Theor Chem Acc (2015) 134:28
DOI 10.1007/s00214-015-1627-5

REGULAR ARTICLE

Chemical bonding analysis in boron clusters by means of localized orbitals according to the electron localization function topology

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Received: 23 October 2014 / Accepted: 23 January 2015

Abstract A series of small planar boron clusters has extensively been studied in the past using different theoretical approximations, and their chemical bonding has been rationalized in terms of aromaticity, antiaromaticity and conflicting aromaticity. Here, we study these systems by means of our recently proposed orbital localization procedure based on the partitioning of the space according to the electron localization function (ELF) topology. The results are compared with those obtained from the adaptive natural density partitioning (AdNDP) method, which is a most extensively tested orbital localization procedure. Minor discrepancies have been found, especially in large clusters. In those cases, an alternative set of localized AdNDP orbitals recovered the representation obtained by ELF localization procedure. These results support the need for multicenter bonding incorporation into the localization models for rationalizing chemical bonding in atomic clusters. Additionally, the aromatic character of the clusters, when it is present, is adequately supported by the more classical treatment based on the ELF topological analysis.

Keywords Electron localization function · Localized orbitals · Chemical bonding · Boron clusters

1 Introduction

We have recently proposed a new orbital localization procedure, within the three-dimensional (3D) physical space partitioning approach, which involves the decomposition of the overlap matrix in accordance with the partitioning of this physical space into basins arising from the topological analysis of the electron localization function (ELF) [1]. This localization procedure provides a straightforward and suitable interpretation of the resulting orbitals in terms of their localization indices and basin occupancies. In Ref. [1], we discussed the advantages of this method compared with previously reported procedures based on other partitionings of the 3D space, i.e., according to Bader's atoms

Published as part of the special collection of articles derived from the XI Girona Seminar and focused on Carbon, Metal, and Carbon–Metal Clusters.

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Published online: 12 February 2015

in molecules (AIM) scheme [2, 3] and the fuzzy atom (FA) treatment [4]. The performance of this new localization procedure has been initially tested on several simple molecules [1]. Subsequently, we used this procedure to analyze the chemical bonding of the $Si_n(BH)_{5-n}^{2-}(n = 0–5)$ series of clusters, which possess identical number of valence electrons and common structural patterns [5]. The orbital localization procedure based on the ELF (ELF-LOC) supported the bonding description previously obtained from adaptive natural density partitioning (AdNDP) method [5, 6]. Interestingly, both orbital localization schemes point out that replacing a BH unit by an Si atom does not alter the chemical bonding pattern of the resulting system, which adequately supports the structural persistence of these clusters through the transformation from Si_5^{2-} to $(BH)_5^{2-}$ [5, 6]. It is important to note that LOC-ELF scheme allowed to distribute the valence electrons, for the series $Si_n(BH)_{5-n}^{2-}$, into lone pairs and two-center two-electron (2c–2e) bonds in contrast to the picture obtained from the ELF domain analysis [7]. Similar results, which correct the chemical bonding description obtained by traditional ELF domain analysis, were obtained within the formalism of the domain-averaged Fermi holes [8].

Atomic clusters are chemical species that, in general, are stabilized through non-classical chemical bonding patterns. Consequently, concepts such as (anti)aromaticity are frequently used to describe them. These concepts have been specially used to describe the stability and structure of metallic clusters [9, 10]. However, there has been an increasing interest in the study of aromatic inorganic clusters conformed by nonmetallic elements [11–15]. Small planar boron clusters and their ions have been extensively and systematically studied both experimentally and theoretically [15–19]. Recently, Boldyrev and coworkers used the AdNDP method to evaluate the chemical bonding of the series of planar clusters: B_4, B_5^-, B_6^{2-}, B_9^-, B_{11}^- and B_{13}^+, which have been classified as aromatic or antiaromatic or with conflicting aromaticity according to that methodology [20]. The variety of chemical bonds exhibited in these clusters, conjointly with the availability of different studies focused on describing their chemical bonding, makes them a suitable set of exotic molecules to test our recently proposed ELF-LOC method.

In the present work, the chemical bonding of the clusters: B_4, B_5^-, B_6^{2-}, B_9^-, B_{11}^- and B_{13}^+ is interpreted in terms of topological analysis of the ELF and their respective localized (ELF-LOC) orbitals. Then, the results are compared with the chemical bonding picture obtained with AdNDP analysis. In first instance, previously reported AdNDP orbitals are used for comparison purposes [20]. In those cases where the ELF-LOC orbitals are clearly different, we have performed a comprehensive search for an alternative set of AdNDP orbitals considering their occupation number as quality indicator, according to the AdNDP method recommendation [20, 21].

2 Theoretical methods

The detailed description of the ELF-LOC algorithm can be found elsewhere [1, 5]. The localization of molecular orbitals within ELF approach has been performed using the GAMESS program [22] and our own routines, at B3LYP [23, 24]/6-311+G* [25] level of theory. We have used DGrid program [26] to calculate the ELF function and derived properties, as overlap integrals over ELF basins. All geometries have been obtained from refs [15, 20] which were recalculated at B3LYP/6-311+G* level of theory using the Gaussian 09 set of programs [27]. The AdNDP analyses were performed using NBO 3.0 [28] (included in Gaussian 09) and MultiWFN 3.2 programs [29]. The ELF-LOC orbitals have been plotted using MacMolPlt program [30]; AdNDP orbitals, ELF isosurfaces and ELF bifurcation analysis have been plotted using the VMD program [31].

ELF topological analysis provides a variety of tools for analyzing chemical bonds, e.g., bifurcation diagrams allow to visualize the hierarchy of splitting of reducible domains into irreducible ones as the ELF value increases [32–35]. The bifurcation value of the ring-shaped domains have been used in the past to assess aromaticity and antiaromaticity in a series of molecular rings [33, 36–42]. In particular, Silvi and collaborators [36] noted that at critical ELF = 0.580 values, it is possible to appreciate a distorted toroidal volume around the C_6 fragment of the benzene, which was identified as "aromatic domain." This aromatic domain splits into six irreducible domains at the critical ELF value of 0.645. In this work, the presence of a ring-shaped domain at ELF values equal to or greater than 0.600 should be taken as sign of aromaticity character. The critical ELF values at which the rings bifurcate should be considered as indicative of electronic delocalization around this region. Then, the localized orbitals, ordered in sets according to their spatial localization and to their molecular fragment assignment, can be used to rationalize the ELF information in terms of simple electron-counting rules, $4n + 2$ and/or $4n$ for aromatic and/or antiaromatic patterns according to the Hückel's rules.

3 Results and discussion

Figures 1, 2, 3, 4, 5 and 6 show the results achieved for the analyzed clusters. Progressive ELF variation, showing the critical ELF values at which the reducible domains split, is shown in part (a). The localized orbitals obtained by ELF-LOC strategy are reported in part (b) of the figures. In the cases where ELF-LOC orbitals were clearly different

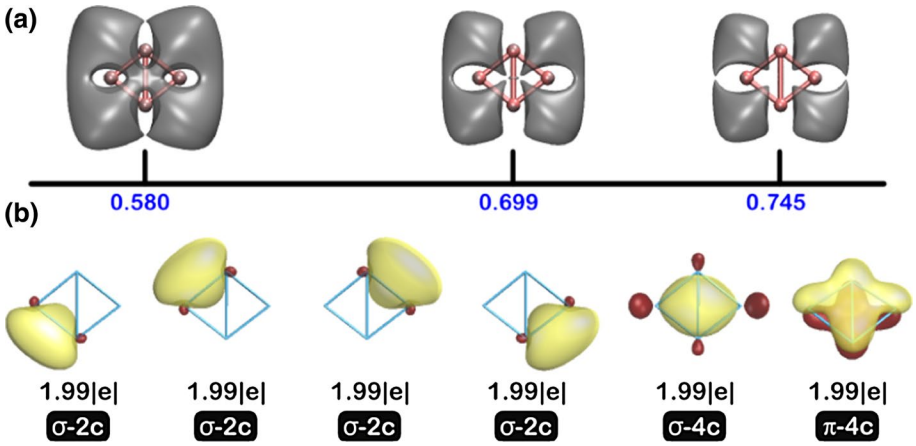

Fig. 1 **a** Isosurfaces at progressive ELF variation for the B_4 (D_{2h}) cluster; **b** ELF-LOC localized orbitals

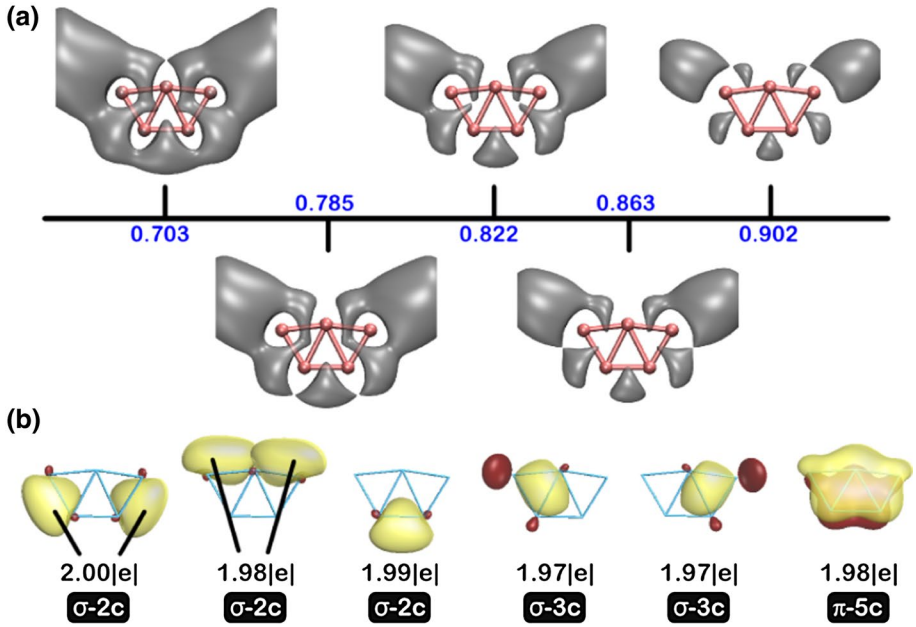

Fig. 2 **a** Isosurfaces at progressive ELF variation for the B_5^- (C_{2v}) cluster; **b** ELF-LOC localized orbitals

from those previously reported AdNDP orbitals, an alternative AdNDP analysis was performed searching for sets of AdNDP orbitals analogues to the ELF-LOC ones, which are shown in part (c). The judgment on the adequacy of the AdNDP localized orbital sets was performed on bases of the assessment of the residual density. At this point it is important to note that ELF-LOC orbitals should contain the same electronic population as the canonical ones. The deviation from the 2.0|e| ideal value does not have a physical or chemical meaning, but is due to numerical errors in the partitioning of the tridimensional space by means of topological analysis on a 3D grid representation of the ELF.

It is important to remark that to simplify the study, some considerations have been taken into account: the ELF and the localized orbital analysis are focused on the valence part of the electronic density. The type and number of centers (atoms), associated with each localized molecular orbital (LMO), are determined according to its relevant occupancy into the ELF basins. The synaptic order of basins with contributions >9 % has been considered to define the number of centers in the cases of multicenter LMOs. The ELF-LOC orbitals are represented by isosurfaces, which have been plotted at adequate values (~0.1 a.u) to visualize the distribution of these orbitals between atomic centers. The bonding localized orbitals are shown in ascending order of delocalization. Those ELF-LOC orbitals that are distributed in more than two centers are called delocalized in the discussion, although they were obtained by a localization procedure.

3.1 B_4 cluster

For the planar B_4 (D_{2h}) cluster, the isosurface at the critical ELF = 0.580 value shows that the domain

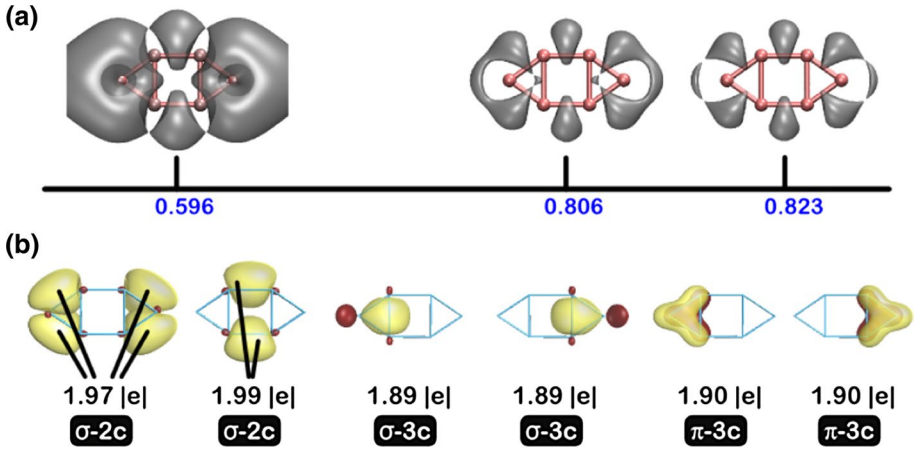

Fig. 3 **a** Isosurfaces at progressive ELF variation for the B_6^{2-} (D_{2h}) cluster; **b** ELF-LOC localized orbitals

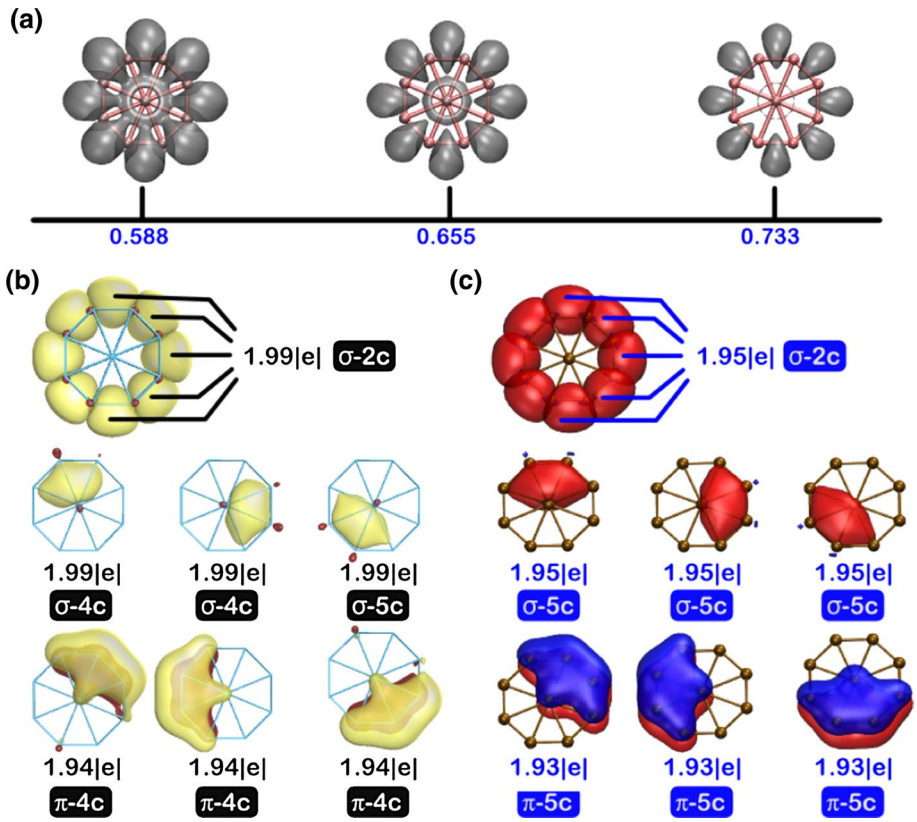

Fig. 4 **a** Isosurfaces at progressive ELF variation for the B_9^- (D_{8h}) cluster; **b** ELF-LOC localized orbitals; **c** AdNDP localized orbitals

surrounding the complete cluster bifurcates on the peripheral region, giving rise to two local and symmetric rings around the triangular B_3 fragments connected between them at the center of the cluster. These local rings bifurcate, on the central region of the cluster, at the critical ELF = 0.699 value. There is no presence of a ring-shaped isosurface involving the complete cluster. The persistence of the local rings at high ELF values suggests a significant electronic delocalization around each one of the B_3 triangular fragments. The global aromatic character of this cluster is not evidenced on the ELF topological analysis.

Previous studies, based on canonical molecular orbitals (CMOs) inspection [43] and AdNDP analysis [20], have classified this cluster as doubly aromatic, due to the presence of one σ and one π completely delocalized orbitals. The ELF-LOC strategy recovers all the localized and delocalized orbitals obtained by AdNDP, supporting this chemical bonding description. The four two-center two-electron (2c–2e) B–B peripheral σ-bonds house a total of eight σ-electrons. Additionally, we have one σ and one π completely delocalized orbitals. Therefore, the doubly aromatic character assignation according to the $4n + 2$ rule is adequately supported by ELF-LOC.

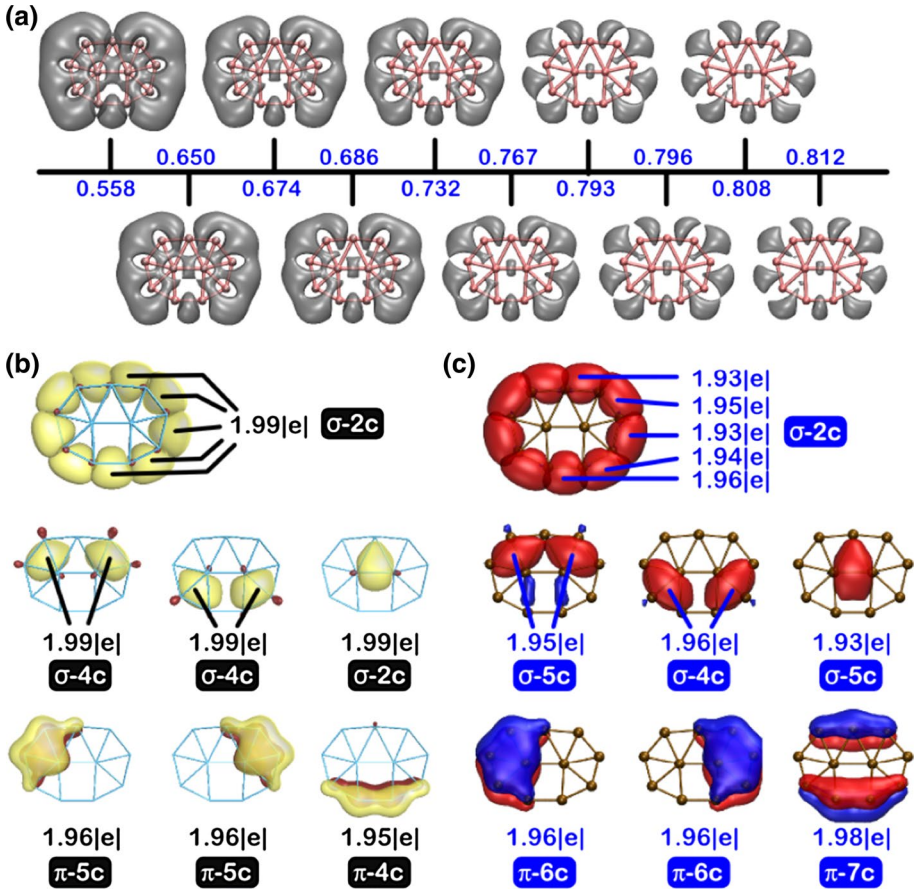

Fig. 5 **a** ELF isosurfaces at progressive ELF variation for the B_{11}^- (C_{2v}) cluster; **b** ELF-LOC localized orbitals; **c** AdNDP localized orbitals

3.2 B_5^- cluster

In the case of the B_5^- (C_{2v}) cluster, the isosurface at the critical ELF = 0.703 value shows a domain with a ring shape bifurcating on the peripheral region. At critical ELF = 0.785 value emerge one disynaptic and irreducible *V*(B,B) basin on the peripheral region of the cluster and two ring-shaped surfaces around the terminal B_3 triangular fragments that bifurcate at critical ELF = 0.822 value. These bifurcation values are even higher than those of the "aromatic domain" on benzene. The ELF analysis suggests global aromatic character and the presence of local aromaticity around the B_3 triangular fragments.

The ELF-LOC procedure allows to localize the σ-electrons into five (2c–2e) B–B σ-peripheral bonds and two delocalized three-center two-electron (3c–2e) σ-bonds [44, 45]. The (3c–2e) σ-orbitals are located on each triangular fragment at the two ends of the clusters, which could be associated with local σ-aromaticity or with global σ-antiaromaticity in agreement with previous assignments [20]. At the end of the figure, the unique five-center two-electron (5c–2e) π-orbital is shown, confirming the presence of π-aromaticity in this cluster. This set of localized orbitals, which represents the valence electrons, is similar to that recovered by AdNDP analysis [20]. The prediction of global and local aromaticity, based on localized orbital evaluation, is consistent with the ELF description. However, the predicted global antiaromatic character due to the four delocalized σ-electrons (on the two (3c–2e) σ-bonds) is not evidenced in the ELF analysis.

3.3 B_6^{2-} cluster

The isosurface at critical ELF = 0.596 value shows a ring-shaped domain that bifurcates on the peripheral region splitting up into four domains: two local rings around each terminal B_3 triangular fragments and two disynaptic and irreducible *V*(B,B) basins on the peripheral region of the cluster. Each local ring bifurcates at critical ELF = 0.806 value. These results suggest a low electronic delocalization around the peripheral region (ELF <0.600) of the B_6^{2-} ring and a higher local electronic delocalization around the B_3 triangular fragments at the ends of the cluster.

The ELF-LOC provides a set of six (2c–2e) peripheral and two delocalized (3c–2e) B–B σ-bonds. The two delocalized σ-orbitals can be interpreted as indicating both: global σ-antiaromatic character ($4n$ system) or doubly local σ-aromatic character ($4n + 2$ system), as was previously

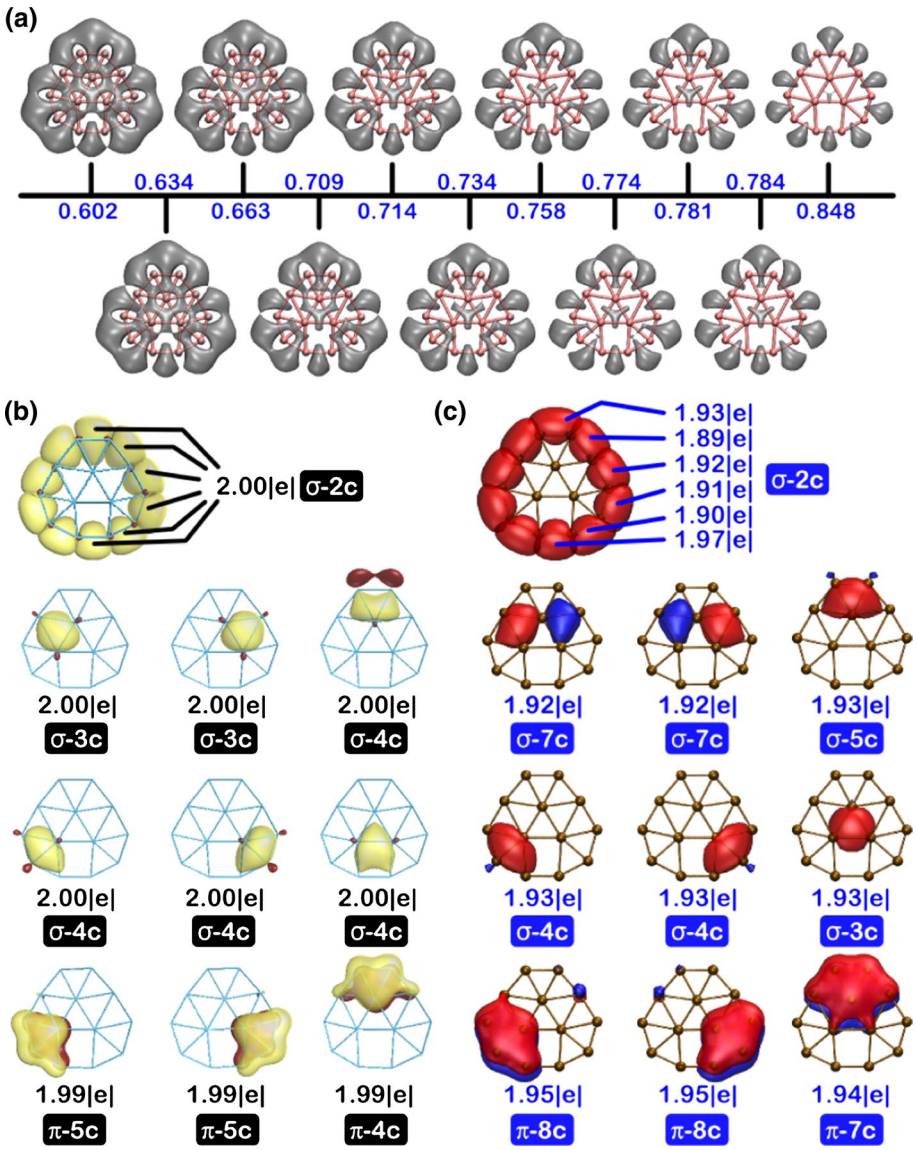

Fig. 6 **a** ELF isosurfaces at progressive ELF variation for the B_{13}^{+} (C_{2v}) cluster; **b** ELF-LOC localized orbitals; **c** AdNDP localized orbitals

discussed by Zubarev and Boldyrev [20]. Additionally, ELF-LOC distributes the π-electrons in two (3c–2e) π-bonds, which are centered on the ending triangular fragments of the cluster. This set of π-orbitals, in a similar way to its σ-orbital set counterpart, could be associated with global antiaromaticity or doubly local aromaticity contribution. According to this description, the B_6^{2-} cluster is globally doubly σ and π antiaromatic. Both the global antiaromaticity and the local aromaticity is supported by the ELF bifurcation analysis.

3.4 B_9^{-} cluster

For the B_9^{-} (D_{8h}) cluster, a flower-shaped isosurface is revealed at critical ELF = 0.588 value. This isosurface is similar to that of benzene, with the toroidal isosurface (aromatic domain), in this case surrounding the central atom of the cluster. At critical ELF = 0.655 value, eight disynaptic *V*(B,B) basins on the peripheral region are separated from the aromatic domain. The aromatic domain bifurcates at critical ELF = 0.733 value. These results suggest that the electrons on the peripheral region of the cluster are well localized, and the presence of an aromatic domain suggests that this cluster is aromatic.

The ELF-LOC allows to localize the σ-electrons into eight (2c–2e) B–B peripheral σ-bonds and one set of three multicenter bonds: one (5c–2e) and two (4c–2e) σ-bonds. The π-electrons are localized into a set of three multicenter (4c–2e) π-bonds. The prediction that single bonds are connecting the peripheral region of the cluster agrees with previous assignation performed by AdNDP analysis [20]; however, the delocalized orbitals are slightly different due to the space partitioning which restricts the symmetry compared with the complete molecular space. Previously reported AdNDP orbitals are completely delocalized

and therefore similar to their CMOs counterparts. The alternative orbital localization procedure using the AdNDP method provides a set of localized orbitals similar to those obtained from ELF-LOC, with a residual electronic population of 0.76|e|, which is small considering the 28 valence electrons. It is important to remark that doubly aromatic character on this cluster, σ and π, is also adequately supported by this alternative set of localized orbitals.

3.5 B_{11}^- cluster

For this cluster, at critical ELF = 0.558 value, the global isosurface bifurcates on its peripheral region revealing a butterfly shape, where it is possible to identify a disynaptic V(B,B) basin connecting, on the peripheral region, two boron atoms at the base of a distorted square B_4 fragment. At critical ELF = 0.650 value, a disynaptic basin V(B,B) connecting the two internal atoms emerges. The peripheral domains are completely defined at critical ELF = 0.793 value. These results suggest that part of the electrons on the peripheral region are delocalized following local ring patterns, with a higher delocalization through the center of the cluster. This analysis does not provide evidence of aromaticity in this cluster.

The previous assignation of conflicting aromaticity made for the B_{11}^- (C_{2v}) cluster, which was based on the visual analysis of the CMOs structure [46], was corrected to doubly (σ- and π-) aromatic following AdNDP analysis [20]. The ELF-LOC strategy recovers the nine (2c–2e) σ-bonds on the peripheral region obtained from the AdNDP method. The localization of the remaining σ-electrons provides a set of four delocalized orbitals around the B_2 internal fragment (four (4c–2e) σ-bonds) and one (2c–2e) σ-bond. The π-electrons are localized in a set of three orbitals [two (5c–2e) and one (4c–2e) π-bonds]. The alternative AdNDP set of orbitals (Fig. 5c) is very similar to that obtained by the ELF-LOC procedure. The residual electronic population associated with this new AdNDP localization is of 0.98|e|, which is small considering the 34 valence electrons. Regarding the set of five σ-delocalized orbitals, the system should be classified as σ-aromatic in agreement with the previous AdNDP assignation [20]. In spite of the differences on the distribution of the π-orbitals, the B_{11}^- cluster should be classified as π-aromatic system in terms of this new set of ELF-LOC localized orbitals.

The doubly (σ- and π-) aromatic character of this cluster is not fully supported by the ELF analysis. An alternative proposal is to classify the σ-delocalized orbitals in two sets. One of them gathers four orbitals around the internal B_2 fragment housing eight electrons and supporting a $4n$ antiaromatic pattern. The other one is constituted by a σ-delocalized orbital contributing to aromaticity. Hence, in this cluster, the presence of conflicting aromaticity is possible, as a consequence of the σ-electronic delocalization.

3.6 B_{13}^+ cluster

For this cluster, the global isosurface bifurcates on the peripheral region, at critical ELF = 0.602 value, revealing a cloverleaf shape where it is possible to identify a disynaptic V(B,B) basin connecting two boron atoms. At critical ELF = 0.709 value, it is possible to discriminate a ring aromatic domain around the central boron atom of the distorted hexagonal B_7 fragment. These results suggest that part of the electrons on the peripheral region is delocalized following local ring patterns. The aromatic character is predicted by the presence of an "aromatic domain" which is displaced to one extreme of the cluster.

The ELF-LOC strategy recovers ten (2c–2e) localized orbitals on the peripheral region of the B_{13}^+ (C_{2v}) cluster, which are similar to those previously recovered by AdNDP analysis [20]. The remaining σ-electrons are localized into a set of six σ-bonds (four (4c–2e) and two (3c–2e) orbitals). The structure and the location of these orbitals forbid a dissection of them in separated sets of localized orbitals as was performed with the AdNDP orbitals [20]. Therefore, our results predict σ-antiaromaticity (twelve electrons, $4n$ system) on this cluster. Further investigation is recommended in this system, in order to clarify this discrepancy. Finally, the ELF-LOC provides a set of three delocalized π-orbitals [two (5c–2e) and one (4c–2e) π-bonds] that are similar to those previously reported by AdNDP [20]. An exhaustive search for a set of AdNDP orbitals equivalent to that obtained from the ELF-LOC method provides a somewhat different set with a residual population of 1.46|e|. This residual population is lower than the original set of AdNDP orbitals (2.32|e|), which in some way validates the ELF-LOC procedure.

The global aromatic character due to the π-electrons is adequately supported by the ELF analysis. However, the aromatic, antiaromatic or conflicting aromatic character due to the σ-electrons is not easy to define within the ELF framework.

Finally, it is important to remark that further systematic studies are necessary to attain a more complete understanding of chemical bond on the analyzed clusters. In this context, we are performing calculations of different aromaticity indexes [47, 48] to provide alternative evidences about aromaticity, antiaromaticity and conflicting aromaticity on these systems; the results should be published elsewhere.

4 Concluding remarks

In this work, we have applied our ELF localization (ELF-LOC) procedure to describe the chemical bonding nature in

exotic molecules such as small boron clusters. The results show that the ELF-LOC method provides additional information complementing that obtained from the classical ELF analysis. Our methodology leads to localized orbitals distributed in more than two centers, which have been identified as delocalized (multicenter) orbitals. These orbitals have been used to interpret and to support the (anti) aromatic character in this series of clusters. In general, the ELF-LOC orbitals are similar to those obtained from the most traditional AdNDP method. However, the information arising from the ELF topological analyses provides, in some cases, interpretations different than those obtained from the AdNDP and ELF-LOC procedures, i.e., the doubly aromatic character (σ and π) assigned to the B_4 cluster is not evidenced in the ELF topological analysis. It is important to remark that the ELF-LOC strategy provides a unique set of localized orbitals, the multicenter localized orbitals; when found, they emerge as a consequence of the localization procedure following the topology of the ELF treatment. Therefore, the ELF-LOC technique seems to be an adequate method to partition the charge density into elements with highest possible localization degree for electron pairs in (*n*c–2e) bonds, allowing to combine Lewis's ideas with (anti)aromaticity concepts. The need for multicenter bonding is quickly growing, and to have a new tool for rationalizing chemical bonding in new chemical systems, as ELF-LOC strategy, is very important.

Acknowledgments This work has been financially supported by the Projects PIP 11220090100061 and 11220090100369 (Consejo Nacional de Investigaciones Científicas y Técnicas, Argentina); UBACYT 20020100100197 (Universidad de Buenos Aires, Argentina); GIU12/09 and UFI11/07 (Universidad del Pais Vasco, Spain). FONDECYT (Grant 1140358), Universidad Andres Bello (Grants DI-01-12/Eq, DI-368-13/R, DI-407-13/I, and DI-619-14/I) CONICYT, PCHA/Doctorado Nacional (Grant 2013-63130043). We thank the Universidad del Pais Vasco for allocation of computational resources.

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