

## Topology of the Effectively Paired and Unpaired Electron Densities for Complex Bonding Patterns: The Three-Center Two-Electron Bonding Case

Rosana M. Lobayan,<sup>†</sup> Roberto C. Boichichio,<sup>\*,‡</sup> Alicia Torre,<sup>§</sup> and Luis Lain<sup>§</sup>

*Facultad de Ingeniería, Universidad de la Cuenca del Plata, Lavalle 50, 3400 Corrientes, Argentina, Departamento de Física, Facultad de Ciencias Exactas y Naturales, Universidad de Buenos Aires, Ciudad Universitaria, 1428 Buenos Aires, Argentina, and Departamento de Química Física, Facultad de Ciencias, Universidad del País Vasco, Apdo, 644 E-48080 Bilbao, Spain*

Received June 2, 2009

**Abstract:** Our previously reported local formalism of the electron density decomposition into effectively paired and unpaired densities is applied to electron deficient molecular systems possessing complex bonding patterns. It is shown that the unpaired density is not only near the nuclear positions, like in classical bonds, but also spills out over the bonding regions, to compensate the electron deficiency. Topological information obtained from the effectively unpaired density, which may not be directly observed from the total density, allows us to establish a procedure to detect complex interactions. This study is complemented with results arising from nonlocal formalism of topological population analyses. The conclusions from both formalisms are in complete agreement and permit to interpret the well-known structural information from Lipscomb *styx* numbers going beyond it in cases where the electronic description becomes ambiguous, pointing out the subtle information contained in the unpaired density. Numerical results for three-center two-electron bondings in the boranes B<sub>2</sub>H<sub>6</sub>, B<sub>4</sub>H<sub>10</sub>, B<sub>5</sub>H<sub>9</sub>, and B<sub>5</sub>H<sub>11</sub> are reported.

### 1. Introduction

The physical information contained in *N*-electron molecular state functions is usually summarized by means of chemical concepts, such as atomic and bondings populations, bond orders<sup>1–4</sup> and ionicities (multiplicities),<sup>4–6</sup> atomic and free valencies,<sup>4,7–12</sup> etc. In the quantitative description of these concepts the electron density<sup>13–16</sup> constitutes a tool of paramount interest. Two complementary methodologies have been developed to deal with this density. On the one hand the *nonlocal or integrated formulations*, which are known as electronic population analysis.<sup>4,13–16</sup> Within these methods, the Mulliken-type partitionings<sup>17</sup> associate an atom with the atomic basis functions centered on the corresponding

nucleus in the molecule; the atomic and bonding regions become automatically defined, regarding the localization of these atomic functions.<sup>18,19</sup> Other methods of population analyses assign real space regions to the atoms, as the “fuzzy” atoms descriptions,<sup>20–23</sup> projection operators techniques<sup>24</sup> or the topological atoms in molecules (AIM) theory.<sup>7,25–30</sup> On the other hand, the electron density  $\rho(\mathbf{r})$  and its associated Laplacian field  $\nabla^2\rho(\mathbf{r})$  can be studied through their topological structures. The localization and classification of their critical points (cp), i.e., maxima, minima, or saddle ones, characterize these fields, providing an alternative and complementary approach to extract and interpret chemical information.<sup>25,26</sup> This approach will be called *local formulation*.

The cp's are classified regarding the value and sign of the three eigenvalues of the Hessian matrix of the density  $\rho(\mathbf{r})$ . This information is featured as  $(r, s)$ , where *r* is the *rank* (the number of nonzero eigenvalues of the Hessian matrix) and *s* is the *signature* (the sum of the signs of its eigenval-

\* Corresponding author e-mail: rboc@df.uba.ar.

<sup>†</sup> Universidad de la Cuenca del Plata.

<sup>‡</sup> Universidad de Buenos Aires.

<sup>§</sup> Universidad del País Vasco.

ues). Any point with all negative eigenvalues is denoted as (3,-3); such a point is called a nuclear critical point (ncp) and indicates a local maximum placed at the nuclear positions. A cp with two negative eigenvalues and a positive one is denoted by (3,-1) and corresponds to a bond critical point (bcp); in this type of cp's the concentration of the electron density shows a bonding interaction between two atoms.<sup>25,26</sup> The first two eigenvalues of the Hessian matrix correspond to the perpendicular curvatures, and the third one provides a curvature along the internuclear axis. In this scenario, a covalent bond is featured by the electron cloud possessing two large negative curvatures perpendicular to the bond line and a small positive curvature along the bond at the position of the bcp.<sup>25,26</sup> Other important cp's which are not present in systems with classical bonding patterns are the *ring* (rcp) and *cage* (ccp) critical points, which appear in molecular systems of complex electronic structure; these points are characterized by rank and signature (3,+1) and (3,+3), respectively.<sup>25,26</sup> The value of  $\nabla^2\rho(\mathbf{r})$  is the sum of the curvatures along the orthogonal coordinate axes. Its sign indicates electron density locally depleted (positive) or locally concentrated (negative) and constitutes valuable information to describe the behavior of the density around a local point<sup>25,26,31</sup> and other features of the electron distribution, as the unpaired electron contributions to the density.<sup>32,33</sup>

In previous works<sup>32,33</sup> we have reported an exact partitioning of the electron density so that  $\rho(\mathbf{r}) = \rho^{(p)}(\mathbf{r}) + \rho^{(u)}(\mathbf{r})$  in which the contributions  $\rho^{(p)}(\mathbf{r})$  and  $\rho^{(u)}(\mathbf{r})$ , possessing different physical character, correspond to the effectively paired and unpaired electron density, respectively.<sup>8-11</sup> We have described the behavior of both contributions to the electron density and the shifts of their (3,-3) and (3,-1)cp's in comparison with those of the total density. Our results show that the positions of the (3,-3)cp's of  $\rho^{(p)}(\mathbf{r})$  are located very close to the total  $\rho(\mathbf{r})$  ncp, while the  $\rho^{(u)}(\mathbf{r})$  (3,-3)cp's are also located close to the nuclear positions but out of the bonding region.<sup>32</sup> The utilization of the Laplacian functions,  $\nabla^2\rho^{(p)}(\mathbf{r})$  and  $\nabla^2\rho^{(u)}(\mathbf{r})$ , shows that nuclear regions possess most of the effectively unpaired electrons. Moreover, both paired and unpaired density fields possess successive regions of concentration and depletion of density, yielding a shell structure.<sup>33</sup> These results have been obtained in systems possessing conventional patterns of bonding. Hence, we have now the challenge to extend this treatment to systems with more complex bonding patterns, such as three-center two-electron (3c-2e) bonds. For this goal, we have chosen several electron deficient boron hydrides, due to the crucial importance of the presence of three-center bondings in the structural description of these compounds.<sup>34-37</sup>

The organization of this article is as follows. The second section briefly reports the theoretical framework of the partitioning of the electron density and the relationships between the density gradients and between the Laplacian fields as well as the tools used to carry out complementary studies of topological population analysis. The third section describes the computational details of the calculations performed over a set of selected boranes and a comparative discussion of the results from both formulations. Finally, the last section is devoted to the concluding remarks.

## 2. Theoretical Background

The electron density,  $\rho(\mathbf{r})$ , in an  $N$ -electron molecular system may be decomposed into two contributions<sup>32</sup>

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

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

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

and

$$\rho^{(u)}(\mathbf{r}) = \frac{1}{2} u(\mathbf{r}|\mathbf{r}) \quad (3)$$

respectively.  ${}^1D(\mathbf{r}|\mathbf{r}')$  means the spin-free first-order reduced density matrix (1-RDM) in the coordinate representation,<sup>14,38</sup> 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  ${}^1D^2(\mathbf{r}|\mathbf{r}') = \int d\mathbf{r}'' {}^1D(\mathbf{r}|\mathbf{r}'') {}^1D(\mathbf{r}''|\mathbf{r}')$ .<sup>8-12</sup> Note that the densities are defined as the diagonal part of the corresponding density matrices, e.g.  $\rho(\mathbf{r}) = {}^1D(\mathbf{r}|\mathbf{r})$ . 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 nonsinglet states) and the other corresponds to the many-body effects or correlation effects that are supported by the Coulomb interaction between the particles.<sup>7,8,28</sup> It may be noted that for state functions having all orbitals doubly occupied, as in the closed-shell Hartree-Fock or the density functional theory (DFT) cases,  $\rho^{(u)}(\mathbf{r})$  is intrinsically zero,<sup>32</sup> and such effects cannot be detected.

The techniques used to study the electron density topology<sup>25,26</sup> may also be applied to its two above-mentioned components, to describe bonding features in a more precise manner. The fundamental information is obtained from the localization of the cp's of each contribution of the electron density. The cp's for the total density are found throughout the gradient of the field by

$$\nabla\rho(\mathbf{r}) \Big|_{\mathbf{r}^c} = 0 \quad (4)$$

or equivalently, according to eq 1

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

where  $\mathbf{r}^c = \{\mathbf{r}_i^c; i = 1, \dots, M\}$  indicates the set of critical points of the total density  $\rho(\mathbf{r})$ . Then the following relation holds

$$\nabla\rho^{(p)}(\mathbf{r}) \Big|_{\mathbf{r}^c} = -\nabla\rho^{(u)}(\mathbf{r}) \Big|_{\mathbf{r}^c} \quad (6)$$

whose physical meaning is that each density field component increases/decreases its value in opposite direction, 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. Hence, no simultaneous increment/decrease of each one may occur at the cp's.<sup>32</sup> The Laplacian field of eq 1 yields

$$\nabla^2 \rho(\mathbf{r}) \Big|_{\mathbf{r}^c} = \nabla^2 \rho^{(p)}(\mathbf{r}) \Big|_{\mathbf{r}^c} + \nabla^2 \rho^{(u)}(\mathbf{r}) \Big|_{\mathbf{r}^c} \neq 0 \quad (7)$$

According to eq 7 both  $\nabla^2 \rho^{(p)}(\mathbf{r}) \Big|_{\mathbf{r}^c}$  and  $\nabla^2 \rho^{(u)}(\mathbf{r}) \Big|_{\mathbf{r}^c}$  contributions do not necessarily follow opposite trends, as the above-mentioned ones for the density gradient. Thus, both density Laplacians may concentrate or deplete at the neighborhood of a cp simultaneously. It is worthwhile to note that the results reported in ref 33 have shown that both  $\rho^{(p)}(\mathbf{r})$  and  $\rho^{(u)}(\mathbf{r})$  densities possess a shell structure as the  $\rho(\mathbf{r})$  one.<sup>33,39</sup>

The nonlocal or integrated formalism is complementary to the above-mentioned local one. This nonlocal formalism deals with classical chemical concepts like atomic charges, bond orders, and valences, etc.<sup>7,8,28–30</sup> We will refer to the nonlocal AIM topological population analysis. We summarize the relations defining the relevant magnitudes to our goal, which have been previously stated within that approach.<sup>7,29</sup> The two-center bond index has been defined as

$$I_{\Omega_A \Omega_B} = \sum_{i,j,k,l} {}^1D_j^i {}^1D_l^k S_{il}(\Omega_A) S_{kj}(\Omega_B) \quad (8)$$

where  $\Omega_A$  and  $\Omega_B$  stand for Bader's atomic domains in the physical space,<sup>25</sup>  ${}^1D_j^i$  are the first-order reduced density matrix elements, and  $S_{ij}(\Omega_A)$  are the elements of the overlap matrix over the region  $\Omega_A$ , in the orthogonal molecular basis set  $\{i,j,k,l,\dots\}$ .<sup>7</sup> In the same context, the three-center bond index is

$$I_{\Omega_A \Omega_B \Omega_C} = \sum_{i,j,k,l,m,n} {}^1D_j^i {}^1D_l^k {}^1D_n^m S_{in}(\Omega_A) S_{kj}(\Omega_B) S_{ml}(\Omega_C) \quad (9)$$

giving rise to the three-center topological bond order as<sup>29</sup>

$$\Delta_{\Omega_A \Omega_B \Omega_C}^{(3)} = \frac{1}{4} \sum_{P(\Omega_A \Omega_B \Omega_C)} I_{\Omega_A \Omega_B \Omega_C} \quad (10)$$

where  $P(\Omega_A \Omega_B \Omega_C)$  indicates the permutations of the three domain contributions.

The theoretical structural index or *styx* number defined by Lipscomb is the indicator commonly used to characterize the reported compounds.<sup>37</sup> According to Lipscomb rules the structure of electron deficient boranes can be summarized by this index where *s* is the number of the 3-center BHB bonds, *t* is the number of 3-center BBB bonds, *y* is the number of 2-center BB bonds, and *x* gives the number of BH<sub>2</sub> groups in the system.

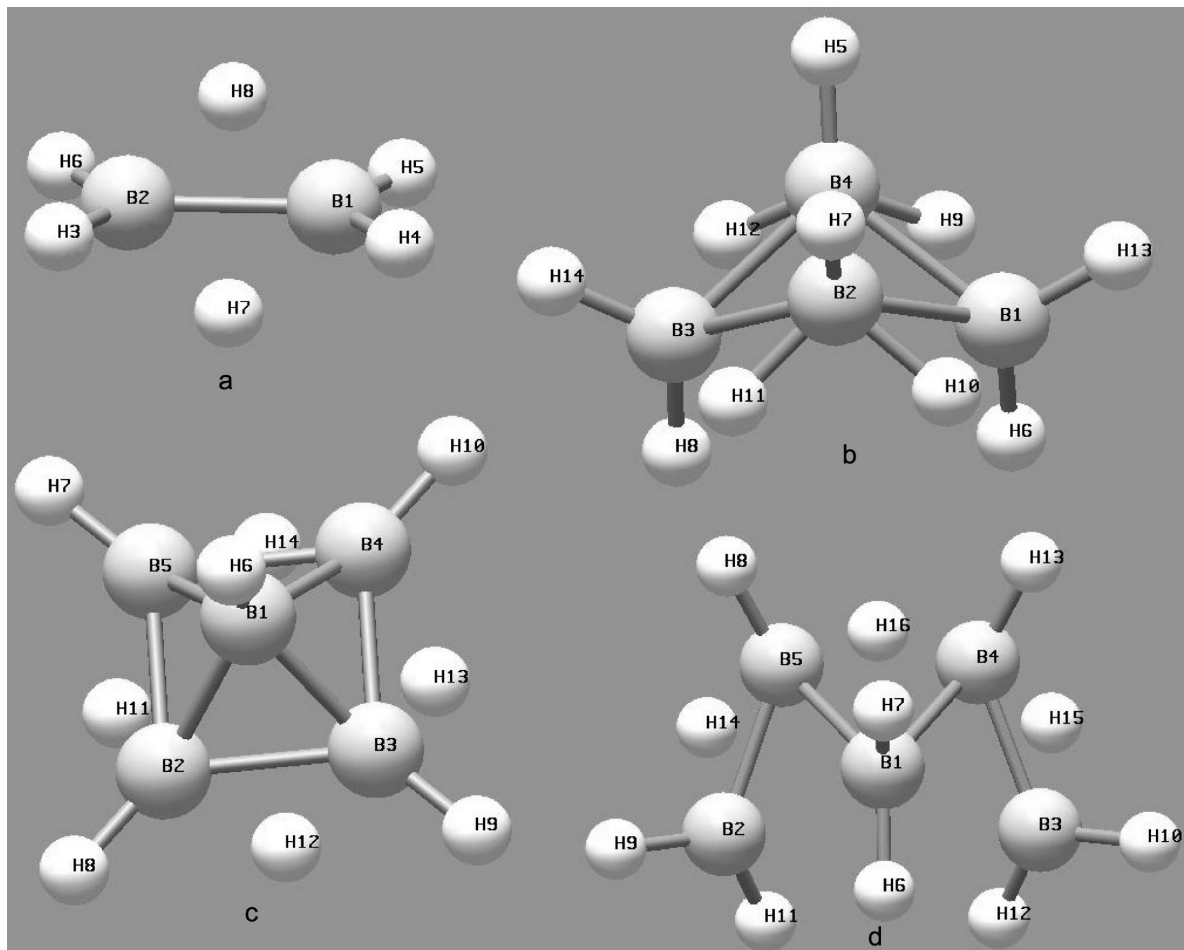
As has been pointed out in the Introduction, the main purpose of this paper is to study the capability of these tools to describe nonconventional bondings as the (3c-2e) ones. The results are reported in the next section.

### 3. Results and Discussion

**3.1. Computational Details and Results.** The state functions used in this work to describe the molecular systems were calculated at the level of configuration interaction with single and double excitations (CISD), using the Gaussian 03 package<sup>40</sup> with the basis sets 6-31G\*\*. The geometries for all systems were optimized within this approximation. 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 appropriately modified AIMPAC modules.<sup>41</sup> The reported systems have been chosen to study the (3c-2e) complex pattern of bonding present in electron deficient boranes<sup>34–36</sup> (some preliminary results for the B<sub>2</sub>H<sub>6</sub> system have been reported in ref 32). The numerical results of populations analysis were obtained with our own codes mentioned in ref 29. For practical reasons, we will use the function  $L(\mathbf{r}) = -\nabla^2 \rho(\mathbf{r})$  in the discussion of results as an indicator of concentration (positive value) or depletion (negative value) of the number of electrons at the point  $\mathbf{r}$ ;<sup>32,33</sup> the terms accumulation and reduction have been proposed for the description of maxima and minima in  $\rho(\mathbf{r})$ .<sup>39,42</sup> 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) in the corresponding systems, 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.<sup>25,26</sup> Figure 1 shows the molecular structure of each of the systems studied in this work.

Table 1 shows a detailed description of the electronic distributions from the topological (local and nonlocal) point of view for these borane systems. We will use diborane molecule, B<sub>2</sub>H<sub>6</sub>, as a test example to show the similar and complementary description of the electron distribution provided by the local and nonlocal formalisms. Table 2 shows the numerical values for each density and its  $L(\mathbf{r})$  field at the bcp's of the total density and at  $\rho^{(u)}(\mathbf{r})$  vs(3,-1) cp's; Tables S1 and S2 of the Supporting Information (SI) show the numerical values for the ncp's and rcp's, respectively.

**B<sub>2</sub>H<sub>6</sub>.** As is indicated in Table 1, the structural number *styx* for this hydride is 2002. It means that this system possesses two (3c-2e) bridge bonds BHB, no BBB bonds, no BB bonds, and two groups BH<sub>2</sub>. The topological structure of the total density  $\rho$  exhibits one ncp located on each nucleus, one bcp for each of the four terminal bond BH, and a bcp defining a bond for each one of the four bridge sequences BH. The absence of bcp's between the boron atoms indicates that this topology does not detect a bond BB in this system. Nevertheless, a rcp defined by the sequence BHBH appears, which is located at the central point of the line joining the boron atoms. These features are coincident with the structural information provided by the



**Figure 1.** Geometrical conformation of borane systems: (a)  $B_2H_6$ , (b)  $B_4H_{10}$ , (c)  $B_5H_9$ , and (d)  $B_5H_{11}$ . Atomic symbols and labels are shown.

number *styx* except for the two bridge bonds BHB, pointed out by its 2002 value, i.e., the bridge BH bcp's and the BHBH rcp, which indicates an intersection point among the BH bridge atomic basins, reveal interactions among all these basins but do not provide enough information to distinguish between two three-center bondings or one four-center bonding involving the atoms forming the ring. The structure of the effectively paired density  $\rho^{(p)}$  is similar to that of the total one  $\rho$ , as may be observed in Table 1, and therefore it cannot introduce any new information about the electronic structure.

Let us now inspect the topology of the effectively unpaired density  $\rho^{(u)}$ . The structure of this density is similar to those of the above commented  $\rho$  and  $\rho^{(p)}$  ones, but it presents some additional subtle and crucial features. As may be observed in Table 1, a  $\rho^{(u)}$  vs(3,-1)cp appears for the sequence BB which is not present for  $\rho$  and  $\rho^{(p)}$ , having the same location than the unique (3,+1)cp of these last densities (see Figure 2). Moreover two vs(3,+1)cp's are detected, one for each of the two bridge bond BHB, which are symmetrically placed on the line joining the bridge H atoms at both sides of the BB vs(3,-1)cp. These features may clearly induce to interpret such new elements as indicators of two (3c-2e) bonds. In view of these considerations let us state *in advance* a rule based on the onset of a vs(3,-1)cp between the boron atoms closing

the bridge sequence BHB and a vs(3,+1)cp associated with that sequence: *in borane systems a (3c-2e) 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 bond*, hereafter called the *local rule*. 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 nonlocal rule*. That criterion settles down the existence of a (3c-2e) bond between atoms ABC when fractional bond orders  $I_{\Omega_A\Omega_B}$  appear between all possible pairs of atoms AB, BC, and AC.<sup>4,43</sup> As is shown in Table 1, the values of  $I_{BB} = 0.056$ , bridge  $I_{BH} = 0.280$ , and  $\Delta_{BHB} = 0.061$  indicate the rule is fulfilled. Hence, the information contained in  $\rho^{(u)}$  permits to fit the structural and local description of the electron distribution, i.e., both formulations have comparable criteria to establish the existence of a (3c-2e) bond. Consequently, the results for this emblematic system show that the local description of the electron distribution is completely coincident with the integrated one as well as with the structural *styx* number, taking into account the information contained in the effectively unpaired electron density. Let us note that the value for the terminal  $I_{BH} = 0.495$  reveals a normal BH

**Table 1.** Structural *styx* Numbers and Local and Integrated (Nonlocal) Topological Features of  $\rho(\mathbf{r})$ ,  $\rho^{(l)}(\mathbf{r})$ , and  $\rho^{(u)}(\mathbf{r})$  Densities for Boranes Systems at the CISD/6-31G\*\* Level of Approximation<sup>c</sup>

cp type	$\rho$ sequences <sup>a</sup>	$\rho^{(l)}$ sequences <sup>b</sup>	$\rho^{(u)}$ sequences <sup>b</sup>	bond	$I_{\Omega_A\Omega_B}$	$\Delta_{\Omega_A\Omega_B\Omega_C}$
<i>B<sub>2</sub>H<sub>6</sub> (styx: 2002)</i>						
ncp	one on each B and H atoms	<i>ibid</i> $\rho$	<i>ibid</i> $\rho$	BB	0.056	
bcp	one per each $BH_{term}$ bond	<i>ibid</i> $\rho$	<i>ibid</i> $\rho$ ;	$H_{term}\dots H_{term}$	0.121	
	one per each $BH_{bridge}$ bond		BB	$BH_{term}$	0.495	
rcp	$BH_{bridge}BH_{bridge}$	<i>ibid</i> $\rho$	$BH_{bridge}B$ (2)	$BH_{bridge}$	0.280	
ccp	no cage critical points present	<i>ibid</i> $\rho$	<i>ibid</i> $\rho$	$B..H_{bridge}..B$		0.061
				$BH_2$		0.051
<i>B<sub>2</sub>H<sub>8</sub><sup>2-</sup></i>						
ncp	one on each B and H atoms	<i>ibid</i> $\rho$	<i>ibid</i> $\rho$	BB	0.167	
bcp	one per each $BH_{term}$ bond	<i>ibid</i> $\rho$	<i>ibid</i> $\rho$	$BH_{term}$	0.670	
	one per each $BH_{bridge}$ bond			$BH_{bridge}$	0.442	
rcp	$BH_{bridge}BH_{bridge}$	<i>ibid</i> $\rho$	<i>ibid</i> $\rho$	$BH_{bridge}B$		0.024
ccp	no cage critical points present	<i>ibid</i> $\rho$	<i>ibid</i> $\rho$	$BH_2$		0.067
<i>B<sub>4</sub>H<sub>10</sub> (styx: 4012)</i>						
ncp	one on each B, H atoms	<i>ibid</i> $\rho$	<i>ibid</i> $\rho$	$B_2B_4$	0.476	
bcp	one per each $BH_{term}$ bond	<i>ibid</i> $\rho$	<i>ibid</i> $\rho$ ;	$B_1H_{10}$	0.245	
	one per each $BH_{bridge}$ bond		$B_1B_2, B_1B_4$	$B_2H_{10}$	0.431	
	$B_2B_4$			$B_1H_{13}$	0.492	
rcp	$B_1H_{10}B_2B_4H_9$	<i>ibid</i> $\rho$	$B_1H_9B_4; B_1B_2B_4$	$B_1H_6$	0.475	
ccp	no cage critical points present	<i>ibid</i> $\rho$	<i>ibid</i> $\rho$	$B_2H_7$	0.577	
				$B_1B_2$	0.095	
				$B_1B_2B_4$		0.056
				$B_1H_{10}B_2$		0.086
				$B_1H_9B_4$		0.087
<i>B<sub>5</sub>H<sub>9</sub> (styx: 4120)</i>						
ncp	one on each B, H atoms	<i>ibid</i> $\rho$	<i>ibid</i> $\rho$	$B_1B_2$	0.385	
bcp	one per each $BH_{term}$ bond;	<i>ibid</i> $\rho$	<i>ibid</i> $\rho$	$B_1H_6$	0.627	
	one per each $BH_{bridge}$ bond;		one per each $B_{eq}B_{eq}$ bond	$B_2H_8$	0.601	
	one per each $B_{eq}B_{ax}$ bond			$B_2B_5$	0.304	
rcp	$B_1H_{10}B_2B_4$	<i>ibid</i> $\rho$	$B_{eq}B_{ax}B_{eq}; B_2H_{12}B_3$	$B_2H_{12}$	0.364	
ccp	no cage critical points present	<i>ibid</i> $\rho$	<i>ibid</i> $\rho$	$B_2H_4$	0.081	
				$B_1B_2B_3$		0.138
				$B_1B_2B_4$		0.049
				$B_2H_{12}B_3$		0.118
<i>B<sub>5</sub>H<sub>11</sub> (styx: 3203)</i>						
ncp	one on each B, H atoms	<i>ibid</i> $\rho$	<i>ibid</i> $\rho$	$B_1B_2$	0.214	
bcp	$BH_{bridge}$ bond	<i>ibid</i> $\rho$	<i>ibid</i> $\rho$	$B_1B_4$	0.459	
	$B_1B_5; B_3H_8; B_2H_9$		$B_1B_2; B_4B_5;$	$B_1H_6$	0.503	
	$B_2B_5; B_1H_7; B_5H_{14}$		$B_2H_{14}$	$B_1H_7$	0.622	
	$B_2H_{11}; B_1H_6$			$B_4H_{13}$	0.574	
rcp	$B_5B_1B_4H_{bridge}$	<i>ibid</i> $\rho$	$B_5H_{bridge}B_4; B_5B_1B_4$	$B_1H_{16}$	0.067	
			$B_5B_1B_2; B_5B_2H_{14}$	$B_2B_3$	0.012	
				$B_2B_5$	0.206	
				$B_2H_7$	0.022	
				$B_2H_6$	0.166	
				$B_3H_{10}$	0.524	
				$B_3H_{12}$	0.496	
				$B_3H_{15}$	0.264	
				$B_3B_4$	0.207	
				$B_4B_5$	0.172	
				$B_4H_{15}$	0.435	
				$B_4H_{16}$	0.348	
				$B_5H_8$	0.571	
				$B_1B_2B_5$		0.137
				$B_1B_2H_6$		0.092
				$B_1B_4B_5$		0.113
				$B_2B_5H_{14}$		0.109
				$B_4B_5H_{16}$		0.105
ccp	no cage critical points present					

<sup>a</sup> Indicate the nucleus at which the **n**cp is located; for **b**cps, the atoms defining the bond; for **r**cps, the atoms giving rise to the ring; for **cc**ps, the atoms defining the cage. <sup>b</sup> Only those of  $\rho$  are *sensu stricto* cps. <sup>c</sup> All quantities are in atomic units.

bonding in the terminal groups, and thus their H atoms may not be involved within (3c-2e) bond.

Table S1 collects the results about the local charge distribution over the nuclear attractors (nuclei) showing electronic charge concentration near the nucleus, as expected.

Table 2 reports the numerical results for the densities at the bcp's of the total density (first line) and at the vs(3, -1)cp's of the effectively unpaired density (second line). The three density fields show electron concentration at the total density bcp's for the BH bonds in each BH<sub>2</sub> group, and the same

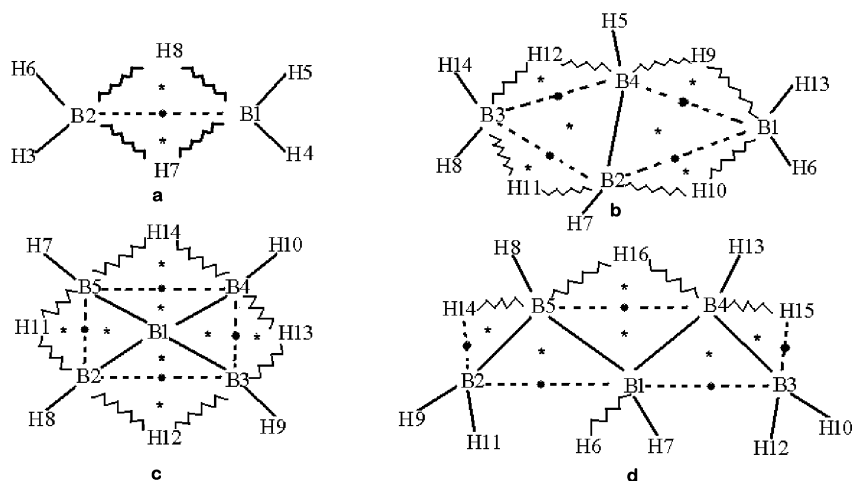
**Table 2.** Density and  $L(\mathbf{r})$  for the Total Density  $\rho$  and Its Contributions  $\rho^{(p)}$ ,  $\rho^{(u)}$  at Bond Critical Points of Total Density at the CISD/6-31G\*\* Level of Calculation<sup>a,e</sup>

system	bond	$\rho(\mathbf{r}) _{bcp}$	$\rho^{(p)}(\mathbf{r}) _{bcp}$	$\rho^{(u)}(\mathbf{r}) _{bcp}$	$-\nabla^2\rho(\mathbf{r}) _{bcp}$	$-\nabla^2\rho^{(p)}(\mathbf{r}) _{bcp}$	$-\nabla^2\rho^{(u)}(\mathbf{r}) _{bcp}$	$\varepsilon^d$	
$B_2H_6$	$BH_{bridge}$	0.12434	0.12031	0.00403	-0.14557	-0.15582	0.01025	0.72166	
		0.13502	0.13126	0.00376	0.24530	0.24071	0.00459	0.12959	
	$BH_{term}$	0.18426	0.17973	0.00454	0.24203	0.22588	0.01616	0.09056	
		0.20088	0.19671	0.00417	0.64524	0.64148	0.00376	0.00977	
$B_2H_6^{2-}$	$BH_{bridge}$	0.11679	0.11371	0.00308	0.04067	0.04151	-0.00084	1.32998	
		0.10871	0.10512	0.00360	0.18834	0.18342	0.00492	0.11459	
	$BH_{term}$	0.14419	0.14012	0.00407	0.12527	0.13634	0.01107	0.67775	
		$B...B^b$							
$B_4H_{10}^c$	$B_2-H_{11(bridge)}$	0.14017	0.13659	0.00357	-0.13225	-0.14131	0.00906	0.49601	
		0.14850	0.14499	0.00351	0.31547	0.30979	0.00568	0.17307	
	$B_3-H_{11(bridge)}$	0.10342	0.10034	0.00309	-0.06856	-0.07604	0.00748	0.85837	
		0.11293	0.11034	0.00258	0.13304	0.13265	0.00039	0.37769	
	$B_2-B_4$	0.13846	0.13518	0.00328	0.25332	0.25203	0.00129	0.33559	
		0.13717	0.13386	0.00331	0.25375	0.25205	0.00170	0.07008	
	$B_3-H_{14}$	0.18500	0.18128	0.00372	0.23376	0.22043	0.01333	0.08766	
		0.20127	0.19783	0.00344	0.64837	0.64501	0.00336	0.01921	
	$B_2-H_7$	0.18213	0.17835	0.00377	0.17064	0.15863	0.01201	0.10678	
		0.19659	0.19304	0.00355	0.61438	0.61055	0.00382	0.08046	
	$B_5H_9^c$	$B_2-B_1$	no bcp						
			0.10028	0.09786	0.00241	0.03854	0.03913	-0.00058	0.87032
		$B_2-H_{12(bridge)}$	0.12062	0.11749	0.00313	-0.06657	-0.07323	0.00666	6.45833
			0.12917	0.12633	0.00284	0.21071	0.20843	0.00228	0.31604
$B_2-H_8$		0.18423	0.18068	0.00354	0.20833	0.19672	0.01161	0.08693	
		0.19879	0.19547	0.33211	0.63582	0.63233	0.00349	0.09007	
$B_1-H_6$		0.17590	0.17242	0.00348	0.09551	0.08554	0.00997	0.00000	
		0.18970	0.18637	0.00333	0.57193	0.56802	0.00391	0.00000	
$B_1-B_2$		0.13859	0.13503	0.00355	0.12304	0.11660	0.00644	3.24034	
		0.13883	0.13559	0.00324	0.20903	0.20757	0.00145	0.11929	
$B_5H_{11}^c$		$B_2-B_3$	no bcp						
			0.11741	0.11481	0.00260	0.07259	0.07327	-0.00069	0.62698
		$B_2-B_4$	no bcp						
			no bcp						
	$B_4-H_{16(bridge)}$	0.11840	0.11537	0.00303	-0.13818	-0.14499	0.00681	1.28377	
		0.12802	0.12520	0.00281	0.21954	0.21663	0.00291	0.27336	
	$B_2-H_6$	no bcp							
		no bcp							
	$B_5-H_{14}$	0.14511	0.14177	0.00334	-0.06305	-0.07182	0.00877	0.69875	
		0.15403	0.15083	0.00320	0.34886	0.34441	0.00446	0.19806	
	$B_1-H_6$	0.15054	0.14699	0.00355	-0.05909	-0.06756	0.00848	0.43287	
		0.15569	0.15217	0.00352	0.32352	0.31736	0.00616	0.24869	
	$B_1-H_7$	0.17958	0.17607	0.00350	0.13166	0.12080	0.01086	0.01518	
		0.19467	0.19136	0.00330	0.59993	0.59627	0.00365	0.00987	
$B_2-H_9$	0.18448	0.18102	0.00346	0.23111	0.21870	0.01241	0.13271		
	0.20062	0.19742	0.00320	0.64844	0.64521	0.00323	0.03314		
$B_2-H_{11}$	0.18310	0.17961	0.00350	0.20816	0.19580	0.01236	0.09965		
	0.19939	0.19614	0.00324	0.63561	0.63224	0.00337	0.02847		
$B_2-H_{14}$	no bcp								
	0.11463	0.11227	0.00236	0.12920	0.12939	-0.00019	0.80530		
$B_5-H_8$	0.18665	0.18312	0.00353	0.22340	0.21159	0.01181	0.07284		
	0.20166	0.19836	0.00330	0.65038	0.64706	0.00332	0.06786		
$B_1-B_2$	no bcp								
	0.10386	0.10142	0.00244	0.09498	0.09494	0.00005	0.37470		
$B_1-B_5$	0.12980	0.12681	0.00299	0.19690	0.19559	0.00131	1.65077		
	0.12863	0.12563	0.00300	0.19073	0.18944	0.00129	0.18989		
$B_2-B_5$	0.11184	0.10905	0.00279	0.12162	0.11896	0.00266	20.37688		
	0.11309	0.11047	0.00262	0.08750	0.08689	0.00061	0.34419		
$B_4-B_5$	no bcp								
	0.10566	0.10325	0.00241	0.03758	0.03825	-0.00067	0.95615		

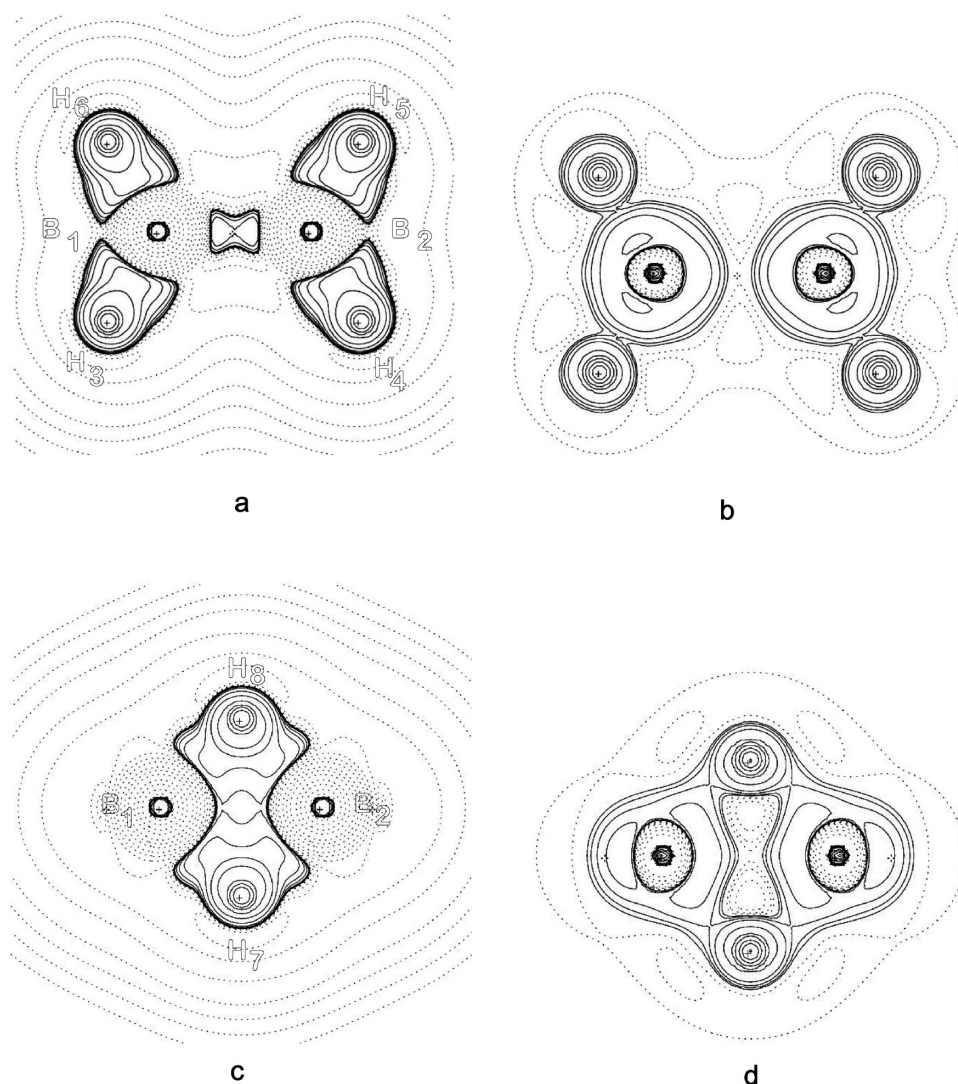
<sup>a</sup> Second line in columns 3 to 9 for each bond indicate the densities and  $L(\mathbf{r})$  at  $\rho^{(u)}(\mathbf{r})$  vs(3,-1)cp. <sup>b</sup> There are no bond critical points for  $\rho(\mathbf{r})$  between the boron atoms. <sup>c</sup> See Figure 1 for atoms labeling. <sup>d</sup> Ellipticity. <sup>e</sup> All quantities are in atomic units.

behavior may be noted at  $\rho^{(u)}$  vs(3,-1)cp's. For the bridge bonds BH the bcp's of the total density show  $\rho$  and  $\rho^{(p)}$  depletion, while  $\rho^{(u)}$  concentrates at those points; but at  $\rho^{(u)}$  vs(3,-1)cp all fields concentrate. The bcp of the  $\rho$  density on the bridge bond BH is closer to the B atom than the corresponding vs(3,-1)cp of  $\rho^{(u)}$  density, which is located

near the midpoint between these atoms (cf. Figure 2). Hence, this density delocalizes over the bonding region, which can be interpreted as a "spill" of  $\rho^{(u)}$  over the bond region, as may be observed in Figure 3(b),(d).  $\rho$  and  $\rho^{(p)}$  have no bcp at the BB sequence. However a rcp appears there, as has been mentioned above, showing a large charge concentration



**Figure 2.** Schematic electronic structure of borane systems: (a)  $B_2H_6$ , (b)  $B_4H_{10}$ , (c)  $B_5H_9$ , and (d)  $B_5H_{11}$ . Solid lines mean all fields possess one bcp between the atoms and concentrate on it; zigzag lines mean all fields possess one bcp between the atoms,  $\rho(r)$  and  $\rho^{(p)}(r)$  show depletion and  $\rho^{(u)}(r)$  shows accumulation; dashed lines mean only  $\rho^{(u)}(r)$  vs(3, -1)cp ( $\bullet$ ) exist between the atoms and this field concentrates on it. Asterisks (\*) indicate vs(3,1)cp locations.



**Figure 3.**  $L(r)$  contour maps of  $B_2H_6$  molecule for effectively paired ((a) and (c)) and effectively unpaired densities ((b) and (d)) in the plane containing the  $BH_2$  groups and the  $H_{bridge}$  atoms, respectively. Positive and negative values are denoted by solid and dashed lines, respectively.

(cf. Table S2 and Figure 3(a),(c)) which justifies the mentioned value of the bond order BB. Nevertheless, the

behavior of  $\rho^{(u)}$  at its own vs(3, -1)cp on this sequence shows a slight concentration, as may be observed in Table 2 and

Figure 3(b),(d). The onset of the two  $vs(3,+1)cp$ 's of  $\rho^{(u)}$  for each bridge bond BHB disrupts the idea of a four-center bond and permits to identify the two (3c-2e) bonds, in agreement with the indicator  $styx$  and the results from the integrated formulation. Besides, the  $vs(3,-1)cp$  of  $\rho^{(u)}$  density at the BB sequence permits to define the above expressed rule for the local formalism.

It is interesting to note the changes on the electron distribution of this system once negative charges are introduced to obtain the anion  $B_2H_6^{2-}$ , which is an electron nondeficient system. As may be seen in Table 1, the topologies of  $\rho$  and  $\rho^{(p)}$  densities remain identical. The pairing and unpairing densities show a remarkable decrease in the bonding regions BB, and consequently a great concentration of these densities appears around the nuclei as shown by Figure S1(a)–(d). Moreover all bonds BH increase their strength, as shown by the increment of the bond orders in Table 1. The topology of  $\rho^{(u)}$  does not exhibit the BB  $vs(3,-1)cp$  as in the compound  $B_2H_6$ , and both  $vs(3,+1)cp$ 's collapse into only one. Therefore, the above established rule seems to be violated by the increments of the two-center bond order values, and consequently the population of the three-center bridge BHB notably decreases. The local view of the broken down (3c-2e) structures in this system may be noted from the contour maps by the lack of concentration zone between boron atoms (Figure S1(a),(c)) and the missing of  $vs(3,-1)cp$  in the line joining the mentioned atoms. It may also be noted that the onset of  $L(\mathbf{r})$  concentration of both  $\rho$  and  $\rho^{(p)}$  fields (cf. Tables 2 and S2) at the bridge bonds BH make them to look like typical terminal bonds BH.

$B_4H_{10}$ . The geometrical structure of this system is shown in Figure 1, and its characterization is given by the  $styx$  number 4012 (see Table 1). Let us analyze each of the structural indicators in view of the hypothesis established for the previous system.  $s = 4$  means that this compound has four bridge three-center bonds BHB. The values of three-center bond index  $\Delta_{BHB}$  shown in Table 1 correspond to four bonds formed by the atoms B(1)H(10)B(2) and B(1)H(9)B(4) and their symmetrical ones, with bond index values of 0.086 and 0.087, respectively. These values are similar to those found in the  $B_2H_6$  system. The bridge two-center bond orders  $I_{BH}$  forming the (3c-2e) bonds have intermediate values in comparison with terminal bonds BH in boranes although one of them, the bond order for the atoms B(2)H(10) and its symmetric B(4)H(12), B(2)H(11), and B(4)H(9) have a value slightly smaller than the normal one for a typical bond BH (cf. the discussion for  $B_2H_6$  system). Thus the nonlocal rule applied to diborane is confirmed for the bonds BHB in this system. Therefore, the structural  $s = 4$  number and the nonlocal results are coincident.

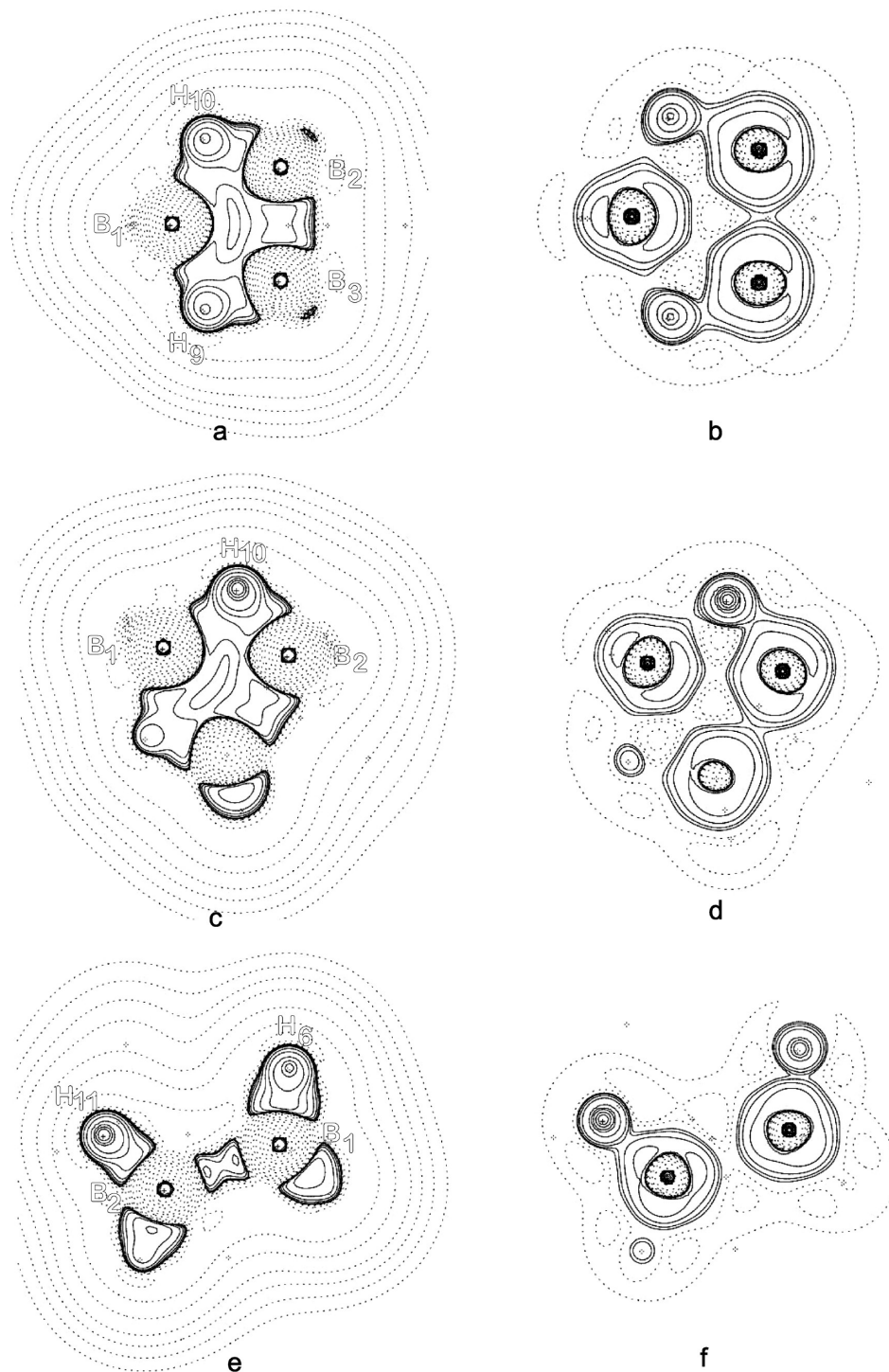
The local information contained in  $\rho$  (and  $\rho^{(p)}$ ) shows ncp's over each of the nuclei and bcp's for each terminal bond BH (B(1)H(6), B(1)H(13), B(2)H(7) and their symmetric ones B(3)H(8), B(3)H(14), B(4)H(5)), for each bridge bond BH and for the B(2)B(4) bond, indicating that the atoms of each mentioned pair are bonded. Besides, an rcp for the total density appears for the B(1)H(10)B(2)B(4)H(9) atomic sequence (see Table 1). As has been discussed for the  $B_2H_6$

system, it may be interpreted as a five-center bond, hiding the existence of (3c-2e) bonds predicted by the integrated formalism and the structural  $styx$  numbers for this structure. However, the information contained in  $\rho^{(u)}$  shows the onset of two  $vs(3,-1)cp$ 's indicating a subtle interaction between the atomic pairs B(1), B(2) and B(1), B(4) (and a similar situation is observed for their symmetric ones B(3), B(2) and B(3), B(4)). This find as well as the onset of two  $vs(3,+1)cp$ 's just defining the sequences B(1)H(9)B(4) and B(1)H(10)B(2), and other two for their symmetrical BHB sequences, seem to indicate four bonds BHB. Consequently there is one  $vs(3,-1)cp$  for each pair of atoms forming the three-center sequences, and besides there is also a  $vs(3,+1)cp$  for each of the mentioned sequences. Hence the local version of the integrated rule for detecting three-center bonds holds, and it is also coincident with both structural and nonlocal descriptors regarding BHB bonds.

The  $t = 0$  number of  $styx$  indicates that this system has no bonds BBB. The normal BB bond order value for the pair B(2)B(4) (0.476) and the small ones for the B(1)B(2) pair and the remaining BB pairs in the system (0.095) break the rule for the three-center bond nonlocal description and is in agreement with a very small (3c-2e) bond B(1)B(2)B(4) of 0.056. Therefore, the structural and nonlocal descriptions are coincident and do not predict these bonds for the system. The local description of  $\rho$  and  $\rho^{(p)}$  shows a bcp for the B(2)B(4) bond but not for B(1)B(2) and B(1)B(4) ones, i.e., the local view shows that there is a bcp only for one of the pairs of atoms in the BBB sequence. However the topology of  $\rho^{(u)}$  shows a  $vs(3,-1)cp$  related with each of these pairs, and we also found a  $vs(3,+1)cp$  for the sequence BBB, insinuating a subtle BBB interaction. This information contained in the  $\rho^{(u)}$  topology is not available from the description provided by  $\rho$  and  $\rho^{(p)}$  densities and may be interpreted as an actual but not too strong interaction between three boron atoms which is not detected by the other descriptions, although is concordant with a very small (3c-2e) population for the sequence BBB. This result would induce to recognize a very weak (3c-2e) bond for both the B(1)B(2)B(4) sequence and its symmetrical B(2)B(3)B(4) and confirms that the information in  $\rho^{(u)}$  goes beyond the structural description by the other methodologies. Figure 4(a),(b) corresponds to maps for  $L(\mathbf{r})$  in the plane containing the boron atoms (1), (2), and (4), while Figure 4(c),(d) refers to the plane defined by the sequence B(1)H(10)B(2). These maps show the concentration of effectively paired density and specially the unpaired one in the bonding regions. The "spillage" of the last density seems to be of crucial importance to form three-center bonds in electron deficient systems, as indicated by the existence of  $vs(3,-1)cp$ 's only in  $\rho^{(u)}$  density.

The value of the  $y$  number predicts only one BB bond. As explained above, the nonlocal description is in agreement with this prediction for the atoms B(2) and B(4). For the sake of completeness we incorporate Figure 4(e),(f) in the plane defined by atoms (1), (2), and (11), which permit to note the pairing density concentration, showing graphically this weak BB interaction; however, as explained above this interaction does not stand for a true BB bond and may be





**Figure 4.**  $L(\mathbf{r})$  contour maps of  $B_4H_{10}$  molecule for effectively paired ((a), (c), and (e)) and effectively unpaired densities ((b), (d), and (f)) in the planes defined by atoms 1-2-4, 1-10-2, and 1-2-11, respectively (Figure 1). Positive and negative values are denoted by solid and dashed lines, respectively.

called a *quasi-bond* because the atoms are involved in BHB bonds. The last number,  $x = 2$ , shows that for  $BH_2$  groups all descriptions are coincident. Similarly to the diborane case, the three density fields show electron concentration at bcp's for the bonds BH of each group  $BH_2$  and for the bonds B(2)H(7) and B(4)H(5). For the bridge bonds BH,  $\rho$  and  $\rho^{(p)}$  show depletion at the bcp's while  $\rho^{(u)}$  concentrates; however, all fields concentrate at  $\rho^{(u)}$  vs(3,-1)cp's. The "spill" of  $\rho^{(u)}$  over the bonding region is again observed at

all bonds (cf. parts (b), (d), and (f) of Figure 4), thus showing positive values of  $L(\mathbf{r})$  (of  $\rho^{(u)}$ ) at all vs(3,-1)cp's (see Table 2). This  $\rho^{(u)}$  behavior was not found in none of the classical bonds analyzed in previous papers<sup>32,33</sup> and therefore seems to be typical of electron deficient systems.

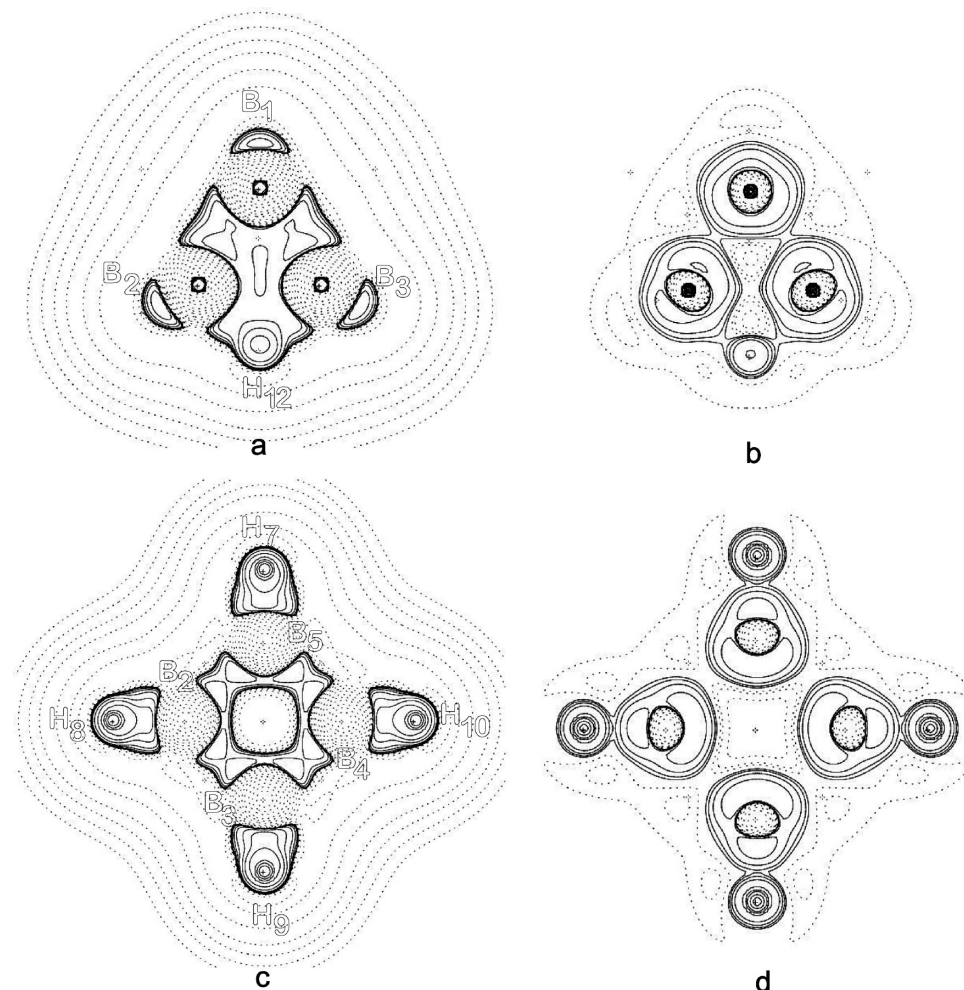
$B_5H_9$ . As illustrated in Figure 1, the hydride  $B_5H_9$  belongs to the  $C_{4v}$  symmetry group and is structurally characterized by the *styx* number 4120 (see Table 1). It means that this compound has four bridge three-center bonds BHB ( $s = 4$ ),

only one bond BBB ( $t = 1$ ), two bonds BB ( $y = 2$ ), and no groups BH<sub>2</sub> ( $x = 0$ ). The sequence B(2)H(12)B(3) and its other three symmetrical ones (cf. Figure 2) have BH bond orders of 0.364, as shown in Table 1. These are intermediate values but not normal values for such a bond (see e.g. the diborane), thus it fulfills the nonlocal rule to form a (3c-2e) bond. Hence, the nonlocal description is coincident with the structural one. From the local point of view, each bond BH in the sequences BHB has (3, -1) cp's for all the densities (bcp for total density), but we only found a vs(3, -1)cp of  $\rho^{(u)}$  between the boron atoms. Accordingly, a  $\rho^{(u)}$  vs(3, +1)cp just defining the sequence B(2)H(12)B(3) is found, which with its symmetrical ones is indicating four bonds BHB. Again, the unpaired density subtly connects these atoms resulting in a (3c-2e) bond and the local rule also holds. In conclusion, the three descriptions are coincident. The  $t = 1$  and  $y = 2$  numbers for this system indicate only a bond BBB and two two-center bonds BB. These results are not compatible with the symmetry group exhibited by the system. However, to rescue such structural indicators, four equivalent resonance structures have been invoked to fit them to quantum concepts.<sup>34,37,43</sup> The nonlocal analysis shows bond orders values of about (0.4) between the axial boron and each equatorial boron atom, which indicates an interaction. The same happens between each pair of equatorial borons, but their bond order values are lower than the formers (of about 0.3). Thus, there are intermediate bond orders between each pair formed by one equatorial boron and the axial boron and consequently four (3c-2e) BBB bonds are present. The nonlocal picture is reinforced from the local point of view by the information of the unpaired electron density, which shows four vs(3, -1)cp's on the equatorial bonds BB and the corresponding four vs(3, +1)cp's, one for each equatorial/axial/equatorial sequence BBB. These results show the usefulness of the local and nonlocal descriptions and a drawback for *styx* numbers, which may not account for the symmetries in a direct manner, i.e., local and nonlocal pictures are able to overcome the ambiguities found in the localization schemes. Each boron atom is also bonded to a hydrogen one by a normal bond (see in Table 1  $I_{B(1)H(6)} = 0.627$  and the four bond indices BH (equatorial boron) with the value 0.601). Hence, the structural description in terms of  $x$  number is coincident with the nonlocal point of view.

In Table 2 it may be noted that at each bcp of the total density for bonds BH of the equatorial boron atoms (hydrogen atoms numbers (7), (8), (9), and (10)), all density fields show concentration and a small ellipticity of 0.08693, which confirms the existence of normal BH bonds as discussed above; a similar behavior of these fields is observed at the vs(3, -1)cp of  $\rho^{(u)}$ . Nevertheless, the bonds equatorial/bridge BH show different behavior than the previous ones; the pairing density field depletes while the unpaired one concentrates at the bcp and an opposite behavior is found for that field at the vs(3, -1)cp of  $\rho^{(u)}$  density. This result is similar to that found in the diborane and once more indicates the "spillage" of the unpaired density over the bonding regions. The graphical representation of these results may be observed on the  $L(\mathbf{r})$  maps of both densities, which are shown in Figure 5(a),(b) on the plane containing the boron

atoms (1), (2), and (3) and in Figure 5(c),(d) on the plane defined by equatorial boron atoms. The analysis of the bonds BB axial/equatorial type (B(1)B(2) in Table 2) permits to observe that at the total density bcp's all fields concentrate, and consequently these bonds are similar to the BB bonds found in the system B<sub>4</sub>H<sub>10</sub>. However, the values of  $L(\mathbf{r})$  for the axial-equatorial boron in this system decrease and the ellipticity values are largely increased for the pairing density, but the  $L(\mathbf{r})$  values for the unpaired density are largely increased, in comparison with the sequence B(2)B(4) in B<sub>4</sub>H<sub>10</sub>. These marked differences may be interpreted as the sharing electron cloud by the atoms involved in the set of four "resonance/fractional bonds",<sup>34,37,43</sup> in the local analysis framework.

**B<sub>5</sub>H<sub>11</sub>.** The geometrical information and the structure representation of B<sub>5</sub>H<sub>11</sub> are shown in Figures 1 and 2, respectively. Table 1 reports the value 3203 for its *styx* number. It means that this system possesses three three-center bonds BHB, two bonds BBB, no two-center bonds BB, and three groups BH<sub>2</sub>. As may be seen in Figure 2, the candidate sequences to form bridge bonds BHB are B(4)H(16)B(5) and B(2)H(14)B(5) (and their symmetrical B(3)H(15)B(4)). The system exhibits only one rcp formed by the sequence B(5)B(1)B(4)H(16) which, as in the previous systems, may not clearly discriminate the (3c-2e) bonds formed by the atoms involved in it. Table S2 shows the behavior of the densities at the rcp. Once again the appearance of the vs(3, +1)cp permits to establish the correct three-center bonds as shown in Table 1. According to this table the sequence B(4)H(16)B(5) shows a three-center population of 0.105, bond orders BH of 0.348 (each of them characterized by a bcp for the total density and a vs(3, -1)cp for the  $\rho^{(u)}$  one), and a bond order BB of 0.172 with only a vs(3, -1)cp of  $\rho^{(u)}$  density (cf. Table 1) indicating any information not available from the total density. The BH bonding regions show similar features to those found in the diborane molecule: depletion of the pairing density while the unpaired density concentrate in the bcp and an opposite behavior for  $\rho^{(p)}$  at the vs(3, -1)cp (cf. Table 2). The density at the bcp is lower than in the other analyzed similar sequences, indicating its weakness, and it also shows a very high ellipticity (Table 2). Similar features are found for the other two above-mentioned bridge sequences BHB. The pair of bondings B(4)H(15) and B(4)H(13) deserve some comments; the first one possesses the topological features which characterize a typical bridge bond BH, i.e., pairing density depletion and unpaired density concentration at the bcp and concentration of the three fields at vs(3, -1)cp. The other one sequence, B(4)H(13), is a typical terminal bond BH as in the diborane, and, thus, the local analysis permits to establish that these two BH bonds do not conform a group BH<sub>2</sub>. Graphically, these considerations may be observed from Figure 6(a),(b) and Figure 6(c),(d) showing  $\rho^{(p)}$  and  $\rho^{(u)}$   $L(\mathbf{r})$  maps in the planes of the atoms (4), (5), and (16) and in the plane of the atoms (4), (5), and (15), respectively. Moreover we found a vs(3, -1)cp between each of the pairs B(4)B(3) (B(2)B(5)), B(2)H(14) (B(3)H(15)), and B(5)H(14) (B(4)H(15)), and a (3, +1)cp for the B(3)B(4)H(15) (B(2)B(5)H(14)) sequences.

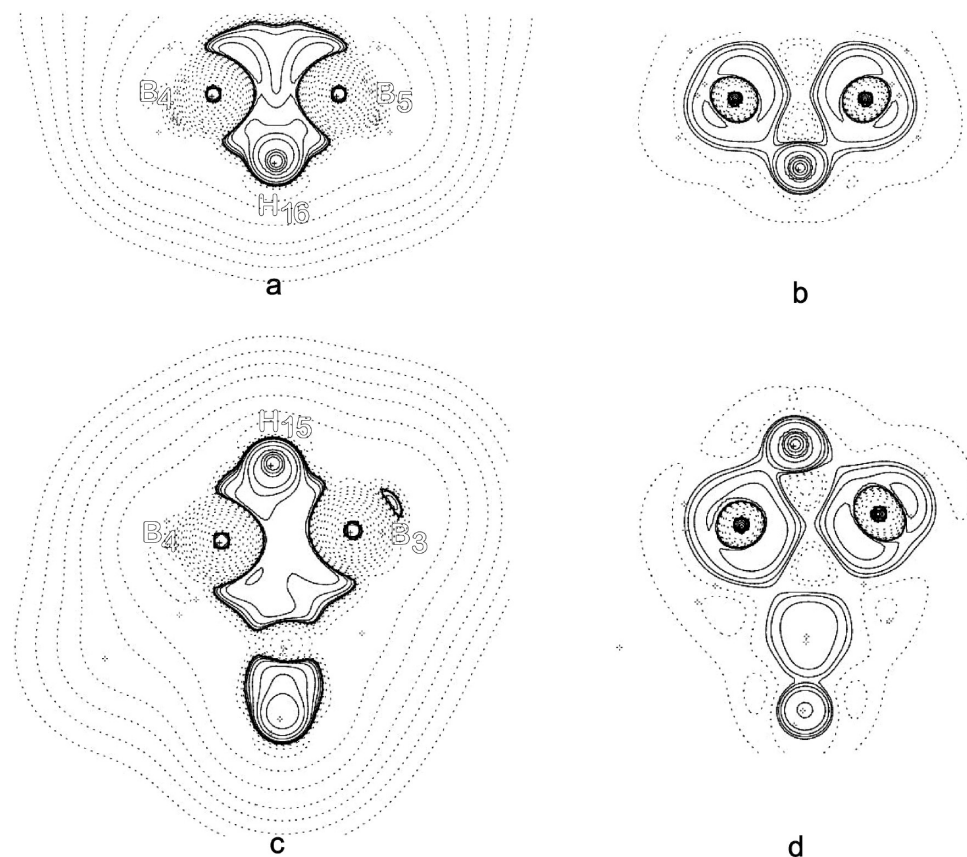


**Figure 5.**  $L(\mathbf{r})$  contour maps of  $B_5H_9$  molecule for effectively paired ((a) and (c)) and effectively unpaired densities ((b) and (d)) in the plane defined by atoms 1-2-3 and 2-3-4-5, respectively (Figure 1). Positive and negative values are denoted by solid and dashed lines, respectively.

Therefore, there are three bridge bonds BHB in this system, and, thus, the structural, local, and nonlocal descriptions coincide.

Let us inspect the BBB sequences B(1)B(4)B(5) and B(1)B(2)B(5) (and its symmetrical B(1)B(3)B(4)). Table 1 shows a three-center population of 0.113 for the sequence B(1)B(4)B(5); the bonds BB involved in this three-center bonding have values of bond order of 0.459 for B(1)B(4) (B(1)B(5)) which are very close to normal values for such a bond (quasi-normal bond) and 0.172 for B(4)B(5) (weak BB bond). The local analysis shows similar features for the two other mentioned BBB series B(1)B(2)B(5) and B(1)B(3)B(4) as reported in Table 1. However, the bond orders for the BB pairs involved in these three-center bonds are lower (see e.g. 0.214 for B(1)B(2) in Table 1). Hence, the fulfillment of the rule of existence of fractional two-center bond orders to identify three-center bondings is better in these cases. It permits to conclude that B(1)B(4)B(5) might be considered as a weak three-center bond thus justifying the value  $t = 2$ . Figure S2(a),(b), in the plane of B(1), B(3), B(4), and Figure S2(c),(d), in the plane of B(1), B(4), B(5), show the accumulation of the densities in the space between those atoms. Regarding the BB bonds, there are four bonds [B(1)B(4) and B(1)B(5) (quasi-normal BB bonds) and

B(2)B(5) and B(3)B(4) (weak BB bonds)] all of them exhibiting a bcp and a  $vs(3,-1)cp$ . These results indicate at first glance four BB bonds. Nevertheless, as all these BB pairs are involved in three-center BBB bondings, they may not be considered as normal two-center bonds, in agreement with the value  $y = 0$  of the *styx* number. It is worthy to note the behavior of the densities for the BB pairs, as shown in Tables 1 and 2. The atom B(4) appears to be bonded to the atoms B(1) and B(3). These sequences show small concentration for the three density fields at bcp and at  $vs(3,-1)cp$  and exhibit a great ellipticity which indicates an unstability interaction between the boron atoms. The interaction B(4)B(1) shows concentration of the three fields at both bcp and  $vs(3,-1)cp$ . Both interactions exhibit low density at these points, indicating a weak character interaction, high ellipticity for the first sequence, and extremely high for the later one, which points out instability; consequently both of them may not be considered as normal bonds from the local point of view. Figure S2(a),(b) shows the density  $L(\mathbf{r})$  maps. For the other B(4)B(5), B(1)B(2), and B(1)B(3) interactions we only found a  $vs(3,-1)cp$ , which means that a true bond between them may not be considered. This scenario induces the formation of three-center bonds BBB, in agreement with the above interpretation of the integrated description. As has been



**Figure 6.**  $L(\mathbf{r})$  contour maps of  $B_5H_{11}$  molecule for effectively paired ((a) and (c)) and effectively unpaired densities ((b) and (d)) in the plane defined by atoms 5-4-16 and 3-4-15, respectively (Figure 1). Positive and negative values are denoted by solid and dashed lines, respectively.

indicated for the system  $B_4H_{10}$ , in which we have used the term *quasi-bonds* for such weak interactions, the concentration of the pairing component between  $B(4)B(5)$  and  $B(1)B(2)$  ( $B(1)B(3)$ ) may clearly be noted in Figure S3(a),(c) in the planes defined by atoms  $B(4)B(5)H(8)$  and  $B(1)B(2)B(3)$ , respectively; Figure S3(b),(d) is the corresponding one to the unpaired density. Concerning the  $BH_2$  groups, previous arguments lead us to consider only the sequences formed by  $B(2)H(9)H(11)$ , its symmetric  $B(3)H(10)H(12)$  and  $B(1)H(6)H(7)$  as candidates to conform such moieties. The bond orders and the bond critical points for the total density associated with each bond  $BH$ , as shown in Table 1, indicate that there are three groups  $BH_2$ . Hence, the local and nonlocal descriptions are in agreement with the value  $x = 3$  in the structural number *styx*.

**3.2. General Discussion.** As a general feature, it may be noted (Table 2) that in the bridge bonds  $BH$  the  $L(\mathbf{r})$  of the pairing density depletes, while the unpaired one concentrates at the bcp. Concerning the  $BB$  and terminal  $BH$  bonds, both of them show Laplacian values of identical sign at the bcp's for the  $\rho^{(p)}$  and  $\rho^{(u)}$  density fields. It was observed in a previous work<sup>33</sup> that this behavior usually indicates an important ionic component of the bond. However, in the present case, the electronic distribution is different since this trend remains at the  $vs(3,-1)cp$ 's. Exception to this feature may be observed at the sequence  $B(1)H(6)$  in the system  $B_5H_{11}$ ; in this case the Laplacian of the pairing density depletes at the bcp while that of  $\rho^{(u)}(\mathbf{r})$  concentrates. At  $vs(3,-1)cp$  both fields concentrate. This behavior is typical

of the bridge bonds  $BH$ , like  $B(3)H(11)$  in  $B_4H_{10}$  or  $B(2)H(12)$  in  $B_5H_9$  one. However, the observation is concordant with the appreciable bond order value between the atoms  $H(6)$  and  $B(2)$  in this  $B_5H_{11}$  system, despite there are not critical points for any field in such sequence, i.e., it does not constitute a bond. Consequently, the small but appreciable three-center population  $B(1)H(6)B(2)$  (see Table 1) can be explained through the population  $B(1)H(6)$  and the  $vs(3,-1)cp$  existing between each pair of atoms in this sequence. These observations indicate a very special "subtle" interaction between all these atoms. The Laplacian density maps for these bonds show a spillage of the unpaired density. Table S1 shows that the pairing density at bridge atoms  $H$ , i.e., the hydrogen atoms involved in the  $(3c-2e)$  bonds, exhibits the greatest concentration in comparison with the terminal hydrogen ones. This can be interpreted as a bigger accumulation of the density on those atoms, even for the total density. Hence, it induces the bridge  $BH$  bcp localizes further from the hydrogen atom than in terminal sequences  $BH$ . It is reinforced by the information in Table 2 and in the contour maps of  $L(\mathbf{r})$  for  $\rho^{(p)}(\mathbf{r})$ , showing that in the valence region there is depletion close to the boron atom while concentration appears close to the hydrogen atoms, while for  $L(\mathbf{r})$  of  $\rho^{(u)}(\mathbf{r})$  it is noted concentration all over bonding region. Conventional covalent and ionic bonds are characterized by concentration of the paired and depletion of the unpaired density Laplacian and depletion of both of them, respectively.<sup>33</sup> The present case of bondings does not exhibit this behavior, but it is featured by the concentration of the unpaired field at all

cp's; the paired component shows concentration at terminal BH and BB bonds and depletion at bridge bonds BH; this is the most important feature of such kind of bonding which physically means that this density is induced toward the interatomic regions, as may be clearly observed in the contour maps.

Regarding the (3c-2e) bonds BHB, in the topological local description the pairing density accumulation between boron atoms in the bridge is relevant. An inspection of all the systems studied reveals the concentration of the pairing component while it is observed depletion for the unpaired one at the vs(3,-1)cp in that kind of bonds. Although no bcp is found, such a situation is typical of a covalent bond. Therefore, it may be considered as subtle information contained in the unpaired density which allows one to infer the existence of a *quasi-bond* between the boron atoms in agreement with the appreciable two- and three-center populations of these atomic sequences. An important relation arises from the data observation of Tables 2 and S1. The Laplacian of the density  $\rho^{(u)}(\mathbf{r})$  presents concentration at the bcp of bridge bonds BH and at the ncp of the bridge atom H; while the integrated populations of the sequences bridge BHB and BB increase, the concentration of that density field at the mentioned points depletes. Another interesting feature to analyze these systems is to introduce the concepts of competitive and cooperative phenomena, due to the fact that boron atoms are involved in different three-center bonds. In Table 1 it may be noted the joint growing tendency of the BHB population and that of the corresponding BB one in the compound series  $B_2H_6$ ,  $B_4H_{10}$ ,  $B_5H_{11}$ , and  $B_5H_9$  with values 0.061, 0.086, 0.105, and 0.118 for three-center bondings and 0.056, 0.095, 0.172, and 0.385 for two-center ones, respectively. To explain this fact, we will choose the system  $B_4H_{10}$  as a reference in which the population BB related with each one of the four bonds BHB is not shared by any other interaction BHB, and consequently there is a relation one to one (1:1) for each type of interaction. In diborane the two (3c-2e) bonds BHB share the BB population, and both populations diminish from the reference value of the compound  $B_4H_{10}$ . A possible interpretation of these situations is to think that the BHB interactions compete to distribute the electrons within the structure with a (2:1) relation. This idea is supported by the analysis of the remaining systems in which the trends noted above are fulfilled, i.e., BHB and BB jointly grow and the increment of BB population is favored if the boron atoms are involved in BBB bonds instead of involved in the BHB ones. Therefore, it seems that BHB bonds are competitive between them and cooperative with BBB bonds.

#### 4. Final Remarks and Conclusions

In this work we have studied electron distributions in some electron deficient molecules (boranes) which are prototype systems possessing no conventional patterns of bonding. The studied systems have been chosen to cover the main features for this type of molecular structures. We have attempted to extend to these systems our methodology, developed and applied in previous works to describe successfully more classical bondings. The challenge is to describe these

nonclassical systems under two approaches: the topological nonlocal (integrated) procedure and the local one, showing the complementary information arising from both treatments. We have compared the results with those provided by the structural indices or *styx* numbers, universally accepted to establish the structure of the boron hydrides. The results reported in this work show that both topological formalisms are in agreement with the structural one and go beyond it in cases where the electronic description becomes ambiguous, pointing out the subtle information contained in the density  $\rho^{(u)}(\mathbf{r})$ , which may not be obtained from the  $\rho(\mathbf{r})$  and  $\rho^{(p)}(\mathbf{r})$  ones. These results allow one to establish the local rule, which has been formulated within the discussion of the  $B_2H_6$  system, in analogy with the nonlocal one for detecting the atomic sequences forming a (3c-2e) bond beyond the Lewis model.

The main difference found between the electron distributions of these systems and those arising from the classical ones is that the paired part of the density remains localized in bonding and nuclear regions while the unpaired one is not only near the nuclear positions but spills out over the bonding regions, as trying to compensate the electron deficiency. Our results prove that the effectively unpaired density,  $\rho^{(u)}(\mathbf{r})$ , provides important information which may not be directly observed from the total and paired densities, constituting a suitable tool to measure the deviations from Lewis bonding models in these compounds.

**Acknowledgment.** This work has been partly supported by the Projects X-017 (Universidad de Buenos Aires), PIP No. 5098/05 (Consejo Nacional de Investigaciones Científicas y Técnicas, República Argentina), the Spanish Ministry of Education (Grant No. CTQ2006-01849/BQU), and the Universidad del País Vasco (Grant No. GIU06/03). We thank the Universidad del País Vasco for allocation of computational resources. R.M.L. acknowledges aid from the Universidad de la Cuenca del Plata (Corrientes, Argentina) for facilities provided during the course of this work.

**Supporting Information Available:** Density and  $L(\mathbf{r})$  of total density  $\rho$  components:  $\rho^{(p)}$ ,  $\rho^{(u)}$  at the nuclear critical points of total density at the CISD/6-31G\*\* level of calculation. All quantities are in atomic units (Table S1); density and  $L(\mathbf{r})$  for the total density  $\rho$  and its contributions  $\rho^{(p)}$ ,  $\rho^{(u)}$  at ring critical points of total density at the CISD/6-31G\*\* level of calculation<sup>a</sup>. All quantities are in atomic units (Table S2).  $L(\mathbf{r})$  contour maps of the  $B_2H_6^{2-}$  molecular anion for effectively paired ((a) and (c)) and effectively unpaired densities ((b) and (d)) in the plane containing the  $BH_2$  groups and the  $H_{bridge}$  atoms, respectively. Positive and negative values are denoted by solid and dashed lines, respectively (Figure S1);  $L(\mathbf{r})$  contour maps of the  $B_5H_{11}$  molecule for effectively paired ((a) and (c)) and effectively unpaired densities ((b) and (d)) in the plane defined by atoms 1-3-4 and 1-4-5, respectively (Figure 1). Positive and negative values are denoted by solid and dashed lines, respectively (Figure S2);  $L(\mathbf{r})$  contour maps of the  $B_5H_{11}$  molecule for effectively paired ((a) and (c)) and effectively unpaired densities ((b) and (d)) in the plane defined by atoms 4-5-8 and 1-2-3, respectively (Figure 1). Positive and

negative values are denoted by solid and dashed lines, respectively (Figure S3). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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CT900281Q