-electron molecular system may be decomposed into two contributions[15,16]

$$\rho(\mathbf{r}) = \rho^{(p)}(\mathbf{r}) + \rho^{(u)}(\mathbf{r}), \quad (1)$$

where $\rho^{(p)}(\mathbf{r})$ and $\rho^{(u)}(\mathbf{r})$ indicate the effectively paired and unpaired densities, expressed by

$$\rho^{(p)}(\mathbf{r}) = \frac{1}{2} \int d\mathbf{r}' \, {}^1D(\mathbf{r}|\,\mathbf{r}') \, {}^1D(\mathbf{r}'|\,\mathbf{r}),$$

$$\rho^{(u)}(\mathbf{r}) = \frac{1}{2} \, u(\mathbf{r}|\,\mathbf{r}), \quad (2)$$

respectively. ${}^1D(\mathbf{r}|\mathbf{r}')$ is the spin-free first-order reduced density matrix (1-RDM) in the coordinate representation,[23,30] its trace (coordinate integration over the whole real space) is the number of electrons in the system, i.e., $tr({}^1D) = \int d\mathbf{r} \, {}^1D(\mathbf{r}|\mathbf{r}) = \int d\mathbf{r} \, \rho(\mathbf{r}) = N$. $u(\mathbf{r}|\,\mathbf{r})$ is the diagonal element of the effectively unpaired density matrix defined by $u(\mathbf{r}|\mathbf{r}') = 2\,{}^1D(\mathbf{r}|\mathbf{r}') - {}^1D^2(\mathbf{r}|\mathbf{r}')$ where ${}^1D^2(\mathbf{r}|\mathbf{r}') = \int d\mathbf{r}'' \, {}^1D(\mathbf{r}|\,\mathbf{r}'') \, {}^1D(\mathbf{r}''|\,\mathbf{r}')$.[15,16,23] The densities are the diagonal part of the corresponding reduced density matrices. The physical meaning of the traces of the effectively paired and unpaired densities is the number of paired (opposite spins) and unpaired (far away) electrons. The unpaired density has two sources, one of them comes from the spin density (only present in non-singlet states) and the other corresponds to the correlation effects.[31] It may be noted that for a single determinant state functions having all doubly occupied orbitals, as in the closed-shell Hartree-Fock or DFT cases, $\rho^{(u)}(\mathbf{r})$ is intrinsically zero[32–36] and then these local finer details or correlation effects cannot be detected. The topological analysis of the density[25,26] is applied to the total electron density as well as to both scalar field components to describe bonding features in a deeper and more precise manner. The fundamental information is obtained from the nature and localization of the cp's of each of the two electron densities and their local accumulation/depletion in space. The cp's for the total density are determined throughout the gradient of the field by

$$\nabla\rho(\mathbf{r})|_{\mathbf{r}^c} = 0, \quad \nabla\rho^{(p)}(\mathbf{r})|_{\mathbf{r}^c} + \nabla\rho^{(u)}(\mathbf{r})|_{\mathbf{r}^c} = 0, \quad (3)$$

where $\mathbf{r}^c = \{\mathbf{r}_i^c; i = 1, \ldots, M\}$ indicates the set of critical points of the total density $\rho(\mathbf{r})$ (cf. Eq. (1)). Then it follows

$$\nabla\rho^{(p)}(\mathbf{r})|_{\mathbf{r}^c} = -\nabla\rho^{(u)}(\mathbf{r})|_{\mathbf{r}^c} \quad (4)$$

whose physical meaning is that the direction of maximum increment of each density field component is opposite, i.e., when $\rho^{(p)}(\mathbf{r})$ increases its value, the other part of the density, the unpaired contribution, properly does it in the opposite direction.[15] The Laplacian field of Eq. (1) yields

$$\nabla^2\rho(\mathbf{r})|_{\mathbf{r}^c} = \nabla^2\rho^{(p)}(\mathbf{r})|_{\mathbf{r}^c} + \nabla^2\rho^{(u)}(\mathbf{r})|_{\mathbf{r}^c} \neq 0. \quad (5)$$

Equation (5) clearly shows that both, $\nabla^2\rho^{(p)}(\mathbf{r})|_{\mathbf{r}^c}$ and $\nabla^2\rho^{(u)}(\mathbf{r})|_{\mathbf{r}^c}$ contributions do not necessarily follow opposite trends, as the density gradient do, i.e., both densities are allowed to concentrate or deplete simultaneously at the neighborhood of a **cp**. It is worthwhile to note that both densities possess a shell structure as well as the total density.[16,37]

On the other side, the *nonlocal* or *integrated formalism* as the complement of local one deals with classical chemical concepts like atomic charges, covalent bond orders, valences, etc.[17,21] We will refer to information contained in these quantities as the nonlocal AIM topological population analysis. Let us summarize the relevant integrated magnitudes which have been previously stated within that approach and that will be used in our study.[19–21,38–40] The covalent bond order (two-center bond index) has been defined as

$$I_{\Omega_A \Omega_B} = \sum_{i,j,k,l} {}^1D_j^i \; {}^1D_l^k \; S_{il}(\Omega_A) \, S_{kj}(\Omega_B), \qquad (6)$$

where Ω_A and Ω_B stand for Bader's atomic domains in the physical space,[25,26] ${}^1D_j^i$ the spin-free first-order reduced density matrix elements, and $S_{ij}(\Omega_A)$ the elements of the overlap matrix over the region Ω_A, in the orthogonal molecular basis set $\{i, j, k, l, \dots\}$.[39,40] Within the same context, the three-center bond population (or three-center bond index) is defined by

$$I_{\Omega_A \Omega_B \Omega_C} = \sum_{i,j,k,l,m,n} {}^1D_j^i \; {}^1D_l^k \; {}^1D_n^m \; S_{in}(\Omega_A) \, S_{kj}(\Omega_B) \, S_{ml}(\Omega_C) \qquad (7)$$

giving rise to the three-center topological bond order[39,40]

$$\Delta^{(3)}_{\Omega_A \Omega_B \Omega_C} = \frac{1}{4} \sum_{P(\Omega_A \Omega_B \Omega_C)} I_{\Omega_A \Omega_B \Omega_C}, \qquad (8)$$

where $P(\Omega_A \Omega_B \Omega_C)$ stands for the permutations of the three domain contributions. The effectively unpaired population is quantified by[19,32–36]

$$u_{\Omega_A} = 2 \sum_{ik} {}^1D_k^i \, S_{ik}(\Omega_A) - \sum_{ijkl} {}^1D_l^i \; {}^1D_k^j \, S_{ik}(\Omega_A) \, S_{jl}(\Omega_A)$$

$$- \sum_{B \neq A} \sum_{ijkl} {}^1D_l^i \; {}^1D_k^j \, S_{ik}(\Omega_A) \, S_{jl}(\Omega_B). \qquad (9)$$

Finally, other fundamental concept is that of unshared populations for an atom A, Q_{Ω_A} as the atomic population from inner shells and/or lone pairs in the atom, i.e., those electrons that are not involved in bonding interactions, defined by[18,19]

$$Q_{\Omega_A} = \left[I_{\Omega_A \Omega_A} - \frac{1}{2} \sum_{\Omega_B \neq \Omega_A} I_{\Omega_A \Omega_B} \right] + \frac{1}{2} u_{\Omega_A}, \qquad (10)$$

where the first and second terms stand for the pairing contributions while the third one stands for the unpaired population contribution to this magnitude.

Finally, although we have not made use of that in this work, it is important to remark the relationships between bond quantities describing the electron distribution as those presented above and bond-energy quantities. For that goal, two main results must be mentioned. The first one is that there is a direct relation between the bond orders concept and the exchange energy between the atoms involved in the bond, i.e., bond orders are also linked to the electron population at the bonding region[44,45] introducing the exchange-correlation terms of correlated state functions.[45] The second one is the concept of pairing y unpairing nature of the density

decomposition (Eq. (1)) applied to the partition of the energy and the consequent definition of the atomic and bond energy.[28,46]

COMPUTATIONAL DETAILS, RESULTS, AND DISCUSSION

The state functions used during the course of this work has been calculated at the level of configuration interaction with single and double excitations (CISD) with the basis sets 6-31G** using the Gamess04 package.[41] The geometries for all systems were optimized within this approximation and have been confirmed to be local minimum in the corresponding energy hypersurfaces. The densities, their critical points and their Laplacian fields $\nabla^2 \rho^{(p)}(\mathbf{r})$ and $\nabla^2 \rho^{(u)}(\mathbf{r})$ were determined by modified AIMPAC modules.[42] Let us express a few words about the topological stability of the **cp**'s with the basis set. There has been pointed out in an extensive and important work that double zeta basis sets are not enough to warrant the stability for the Laplacian **cp**'s and basis set of higher hierarchy for the study of such field are needed.[43] Nevertheless, in the present work only **cp**'s of the electron densities are used and their topology is not modified as we have noted in this and previous works.[5,14–16,29,31] The numerical results of population analysis were obtained with our own codes mentioned in Refs. 17–21. For practical reasons, we will use the function $L(\mathbf{r}) = -\nabla^2 \rho(\mathbf{r})$ in the discussion of the results as an indicator of local concentration (positive value) or local depletion (negative value) of the number of electrons at the point of space $\mathbf{r}$.[25,26,37] The terms accumulation and depletion have been proposed for the description of $\rho(\mathbf{r})$.[25,26,37] Because of the complex structure of the $\rho^{(u)}(\mathbf{r})$ topology, we will only deal with critical points associated with its valence shells (vs) and no reference will be made to those of the inner shells of this density; in fact, only the former ones are involved in bonding phenomena. The terminology vs(3,−1)cp, vs(3,+1)cp, and vs(3,+3)cp will refer to (3,−1), (3,+1), and (3,+3) critical points of $\rho^{(u)}(\mathbf{r})$ valence shell, in analogy with the bcp, rcp, and ccp's of the total density. Nevertheless, it is important to note that such points are not *sensu strictu* bcp, rcp, or ccp's because only the cp's of the total density are able to define a bond in the AIM topological formalism.[25,26] The discussion of the results about the existence of the complex 2e-3c patterns of bonding will be performed taking into account our prior results that have been condensed in a quantum rule which we have successfully built on the basis of well known systems possessing such patterns, like boron hydrids[5] and then applied to some evolved structures, the closo-boranes.[14]

As it was mentioned in the Introduction, some important organic compounds commonly considered as possessing 2e-3c patterns of bonding will be discussed to describe their electronic distributions in light of the established quantum rule. For that goal, let us introduce this rule in a general manner as: *a 2e-3c bond between atoms* ABC *exists if there is a vs(3,−1)cp of* $\rho^{(u)}$ *between each pair of atoms involved in the three-center* ABC *sequence and a vs(3,+1)cp defined only by the atoms involved in the three center sequence*, hereafter called the *local rule*.[14] This result seems to be the local

version of the criterion of the integrated formalism of population analysis for detecting three-center bonding, hereafter *the integrated or non-local rule*. That criterion settles down *the existence of a 2e-3c bond between atoms* ABC *when fractional covalent bond orders* $I_{\Omega_A \Omega_B}$ *appear between all possible pairs of atoms* AB, BC, *and* AC *and an appreciable* $\Delta^{(3)}_{\Omega_A \Omega_B \Omega_C}$ *defines its strength*.[39,40] Because of the detailed description of the distribution from the topological (local) view, we will adopt this form of the rule as the indicator of the quality of the interaction between the atoms while the integrated form is interpreted as an indicator of the strength of such interaction, i.e., the local rule defines and typifies the existence of such a type of interaction between the atoms while the integrated (nonlocal) form of the rule adjudicates the strength of the interaction by means of the population shared by the atoms involved. It may be noted that in the cases in which $\rho^{(u)}$ vanishes identically as mentioned above, the local part of the rule cannot be applied and consequently only a 3c populations indicators of the interactions may be considered from the non-local one. This is a consequence of the double occupation of the molecular orbitals which makes the "hole" distribution described by $\rho^{(u)}$ [32] to vanish and thus the "expansion" of the electron cloud out of the core region of the atoms cannot be detected. This situation is of high importance in the treatment of the type of 2e-3c interactions present in deficient electron compounds which we are dealing with. This means that although the 2e-3c type interactions can be detected by an uncorrelated or a correlated single determinantal state function models it may fail, i.e., an appreciable 3c population

may not be enough by itself to confirm a 2e-3c bonding interaction,[14,29] namely, only non-local part applied to this type of studies has no enough information to conclude about existence or not of such interactions.[29] It indicates the importance of the correlation effects that admits the "holes" to enter as a fundamental magnitude in the electron deficient phenomena in molecular compounds.

As it was pointed out in the Introduction, carbonium and butonium organic ions are proposed as systems which possess complex patterns of 2e-3c bonding interactions.[6,7] Our results indicate that these bonding interactions have different characteristics from those well known electron deficient boron hydrids and hence they admit an important new feature which induces a wider interpretation of the rule. To this end, the information obtained may be interpreted as it is not necessary that both views of the rule, i.e., the local and the non-local conditions, ought to be satisfied in order to recognize a 2e-3c interaction. This is the main result of the present work which will be properly explained and discussed by means of a set of selected organic systems to reach a novel interpretation of the rule which enable us to perform an attempt to classify these bonding interactions. Figure 1 shows the geometrical conformation of the four selected systems used in this work to describe these phenomena. They are two 2-C-n-butonium isomers, ethonium ($C_2H_7^+$), and methonium (CH_5^+) ions.[6,13]

Table I contains the topological information concerning the total density $\rho(\mathbf{r})$ which summarizes the main parameters describing the structure of the systems. It shows the localization of the cp's, their type and the atomic sequence defining
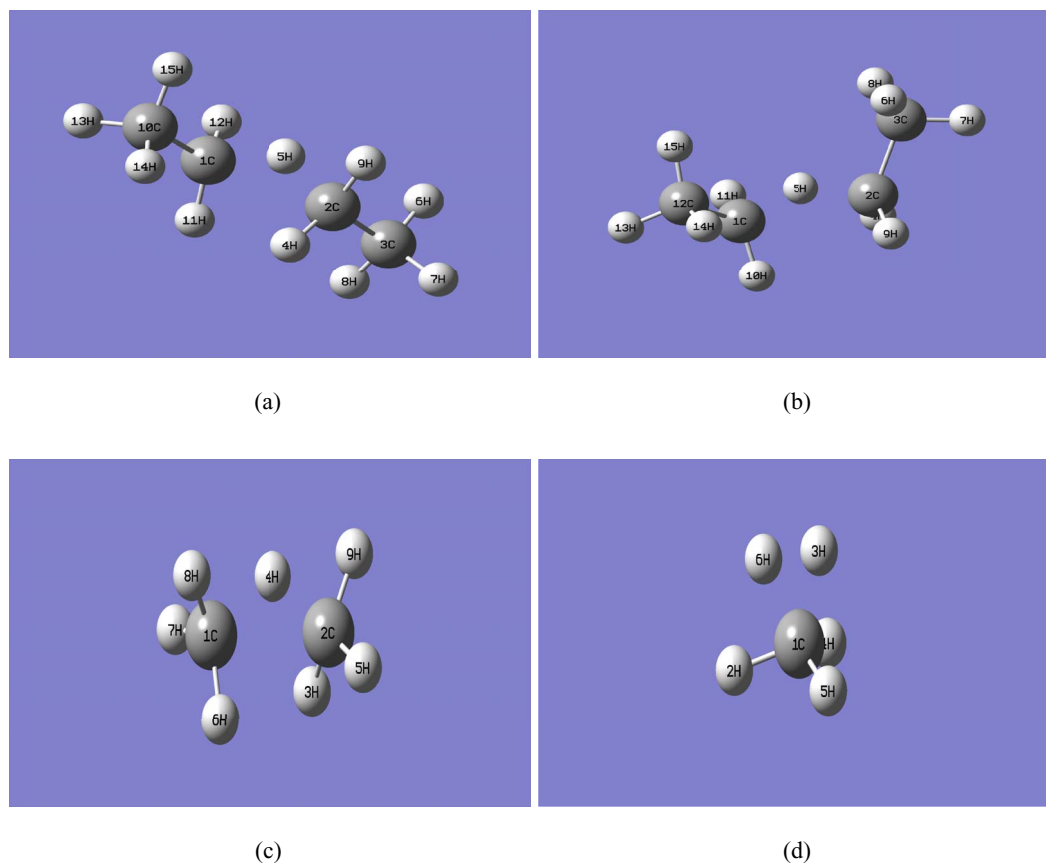

(a)

(b)

(c)

(d)

FIG. 1. Geometrical conformation of the two $n - C_4H_{11}^+$ isomers (butonium cations) (a) and (b), ethonium ($C_2H_7^+$) (c), and methonium (CH_5^+) (d).

TABLE I. Electronic structure of selected organic systems: carbonium ions. Local and integrated (non-local) topological features of $\rho(\mathbf{r})$ density at CISD/6-31G** level of approximation. All quantities are in atomic units.

cp type	ρ sequences[a]	Bond	$I_{\Omega_A \Omega_B}$	$\Delta^{(3)}_{\Omega_A \Omega_B \Omega_C}$
		$C_2H_7^+$ (twisted)		
ncp	One on each C, H atoms			
bcp	One on each CH[b] sequence	CH[b]	≈ 0.9	
	One on each CH_b[c] sequence	$C(1)H_b$	0.525	
		$H_bC(2)$	0.518	
		CC	0.297	
rcp	No present	C(1)H(4)C(2)		0.281
ccp	No present			
		2-C-n-butonium (structure I)		
ncp	One on each C, H atoms			
bcp	No on $C_{bh}C_{bh}$ sequence	$C_{bh}C_{bh}$		0.190
	One for each $C_{bh}C$ sequence	$C_{bh}H_b$	0.512	
	One per each of $C_{bh}H_b$ sequence	$C_{hb}H_bC_{hb}$		0.239
	One per each of CH sequence			
rcp	No present			
ccp	No present			
		2-C-n-butonium (structure II)		
ncp	One on each C, H atoms			
bcp	No on $C_{bh}C_{bh}$ sequence	$C_{bh}C_{bh}$	0.203	
	One for each $C_{bh}C$ sequence	$C_{bh}H_b$	0.512	
	One per each of $C_{bh}H_b$ sequence	$C_{hb}H_bC_{hb}$		0.246
	One per each of CH sequence			
rcp	No present			
ccp	No present			
		CH_5^+		
ncp	One on each C, H atoms			
bcp	One on each CH[d] sequence	CH(4 and 5)	0.880	
	(No present for CH(6))	CH(2)	0.822	
		CH(3)	0.551	
		CH(6)	0.507	
	One for HH[e] sequence	H(3)H(6)	0.350	
		H(3)CH(6)		0.318
rcp	No present			
ccp	No present			

[a]Indicate the nucleus at which the **ncp** is located; for **bcp**'s, the atoms defining the bond; for **rcp**'s, the atoms giving rise to the ring; for **ccp**'s, the atoms defining the cage.
[b]CH sequence in CH_3 group (see Figure 1(c)).
[c]H_b stands for the *bridge* atom labeled 4 in Figure 1(c).
[d]H stand for the hydrogen atoms labeled 2, 3, 4, 5 (see Figure 1(d)).
[e]HH stand for the hydrogen atoms labeled 3 and 6 (see Figure 1(d)).

each of them. Also the non-negligible values of the two-center covalent bond indices $I_{\Omega_A \Omega_B}$ and the three-center populations $\Delta^{(3)}_{\Omega_A \Omega_B \Omega_C}$ are shown in this table. Table II is dedicated to the topological structure of $\rho^{(u)}(\mathbf{r})$ and also reports the unshared Q_{Ω_A} and the effectively unpaired populations u_{Ω_A}. No reference to the effectively paired density $\rho^{(p)}(\mathbf{r})$ is made in the tables because as shown in previous articles, its structure is similar to that of $\rho(\mathbf{r})$ and therefore it does not introduce any new information.[5,14] Table III collects the values of the total and the unpaired densities and their associated Laplacian fields at the neighborhoods of the bcp's and vs(3,−1) cp's. The density maps shown in Figures 2– 4 complete the description of the analyzed electron distributions.

In the present discussion, the studied systems are considered into two groups according to the similarity of the molecular structures in the region of interest; the first group involves the two isomers of the 2-C-n-butonium (Figures 1(a) and 1(b)) and the twisted form of the $H_3C \cdots H \cdots CH_3$ (Figure 1(c)); the other group deals with the simplest but no less important methonium (CH_5^+) ion (Figure 1(d)) as will become clear latter.

Despite the different conformational structure of the two isomers and the ethonium ion all them share the main electronic features at the CHC bridge region. All nuclei have an associated **ncp** and all traditional CH sequences are bonded because of the existence of a **bcp** between each pair of atoms of the bridge. The most important spatial region in these systems is defined by the two carbon C_{bh} bridgehead atoms and the hydrogen H_b bridge atom building the bridge structure which connects the two $H_3C - H_2C$ and H_3C groups, in the 2-C-n-butonium isomers and *ethonium*, respectively. The $C_{bh}H_b$ sequences are bonded for all systems, as shown in Table I and

TABLE II. Electronic structure of selected organic systems: carbonium ions. Local and integrated (non-local) topological features of $\rho^{(u)}(\mathbf{r})$ density at CISD/6-31G** level of approximation. All quantities are in atomic units.

cp type	$\rho^{(u)}$ sequences[a]	Atom	Q_{Ω_A}	u_{Ω_A}[b]
		$C_2H_7^+$ (twisted)		
vs (3,−3) cp	One on each C, H atoms	C(1)	2.249	0.181
		C(2)	2.250	0.179
vs (3,−1) cp	One for each CH sequence	H_b	− 0.140	0.054
		H	≈ − 0.140	≈ 0.055
vs (3,+1) cp	No present			
vs (3,+3) cp	No present			
		2-C-n-butonium (structure I)		
vs (3,−3) cp	One on each C, H atoms	C_{bh}	2.130	0.151
		H_b	− 0.079	0.051
vs (3,−1) cp	No on the $C_{bh}C_{bh}$[c] sequence	C	≈ 1.940	≈ 0.140
	One for each $C_{bh}C$ sequence	$H(CH_2)$	≈ − 0.120	≈ 0.040
	One for each $C_{bh}H_b$[d] sequence	$H(CH_3)$	≈ − 0.090	≈ 0.050
	One per each of CH sequence			
vs (3,+1) cp	No present			
vs (3,+3) cp	No present			
		2-C-n-butonium (structure II)		
vs (3,−3) cp	One on each C, H atoms	C_{bh}	2.130	0.151
		H_b	− 0.086	0.052
vs (3,−1) cp	No present for the $C_{bh}C_{bh}$[c] sequence	C	≈ 1.940	≈ 0.140
	One for each $C_{bh}C$ sequence	$H(CH_2)$	− 0.130	≈ 0.080
	One for each $C_{bh}H_b$[d] sequence	$H(CH_3)$	− 0.080	≈ 0.130
	One per each of CH sequence			
vs (3,+1) cp	No present			
vs (3,+3) cp	No present			
		CH_5^+		
vs (3,−3) cp	One on each C, H atoms	C	2.383	0.196
		$H_b(3)$[e]	− 0.201	0.057
		$H_b(6)$	− 0.228	0.051
vs (3,−1) cp	One for each CH sequence	H[f]	− 0.16,−0.19	0.05,0.06
	One for the H_bH_b[d] bridge sequence			
vs (3,+1) cp	One for the H_bCH_b			
vs (3,+3) cp	No present			

[a]Indicate the nucleus at which the vs(3,−3)**cp** is located; for vs(3,−1)**cp**'s, the atoms defining the bond; for vs(3,+1)**cp**'s, the atoms giving rise to the ring; for vs(3,+1)**cp**'s, the atoms defining the cage.
[b]Effectively unpaired atomic electron index.
[c]C_{bh} the *bridgehead*-carbon atom.
[d]H_b the *bridge*-hydrogen atoms.
[e]$H_b(3)$, $H_b(6)$ stand for the *bridge* hydrogen atoms labeled 3 and 6 in Figure 1(d), respectively.
[f]H atoms not involved in the *bridge*.

their covalent bond population are fractional numbers, 0.525 and 0.512 for both isomers (structures I, Figure 1(a) and II, Figure 1(b)), respectively, and 0.512 for $C_2H_7^+$ (Figure 1(c)). The covalent bond order for $C_{bh}C_{bh}$ is 0.190 in both isomers and 0.297 for $C_2H_7^+$ but they are not bonded each other, i.e., no **bcp** is present between them. Neither **rcp**, nor **ccp** appear in the structures. Notably, 0.239, 0.246, and 0.281 2e-3c populations are found for the $C_{bh}H_bC_{bh}$ bridge sequence of isomeric structures I, II, and ethonium ion, respectively.

The remaining covalent bond orders (populations) for all other bonded sequences are not reported in the table because they are as expected close to unity for linked atoms and close to zero for unlinked ones. Table II shows that the values for the non-shared populations Q_{Ω_C} of carbon atoms are greater than 2.0 and H and H_b atoms look positively charged. This means that the most of the electrons in the core region of the C_{bh} atoms are paired (cf. Eq. (10)), and also there are some

flux of electrons from the H atoms regions of the molecule to the bridging neighborhood, most highly marked in $C_2H_7^+$. These results perfectly agree with the non-local view of the quantum rule aforementioned. Nevertheless, as may be noted from Table II, the $\rho^{(u)}$ exhibits a vs(3,−1)cp's for each $C_{bh}H_h$ sequences but there is not a vs(3,−1)cp present for the $C_{bh}C_{bh}$ sequence. Also no vs(3,+1)cp appears for $C_{bh}H_hC_{bh}$ sequence and therefore the local rule is not fulfilled for these compounds. This is a first novelty in comparison with 2e-3c interactions in inorganic systems previously studied, i.e., borane hydrids and closo-borane systems.[5,14] The densities and $L(\mathbf{r})$ at both, bcp and vs(3,−1)cp are shown in Table III. The values for the pairing density (very close to the total density) are several orders of magnitude greater than that of the unpairing one at both points, i.e., bcp and vs(3,−1)cp. Other important feature is that the values for ρ and $\rho^{(u)}$ are very similar when evaluated at these points, hence it indicates they

TABLE III. Density and $L(\mathbf{r})$ of the total density ρ and $\rho^{(u)}$ for carbonium ions at bond critical points of the total density at CISD/6-31G** level of calculation.[a] All quantities are in atomic units.

System[b]	Bond	$\rho(\mathbf{r})\|_{bcp}$	$\rho^{(u)}(\mathbf{r})\|_{bcp}$	$-\nabla^2\rho(\mathbf{r})\|_{bcp}$	$-\nabla^2\rho^{(u)}(\mathbf{r})\|_{bcp}$	ε[c]
$C_2H_7^+$	$C(1)H_b$	0.1735	0.0056	0.2893	0.0071	0.2385
(twisted)		0.1781	0.0053	0.3148	0.0056	0.0082
	$C(2)H_b$	0.1733	0.0056	0.2889	0.0071	0.2348
		0.1779	0.0053	0.3142	0.0056	0.0084
	C(1)H(6)	0.2993	0.0052	1.2173	-0.0050	0.0346
		0.2992	0.0052	1.2052	-0.0053	0.0393
	C(1)H(7)	0.2987	0.0051	1.2132	-0.0053	0.0341
		0.2985	0.0051	1.1998	-0.0055	0.0371
	C(1)H(8)	0.2907	0.0053	1.1491	-0.0036	0.0282
		0.2898	0.0053	1.1202	-0.0038	0.0270
2-C-n-butonium	$C(1)H_b$	0.1625	0.0047	0.2605	0.0073	0.0510
(structure I)		0.1687	0.0045	0.2810	0.0062	0.0167
	$C(2)H_b$	0.1624	0.0047	0.2598	0.0073	0.0452
		0.1685	0.0045	0.2802	0.0062	0.0173
	C(2)C(3)	0.2578	0.0044	0.6774	0.0053	0.0116
		0.2595	0.0042	0.6566	0.0071	0.0340
	C(1)C(12)	0.2575	0.0044	0.6760	-0.0053	0.0118
		0.2592	0.0043	0.6553	-0.0070	0.0332
	C(2)H(4)	0.3021	0.0042	1.2200	-0.0043	0.0378
		0.3020	0.0042	1.2326	-0.0043	0.0256
	C(2)H(9)	0.3001	0.0042	1.2066	-0.0044	0.0356
		0.2999	0.0042	1.2137	-0.0041	0.0278
	C(3)H(6)	0.2900	0.0042	1.0827	-0.0040	0.0197
		0.2904	0.0042	1.1314	-0.0035	0.0199
	C(3)H(7)	0.2825	0.0043	1.0323	-0.0029	0.0122
		0.2825	0.0043	1.0623	-0.0025	0.0216
	C(3)H(8)	0.2896	0.0042	1.0790	-0.0040	0.0197
		0.2900	0.0042	1.1286	-0.0035	0.0197
2-C-n-butonium	$C(1)H_b$	0.1629	0.0046	0.2547	0.0068	0.0965
(structure II)		0.1687	0.0044	0.2755	0.0057	0.0218
	$C(2)H_b$	0.1629	0.0046	0.2548	0.0068	0.0958
		0.1687	0.0044	0.2756	0.0057	0.0218
	C(2)C(3)	0.2611	0.0043	0.6957	-0.0057	0.0089
		0.2629	0.0042	0.6744	-0.0075	0.0441
	C(1)H(10)	0.2611	0.0043	0.6958	-0.0058	0.0089
		0.2629	0.0042	0.6745	-0.0075	0.0442
	C(2)H(4)	0.3024	0.0043	1.2214	-0.0045	0.0381
		0.3024	0.0043	1.2355	-0.0042	0.0166
	C(2)H(9)	0.2961	0.0043	1.1779	-0.0037	0.0304
		0.2957	0.0043	1.1753	-0.0035	0.0232
	C(3)H(6)	0.2898	0.0042	1.0845	-0.0040	0.0196
		0.2901	0.0042	1.1286	-0.0035	0.0174
	C(3)H(7)	0.2832	0.0043	1.0370	-0.0030	0.0124
		0.2832	0.0043	1.0677	-0.0026	0.0200
	C(3)H(8)	0.2888	0.0042	1.0697	-0.0039	0.0202
		0.2893	0.0042	1.1220	-0.0034	0.0180
CH_5^+	H_bH_b	0.2173	0.0043	0.4409	-0.0126	4.3608
		0.1982	0.0047	0.4679	-0.0013	0.4291
	CH(2)	0.2727	0.0060	1.0199	-0.0009	0.0017
		0.2724	0.0060	0.9617	-0.0023	0.0036
	$CH_b(3)$	0.2174	0.0046	0.4119	-0.0113	3.9046
		0.2015	0.0051	0.3696	-0.0022	0.1564

[a]Second line in Columns 3–7 for each bond indicates the densities and $L(\mathbf{r})$ at $\rho^{(u)}(\mathbf{r})$ vs(3,−1)cp.
[b]See Figure 1 for atoms labeling.
[c]Ellipticity.
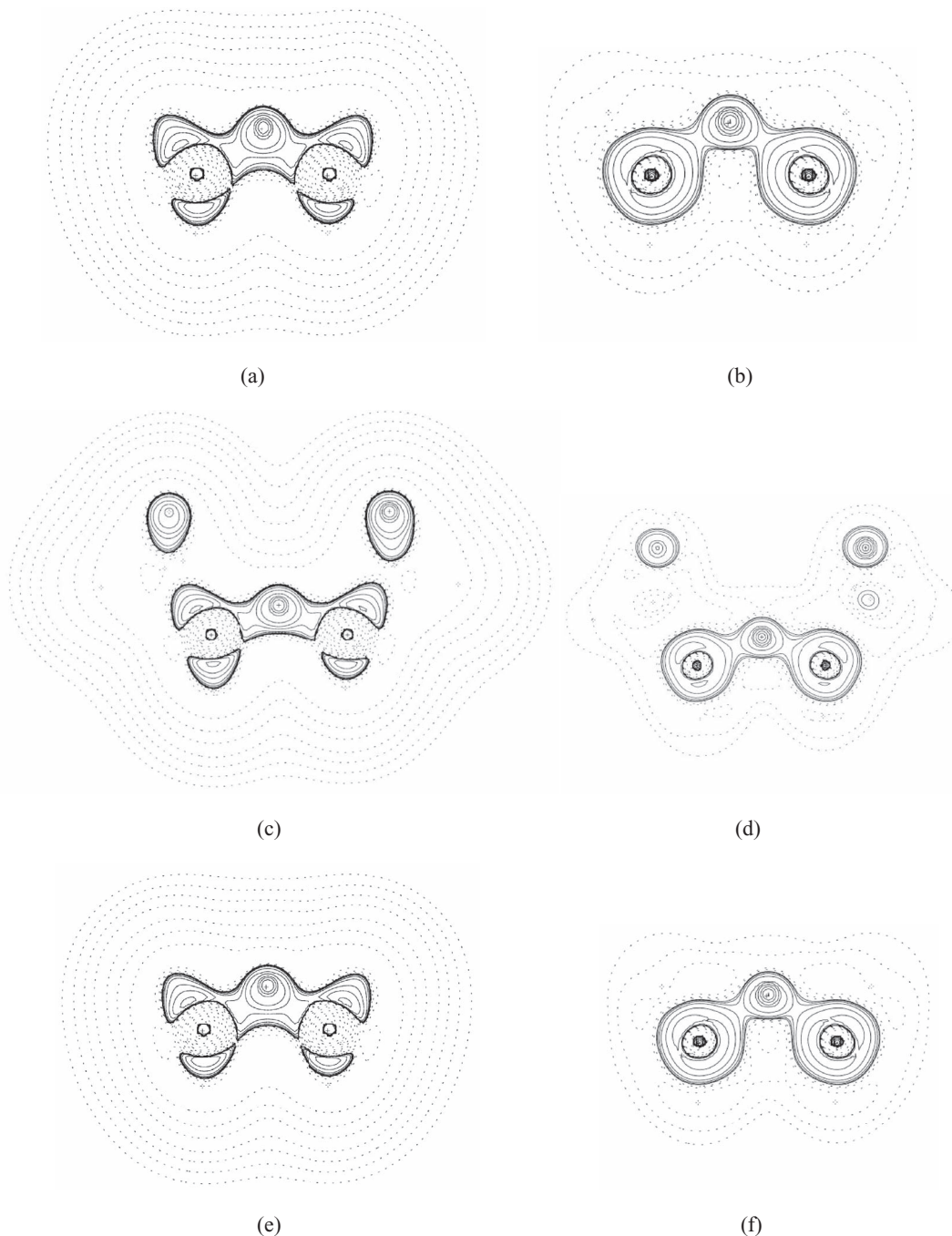
(a)

(b)

(c)

(d)

(e)

(f)

FIG. 2. $L(\mathbf{r})$ contour maps for total density (a), (c), and (e) and effectively unpaired densities (b), (d), and (f) in the plane defined by bridge atoms of $n - C_4H_{11}^+$ isomers (butonium cations), and ethonium ($C_2H_7^+$), respectively. Positive and negative values are denoted by solid and dashed lines, respectively.

are close together. Moreover, however both densities accumulate at bcp's of $C_{bh}H_b$ sequences, the unpaired density is very close to a null value. Thus, these bonds may be considered as quasi-covalent, i.e., a typically covalent would show a depletion of the unpaired density.[16] It may be noted that the CH bridge bond at $C_2H_7^+$ seems to be very unstable because of the high values of its ellipticity (cf. Refs. 25 and 26, p. 84 and 77, respectively.); this is not the case for the 2-C-n-butonium isomers. The contour maps of the Laplacian function $L(\mathbf{r})$ of the density fields at the bridge region in its own plane are shown in Figure 2. All of them are very similar for the three systems. The ρ contours show accumulation over the inter-

atomic region $C_{bh}H_b$ and depletion between the $C_{bh}C_{bh}$ atoms (Figures 2(a), 2(c), and 2(e)) which does not show bonding interactions. The Laplacian contour maps of $\rho^{(u)}$ show similar accumulation/depletion behavior as ρ (Figures 2(b), 2(d), and 2(f)). This is another important feature which also appears as a novelty in comparison with 2e-3c interactions in inorganic systems previously studied, i.e., borane hydrids and closo-borane systems.[5,14] Hence, it seems to be the conductive thread expressing this different type of 2e-3c patterns of bonding interactions appearing in organic systems.

The results analyzed above suggest that the 2e-3c interaction mechanism bifurcate into two different kind of
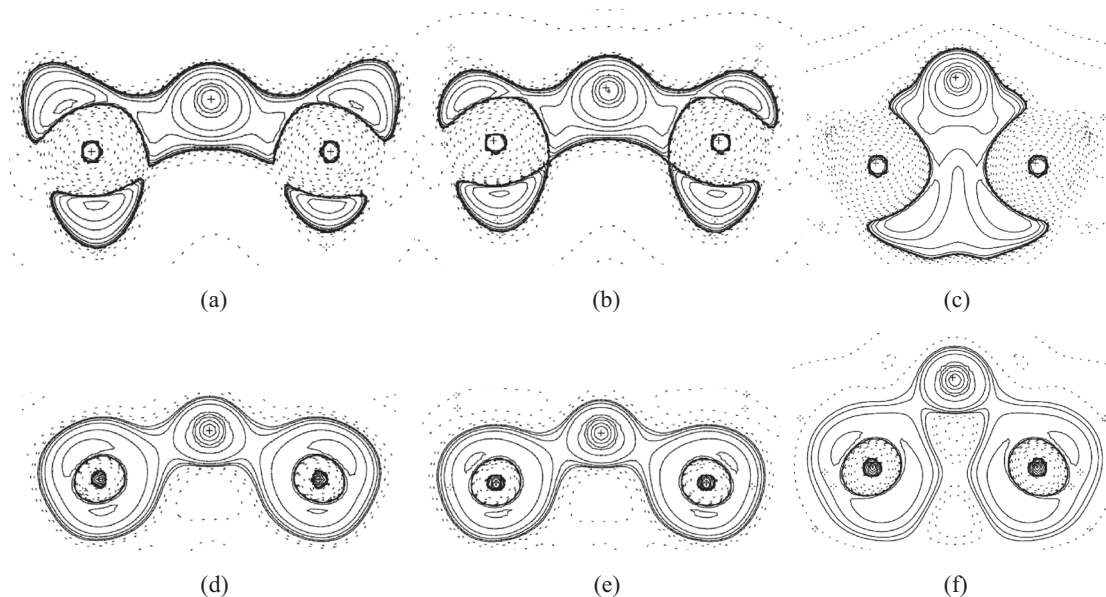
FIG. 3. $L(\mathbf{r})$ contour maps for total density (a)-(c) and effectively unpaired densities (d)-(f) in the plane defined by bridge atoms of $n - C_4H_{11}^+$ isomers (butonium cations), and B_5H_{11} boron hydrid for comparison of **TB** and **TS**, respectively. Positive and negative values are denoted by solid and dashed lines, respectively.

interactions. For boron hydrids[5] and closo-boranes,[14] such interactions may be interpreted from both views of the quantum rule, i.e., local and non-local. Nevertheless, this type of interactions in the organic systems which have been analyzed seems to be interpreted only from the non-local point of view. Let us now to discuss in more detail the similarities and differences between both types of electron distributions.

Figure 3 shows the $L(\mathbf{r})$ contour lines of ρ (Figures 3(a)–3(c)) and $\rho^{(u)}$ (Figures 3(d)–3(f)) for the two 2-C-n-butonium ion isomers and the B_5H_{11} boron hydrid,[5] in the plane of the $X \cdots H_b \cdots X$ (X = C, B) bridge, respectively (see Figure 1 of this work and Figure 1(d) of Ref. 5), for comparison. At $X \cdots H_b$ regions, the total density ρ shows a similar structure for both kinds of systems, i.e., the corresponding inner shell structure and the density accumulation in the internuclear XH_b region. Nevertheless, the differences between the two types of systems appear at $X \cdots X$ regions for $\rho^{(u)}$ which does not show "spillage" between the two C_{bh} atoms while this is true for the boron hydrids (Figure 3(f)). Also, the pairing density does not show accumulation at internuclear $C_{bh} \cdots C_{bh}$ regions while it has been always found concentration of pairing density in $B \cdots B$ region.[5, 14] Other important
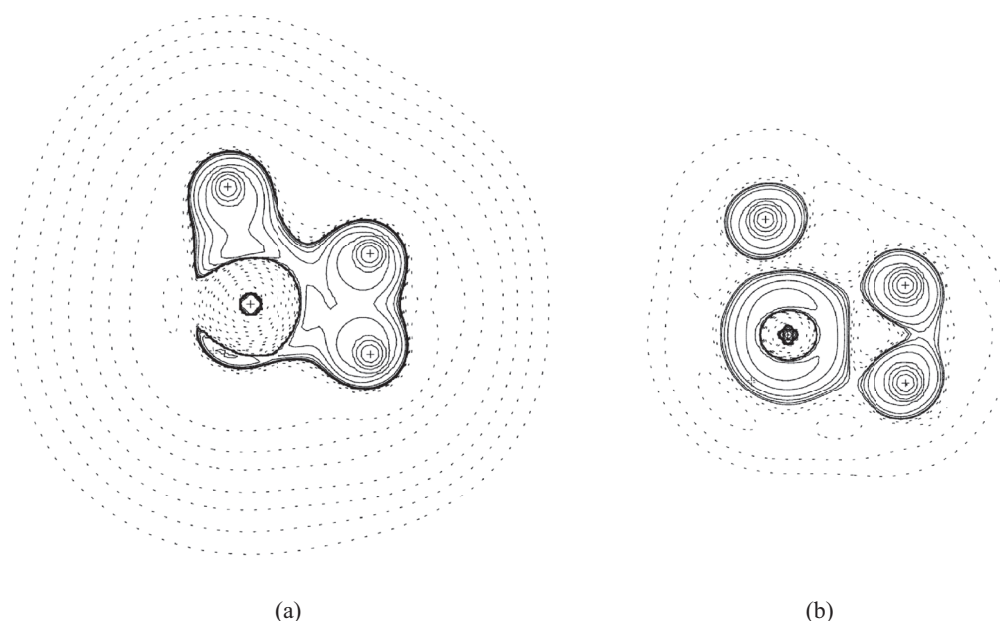

FIG. 4. $L(\mathbf{r})$ contour maps for total density (a) and effectively unpaired densities (b) in the plane defined by bridge atoms of methonium (CH_5^+). Positive and negative values are denoted by solid and negative values are denoted by solid and dashed lines, respectively.

feature to be noted is the greater strangulation of solid contour lines at valence regions at the internuclear region of the XH_b bonded sequence for the boron hydrids in comparison with those of the organic ions (cf. Figs. 3(d) and 3(e) with 3(f)) which seems to be related to the 2e-3c XH_bX population decrement in boron hydrids in comparison with the organic ions, i.e., 2-C-n-butonium (0.28-0.24) > B_5H_{11} (0.105) > B_2H_6 (0.061) (the B_2H_6 bridge contour is not shown in Figure 3 because it is similar to the B_5H_{11}).[5] This situation may be interpreted as follows. A greater strangulation of the accumulation lines of $\rho^{(u)}$ present in the boron hydrids in comparison with organic ions and the "spillage" over the physical region of the three centers, i.e., the two headbridge B atoms and the bridge H_b atom give rise to the $vs(3, +1)cp$ which is in agreement with the local rule for 2e-3c bonding interactions. On the other side, for the organic ions there is no such "spillage" between the two headbridge C_{bh} atoms, therefore no $vs(3, +1)cp$ arises. It is of crucial importance to note that the features described above indicate that the conditions invoked for the local view of the rule for boron hydrids are not present in the organic ions. Then, it becomes clear that this situation is an indicator of the sensitive character of the local view allowing to establish that all 2e-3c interactions have not the same nature in all of the systems. Regarding the studied structures the main difference appears considering the regions in which $\rho^{(u)}$ accumulates, i.e., around the bond path between the nuclei in the three center sequence or "spilled" over the interatomic physical space involving the three centers.

In fact, the results discussed above allow conjecturing a possible classification of the 2e-3c interactions based in the features arisen from the two type of systems, i.e., the present organic ions (2-C-n-butonium cations) and the boron hydrids. Therefore, according to what was described above, the distribution types can be classified as follows:

- **TS**: The $\rho^{(u)}$ is spilled over the spatial region involving the atoms of the sequence. Consequently, it accumulates beyond the surroundings of the bonded nuclei which allows to form a $vs(3, -1)cp$'s between the three pairs of atoms and a $vs(3, +1)cp$ formed by the atoms involved in the pattern. It indicates that there is a non-negligible unpairing electron density concentration at the inter-atomic regions correspondent to no linked atoms, i.e., those atoms which between them no **bcp** exists. Thus, the interaction is also produced through a localized physical region where there are no bcp and then it is called *through space*.

- **TB**: Between each pair of the three atoms involved in this interaction neither $vs(3, -1)cp$'s nor $vs(3, +1)cp$'s appear. There are no "spillage" of $\rho^{(u)}$ over the whole region involved in the 2e-3c interaction, i.e., the three pairs of atoms. The unpaired electron cloud is localized only close to the internuclear "headbridge-bridge" joining line and not within the two "headbridge" ones. Therefore, $\rho^{(u)}$ concentrates only in the interatomic linked nuclei regions, i.e., those which has a **cp** indicating a bonding interaction. Therefore, it is called *through bond*.

Let us make some remarks about the distinctions for these two types of 2e-3c interactions. At non-local level of description, both types of interactions share the fact that covalent bond orders I_{AB} for any two atoms in the three center sequence are fractional numbers and the 2e-3c populations $\Delta^{(3)}_{\Omega_A\Omega_B\Omega_C}$ are non-negligible. The 2e-3c populations are generally greater for **TS** than for **TB** type interactions. In like manner, the unpairing populations u_Ω are minor for **TS** than for **TB** because at the former type the unpaired electron cloud is spread out over the whole internuclear regions while at the latter it concentrates around the bond paths and close to the nuclei. Namely, such population indicators show that the unpaired electron cloud localizes at different regions in physical space.

Finally, the analysis of the remaining system, CH_5^+ is carried out. It is the simplest system of this type of ions but its electron distribution adds an important feature that emphasizes the above classification and merits its analysis. To begin with, it may be noted that its conformational structure differs from the above discussed ones in that it also possesses a bridged structure but unlike the other systems, it is formed by a $H \cdots C \cdots H$ sequence, i.e., the C atom would be considered the bridge while the headbridge are the two H atoms as shown in Fig. 1(d). Its topological characteristics defining the electronic distribution can be observed from Table I. All nuclei has an associated **ncp** and all CH sequences are bonded, i.e., a **bcp** exist between each pair of atoms, except that formed by the C atom and one of the H atoms of the bridge (label 6 in Fig. 1(d)). The two bridging H_b atoms are linked, a **bcp** is defined by them. Similarly as in the first group of systems, there are no **rcp**, neither **ccp**'s. The covalent bond orders between the atoms which are not involved in the bridge are ≈ 0.88, a little weaker than in normal reference CH_4 system. The total difference of population of the three atoms in the CH_3 group respect to the unit (0.36) is close to the excess population in C (more than the two electrons which it normally houses in the inner shell), ≈ 0.38 which may be observed from the Q_C in Table II. Therefore, it may be interpreted as a flux of electrons from the CH bonds to the atomic C domain. For the CH_b bridge sequences, the values are 0.551 for the bonded atoms and 0.507 for those which are not bonded (cf. Table I and Fig. 1(d), labels 3 and 6, respectively). The bonded $H_b \cdots H_b$ sequence (Table I and Fig. 1(d), labels 3 and 6) show a notable value of 0.35. Note that such values are fractional and as the 2e-3c population of the bridge $H_{hb}CH_{hb}$ is high, 0.318, the non-local rule is then fulfilled. Table II collects the information for $\rho^{(u)}$ topology which stands for the fulfillment of the local view of the quantum rule. The non-shared populations Q_{Ω_A} for the C atom of 2.38 is appreciable greater than to 2.0 and because the contribution of u_{Ω_A} in C is 0.196, it indicates that an important fraction of the electrons in the core region of the C atom is effectively unpaired. H_{bh} and H_b, as well as the other Hs have high positive unshared charges, ≈ -0.2 and $\approx -0.16, -0.19$, respectively. They also exhibit not so high unpaired populations in comparison with those in the other group of systems. The density maps of ρ and $\rho^{(u)}$ for this system in the plane of the bridge are shown in Fig. 4. Fig. 4(a) shows the charge accumulation in the internuclear region joining the $H_b \cdots H_b$, $H_{bh} \cdots H_b$, and $C_{hb} \cdots H_{hb}$

atoms. The corresponding $\rho^{(u)}$ maps (Fig. 4(b)) are similar to those of boron hydrids (cf. Fig. 3)[5] in which the unpaired electron cloud spills over the three centers and their surroundings regions giving rise to the $vs(3,-1)cp$'s between each of the pairs of atoms forming the bridge (C_hH_{bh} and $H_{bh}H_{bh}$) and a $vs(3,+1)cp$, as reported in Table II. These results perfectly agree with a not so high accumulation of the unpaired density in the atomic and bond path regions and the consequent "spillage" of that cloud over the three center involved in the interaction are the onset of the vs(3,−1) and vs(3,+1)cp's, in comparison with the previous described systems. Therefore, the local view of the rule is fulfilled. Let us inspect the densities and their Laplacian values at **bcp** and vs(3,−1)cp from Table III. The most important features to be remarked are that, on one side, ρ is of one order of magnitude greater than $\rho^{(u)}$ at both points. Also, the values of both fields at these points are very similar, which indicates as in the 2-C-n-butonium cations, that they are close together each other. Looking at their Laplacian fields, it may be noted that the pairing density (not explicit shown in the table because of the explanation given at beginning of this section) accumulates at the aforementioned points while $\rho^{(u)}$ diminishes. Note that the bridge bonding interactions between C_hH_{bh} and $H_{bh}H_{bh}$ exhibit high ellipticity, so that they may be considered as unstable or defining a system near to undergo a structural change (cf. Ref. 25, p. 84). To finish our discussion, let us make an important observation which completes the description of the proposed interaction mechanisms of the 2e-3c type. The first group of systems discussed in this section makes us able to establish what we called the **TB** interactions because of the comparison with other types of systems, the boron hydrids and closo-boranes described in Refs. 5 and 14, which gives rise to other type of mechanism called **TS** interactions. The second group includes in the discussion the simplest CH_5^+ ion which fulfills the conditions of both versions of the quantum rule. On one side, this system admits the formation of the $vscp$'s and also the integrated magnitudes are according to the physical conditions defined by the rule. However, the value of the 2e-3c population $\Delta^{(3)}_{\Omega_A\Omega_B\Omega_C} = 0.318$ seems to be typical of the **TB** type of interaction despite this system possess a widespread of $\rho^{(u)}$ over the whole bridge region typical of the **TS** mechanisms. Hence, this situation may be interpreted as intermediate between the two well established cases. This result gives an emphasis to the proposed mechanisms of interaction to form the complex 2e-3c pattern.

CONCLUDING REMARKS

The electron distributions of some organic systems which are considered as possessing 2e-3c complex pattern of bonding has been described in detail. The present analysis extends the previous one performed on the emblematic boron hydrids which gave rise to a quantum rule to characterize this type of bonding interactions from local and non-local views. Hence, the analysis of the present systems provides a challenge to the interpretation of the non-local view of the quantum rule and consequently the understanding of these interactions. To characterize the interactions, thus giving a set of features that describe different environments an attempt of classification

into two main types as **TS** and **TB** has been proposed in order to understand the differences and similarities of these distributions. Both types are similar at the non-local point of view but the strength of the interactions measured by the 2e-3c populations are of different orders of magnitude. The essential differences between both types of interactions become clear from the local view, i.e., the **TS** type shows the onset of $vs(3,-1)cp$'s and the $vs(3,+1)cp$ associated to the three center sequences which expresses the accumulation of $\rho^{(u)}$ cloud over the whole region of the involved atoms, while in the **TB** type these critical points are not present, and the $\rho^{(u)}$ only shows a non-negligible accumulation over the interatomic region of interacting atoms. It permits to conclude that this main difference is the physical region over which the $\rho^{(u)}$ density localizes. It is of great importance to note that this attempt of classification may not be interpreted as that the bonding interactions of inorganic compounds are of **TS** type while the organic ones of **TB**, but for any type of systems. The intermediate situations between both types of interaction features may be observed from the inclusion of CH_5^+.

The main conclusion from all the remarked results can be condensed in that the knowledge about many-atoms interactions like the present 2e-3c case is supported by the behavior of the $\rho^{(u)}$ density localization and the onset of its vscp's. Therefore, it made us able to extend our knowledge to confirm for a wider class of molecular systems that some subtle and crucial information is hidden in the total density and may be extracted from it throughout the unpaired density matrix. These important consequences from the detailed study for complex interactions between atoms that give rise to the different molecular structures, i.e., organo-metallic, pnicogen, hydrogen, van der Waals, small clusters, and metallic interactions among others constitute a natural scenario for the application of these techniques and are being studied in our laboratories.

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