Orbital Localization Criterion as a Complementary Tool in the Bonding Analysis by Means of Electron Localization Function: Study of the $Si_n(BH)_{5\text{-}n}^{2-}$ ($n = 0-5$) Clusters

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ABSTRACT: A recently proposed molecular orbital localization procedure, based on the electron localization function (ELF) technique, has been used to describe chemical bonding in the cluster series $Si_n(BH)_{5\text{-}n}^{2-}$ ($n = 0-5$). The method combines the chemically intuitive information obtained from the traditional ELF analysis with the flexibility and generality of canonical molecular orbital theory. This procedure attempts to localize the molecular orbitals in regions that have the highest probability for finding a pair of electrons, providing a chemical bonding description according to the classical Lewis theory. The results confirm that conservation of the structures upon isoelectronic replacement of a B–H group by a Si atom, allowing evolution from $B_5H_5^{2-}$ to Si_5^{2-}, is in total agreement with the preservation of the chemical bonding pattern.

$B_5H_5^{2-}$ (D_{3h}, $1A_1'$) Si_5^{2-} (D_{3h}, $1A_1'$)
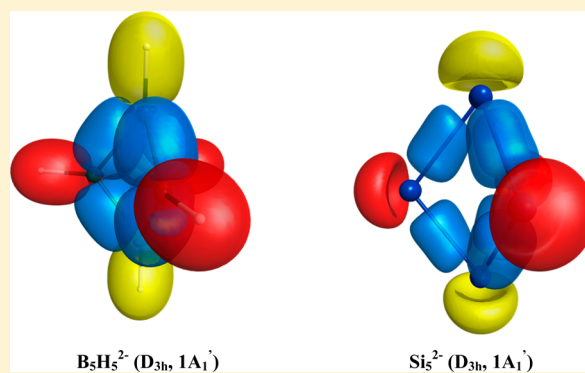
I. INTRODUCTION

More than nine decades ago Lewis proposed the most successful and generally accepted model to describe the chemical bonding, using localized bonding elements such as lone pairs and two-center two-electron (2c-2e) bonds.[1] For many simple molecules and especially for organic molecules, the Lewis proposal is the simplest and most powerful way to rationalize the chemical bonding of these species. Furthermore, even in systems that present electronic delocalization, the clearest and most didactic representations of their bonds arise from combination of several resonant structures, each of them corresponding to a simple Lewis scheme. Since then, the diversity of concepts proposed to gain an insight into chemical bonding has coexisted with the main ideas of the Lewis framework. The theory of molecular orbitals (MO) by Mulliken,[2] Hund,[3] and the pioneering works of Lennard-Jones[4,5] describes the electrons as entities delocalized among the fragments of a system. This theory turned out to be compatible with the more intuitive and practically applicable Lewis description after utilizing various localization techniques. The well-known localization procedures proposed by Foster and Boys,[6] Edmiston and Ruedenberg,[7] Pipek and Mezey,[8] and

others[9,10] are based on the fact that the wave function is invariant under unitary transformations among molecular orbitals. On the other hand, a huge segment of the chemical bonding field belongs to theories, which avoid any reference to "chemical bonds", since these entities have not a clear and precise physical definition. Instead, these theories rely on different forms of analysis of charge density, such as topological analysis of the Laplacian of the electron density within the framework of quantum theory of atoms in molecules (QTAIM),[11] or local quantum-mechanical functions, related to the Pauli exclusion principle, i.e., Fermi hole (FH),[12−22] approaches or electron localization function (ELF).[12,17,23−29] In particular, the ELF procedure provides information about the regions of the space where it is more probable to find an electron or a localized electron pair.[30−32] Therefore, this method enables us a chemical bonding description in agreement with the Lewis model.

We have recently proposed a new localization procedure that involves the partitioning of the molecular space according to the ELF technique, with a subsequent orbital localization into these regions.[33] This localization procedure has the advantage of providing a straightforward and suitable interpretation of the resulting orbitals in terms of their localization indices and basin occupancies. The method has been tested in some benchmark molecules, and the obtained results are in agreement with the genuine chemical expectations of the classical bonding paradigms exhibited by these systems.[33] In the present work, we apply our localization scheme to describe the chemical bonding in the $Si_n(BH)_{5-n}^{2-}$ ($n = 0-5$) set of clusters, which possess identical number of valence electrons and common structural patterns.[34] The chemical bonding for $B_5H_5^{2-}$ and Si_5^{2-} ions is frequently represented by structure I (see Scheme 1: X =

Scheme 1
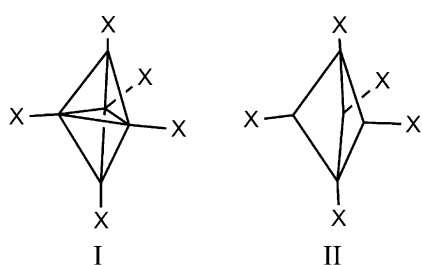
H for $B_5H_5^{2-}$ and X = lone pair for Si_5^{2-}).[35−37] Nevertheless, in clusters it is common to connect atoms, in the corresponding structures, following only distance criteria. Zubarev et al. have described the chemical bonding in $B_5H_5^{2-}$ and Si_5^{2-} species using ELF, canonical molecular orbitals, and atomic charges obtained from natural population analysis (NPA).[37] These authors have proposed a chemical bonding framework in the Si_5^{2-} ion like structure I in Scheme 1 (X = lone-pair electrons), whereas in the $B_5H_5^{2-}$ one, they have not detected equatorial B−B bonds and have proposed structure II in Scheme 1. In a later work, Osorio et al.[34] have used adaptive natural density partitioning (AdNDP)[38,39] method to describe the chemical bonding of the $Si_n(BH)_{5-n}^{2-}$ ($n = 0-5$) series of clusters. These authors concluded that both $B_5H_5^{2-}$ and Si_5^{2-} ions present an identical bonding pattern into the cage of the cluster, which resembles structure II, with two-center two-electron bonds between equatorial and axial atoms and an absence of bonds between equatorial atoms.

The results reported in the present work suggest that the localized orbitals arising from the ELF domains lead to similar bonding patterns than those obtained by the AdNDP approach, allowing a more intuitive description of chemical bonding according to Lewis theory. This localization scheme turns out to be an adequate alternative which complements the traditional information obtained by ELF analysis; it can be very useful in the study of exotic molecules, like atomic clusters.

II. LOCALIZATION CRITERION BASED ON TOPOLOGYCAL ANALYSIS OF ELF

The localization procedures are based on the fact that a wave function is invariant with respect to any unitary transformation among molecular orbitals. Therefore, the localization of these orbitals is equivalent to find an isopycnic orbital transformation matrix U that maximizes the localization sum

$$L = \sum_\mu \sum_{klm} U_{\mu k}^* U_{\mu l} U_{\mu m}^* U_{\mu n} T_{klmn} \tag{1}$$

where the tensor T defines the localization procedure. The matrix U, that relates localized molecular orbitals $\{\mu\}$ with canonical ones $\{k,l,m,n\}$, is usually computed throughout consecutive $\{2 \times 2\}$ rotations[7] or by a second-order maximization procedure.[40] Recently, we have proposed a new localization procedure with the tensor T defined through the ELF theory, which carries out a partitioning of the physical space based on the topological properties of the ELF.[33] The whole three-dimensional space is divided into disjoint basins Ω_A, having a clear chemical meaning, which are classified into core basins organized around nuclei and valence basins in the remaining space.[23,29] Thus, within this procedure the tensor T is defined as

$$T_{klmn}^{ELF} = \sum_{\Omega_A} \langle k|l \rangle_{\Omega_A} \langle m|n \rangle_{\Omega_A} \tag{2}$$

which yields maximization of the ELF charge-density overlap functional and where $\langle k|l \rangle_{\Omega_A}$ are the overlap integrals over the ELF domains Ω_A ($\langle k|l \rangle_{\Omega_A} = \int_{\Omega_A} \psi_k^*(\mathbf{r}) \, \psi_l(\mathbf{r}) \, d^3r$ is limited to this kind of basins). The ELF basins let one express the Kronecker deltas as $\delta_{kl} = \langle k|l \rangle = \sum_{\Omega_A} \langle k|l \rangle_{\Omega_A}$ and the quantity $\langle k|l \rangle_{\Omega_A}$ defines the population of the kth orbital on the basin. The localized orbitals resulting from this procedure have many attributes usually associated with chemical concepts (appropriate spatial localization, high transferability, etc.) so that they can be regarded as the theoretical counterpart of the classical chemical pictures such as bonds, nonbonding electron pairs, core orbitals, valences and so forth, as it has been shown in ref 33.

III. COMPUTATIONAL DETAILS

The localization of molecular orbitals within the ELF approach has been performed using the GAMESS program[41] and our own routines, at the B3LYP[42,43]/ 6-311+G*[44] level of theory. We have used DGrid program[45] to calculate the overlap integrals over ELF basins, required for these calculations. All geometries have been obtained from ref 34, where the isomers of minima energy have been identified using the gradient embedded genetic algorithm (GEGA)[46,47] program following a geometry reoptimization at the B3LYP/def2-TZVPP[48] level of theory with final single-point energy calculation at the CCSDT/def2-TZVPP level of theory. The nuclear independent chemical shifts (NICS)[49] were computed using the B3LYP/def2-TZVPP level in the Gaussian 09 program.[50]

The cluster geometries and the position at which the ELF and orbitals are plotted are shown in Figure 1. The orbitals and ELF isosurfaces have been plotted using MacMolPlt[51] and Vesta[52] programs.

IV. RESULTS AND DISCUSSION

As has been mentioned above, the first step of our molecular orbital localization strategy is to calculate the ELF and evaluate its topology according to the Silvi and Savin approach.[29] Selected isosurface values, which represent all irreducible localization domains, are reported in Figures 2 and 3; it means that each localized volume in those figures represent a localized region into a basin. According to the traditional ELF topological analysis and following the Silvi and Savin definitions
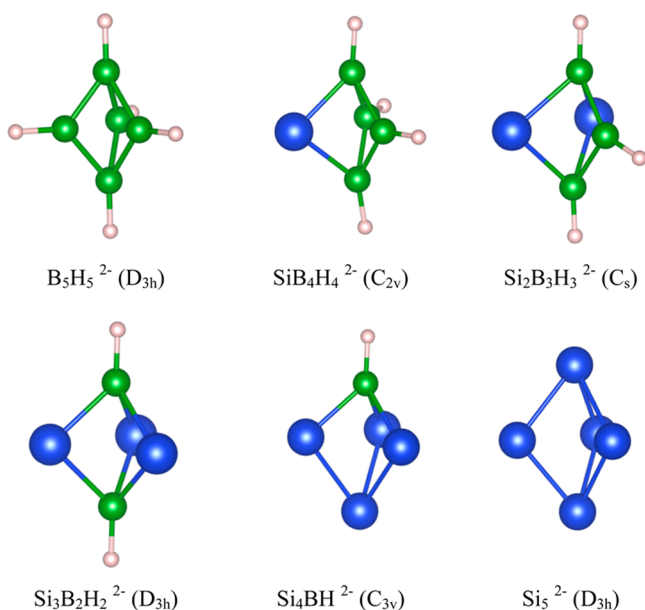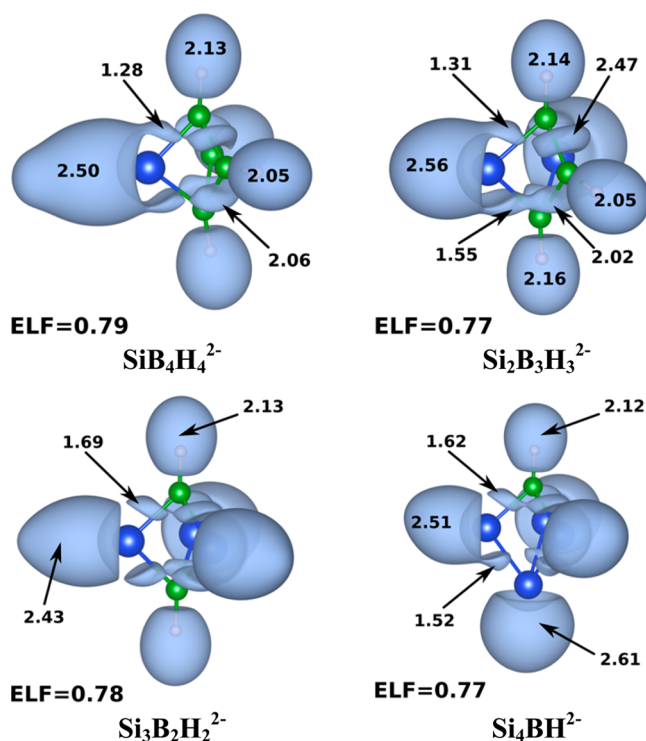
Figure 1. Global minimum structures of the $Si_n(BH)_{5-n}^{2-}$ ($n = 0-5$) clusters at the CCSDT/Def2-TZVPP//B3LYP/Def2-TZVPP level (from ref 34).
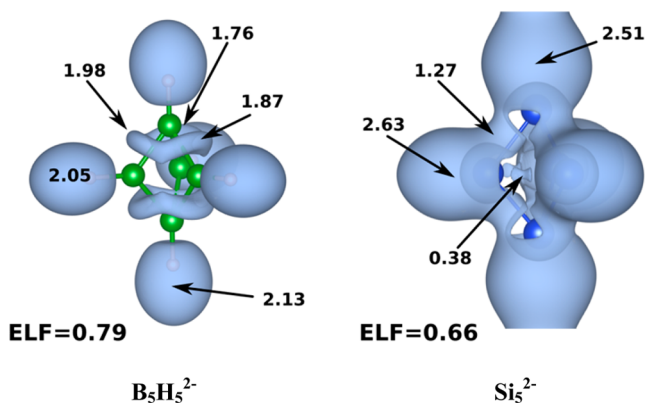
Figure 2. ELF isosurfaces showing all of the irreducible localization domains for $B_5H_5^{2-}$ (D_{3h}, $1A_1'$) and Si_5^{2-} (D_{3h}, $1A_1'$) calculated at the B3LYP/6-311+G* level of theory. The electron density integrated in each region is also reported.

Figure 3. ELF isosurfaces showing all the irreducible localization domains for $Si_n(BH)_{5-n}^{2-}$ ($n = 1-4$) clusters, computed at the B3LYP/6-311+G* level of theory. The electron density integrated in each region is also reported.

about basin synaptic order, we have found three types of basins in the studied systems: core basins $C(X_i)$ which involve the electron density of the core electrons over the X_i atom, monosynaptic valence basins $V(X_i)$ associated with lone pairs electrons over the X_i center, and disynaptic valence basins $V(X_i,X_j)$ which represent chemical bonds involving X_i and X_j atoms. The ELF topological analysis of the $B_5H_5^{2-}$ ion reveals six equivalent and irreducible localization domains corresponding to $B_{eq}-B_{ax}$ bonds, plus five monosynaptic basins over the H atoms corresponding to the polarized B−H covalent bonds. In contrast, the same analysis for the Si_5^{2-} species reveals three types of localization domains corresponding to three $Si_{eq}-Si_{eq}$ bonds, six $Si_{eq}-Si_{ax}$ bonds and five lone pairs, one over each Si atom. These findings are in total agreement with the results previously reported by Zubarev et al.[37] It is important to remark that core basins are also obtained from the ELF analysis, but our discussion will be focused on describing the chemical bonding, i.e., on the distribution of the valence electrons. Integration of the electron density into each basin is reported in

the same figures. As can be seen in Figure 2, the electron density is distributed in quantities close to a pair of electrons in each of the ELF basins of $B_5H_5^{2-}$. The skeletal bonding basins $V(B_{eq},B_{ax})$ have an electronic population of 1.87 |e⁻| and the B−H bonding basins $V(B,H)$ have an electronic population of 2.05 |e⁻| and 2.13 |e⁻|, corresponding to equatorial and axial atoms, respectively. Therefore, following the information provided by the classical analysis of the ELF, the bonding pattern in $B_5H_5^{2-}$ should be adequately represented by structure II (Scheme 1). This simple chemical bonding interpretation disappears when Si_5^{2-} is analyzed; the lone pair basins involve 2.63 |e⁻| and 2.51 |e⁻|, corresponding to equatorial and axial atoms, respectively. The bonding basins, which connect equatorial and axial atoms, enclose 1.27 |e⁻| and the bonding basins in the equatorial region have the smallest electronic population of 0.38 |e⁻|. The $Si_n(BH)_{5-n}^{2-}$ ($n = 1-4$) have also been included in the analysis, with the aim of evaluating the ELF interpretation of chemical bonding as the system evolves from $B_5H_5^{2-}$ to Si_5^{2-}; the results are reported in Figure 3. In general, the systems that involve silicon atoms in their conformations allow the presence of lone pair basins with an electronic population between 2.4|e⁻| and 2.6 |e⁻|. Additionally, the bonding basins involving silicon atoms have electronic populations between 1.3|e⁻| and 1.7 |e⁻|. This prevents a clear interpretation of the chemical bonding, generating some questions like: what is the meaning of a chemical bond with an electronic population of 0.38|e⁻|? Most importantly, will this result lead to erroneous interpretations of chemical bonding, e.g., the presence of equatorial bonds in Si_5^{2-} and the absence of these bonds in the other analyzed systems, even in $Si_3B_2H_2^{2-}$ and Si_4BH^{2-} clusters which present the same Si_3 equatorial ring as in Si_5^{2-}? The difference in the chemical bonding patterns

described by the traditional ELF analysis disagrees with the fact that the isoelectronic substitution of a B−H unit for a Si atom along the transformation from $B_5H_5^{2-}$ to Si_5^{2-} does not affect the overall structure of the clusters, which was attributed to the similarities in the bonding patterns of these species.[34]

The above-mentioned orbital localization procedure generates a set of localized core and valence orbitals, the later being graphically represented in Figure 4. That figure shows selected
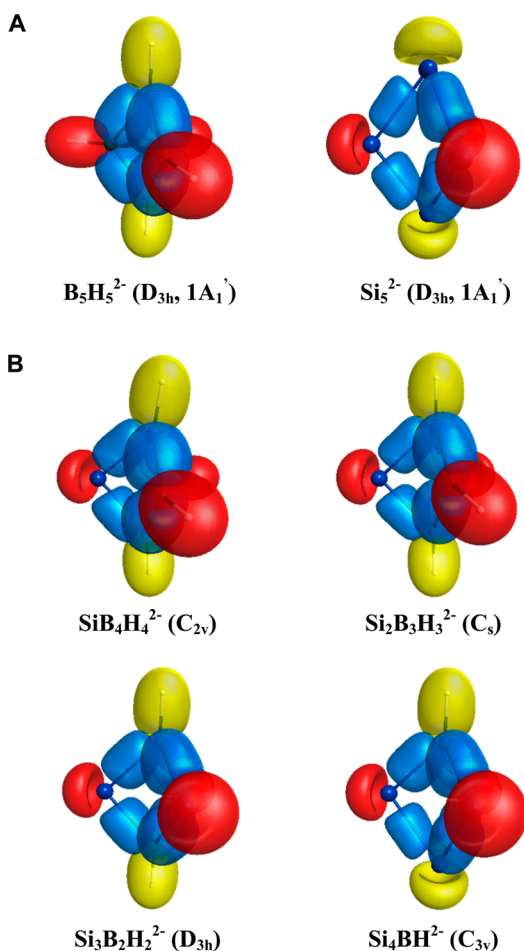
Figure 4. Isosurfaces of the localized orbitals for $Si_n(BH)_{5-n}^{2-}$ ($n = 0-5$) clusters. The colors have been chosen to distinguish the orbitals according to their chemical bonding interpretation (see text). The isovalues are ±0.135 au, and negative or positive orbitals of the same kind are represented by the same color.

isosurfaces of the localized orbitals for the clusters $B_5H_5^{2-}$ and Si_5^{2-} (in part A) and $Si_n(BH)_{5-n}^{2-}$ ($n = 1-4$) (in part B). We have included the $Si_n(BH)_{5-n}^{2-}$ ($n = 1-4$) clusters in our discussion, in order to evaluate the bonding description in B−Si mixed clusters. In the figure, the localized orbitals are classified by colors according to the following criteria:

(1) The X_i-X_j bonding orbitals that connect the atoms in the cage of the clusters are represented in blue. In $B_5H_5^{2-}$ and Si_5^{2-} six orbitals have been obtained, which are principally localized into the dysinaptic, $V(X_{eq}, X_{ax})$, ELF basins. These orbitals clearly represent two-center two-electrons (2c-2e) chemical bonds.

(2) The peripheral lone pairs or/and B−H bonding orbitals are represented in yellow or red, according to their location, axial or equatorial, respectively. In $B_5H_5^{2-}$ and Si_5^{2-}, five 2c-2e

B−H bonding orbitals and five lone pairs were obtained, respectively.

Interestingly, the localization procedure does not predict orbitals into the equatorial region in the $B_5H_5^{2-}$ or Si_5^{2-} clusters, although in the later one the ELF topological analysis provides a localized basin in this region (see Figure 2). Therefore, from localized orbitals analysis the chemical bonding in the clusters $B_5H_5^{2-}$ and Si_5^{2-} fits better within the structure II (Scheme 1). The same analysis was performed in $Si_n(BH)_{n-5}^{2-}$ ($n = 1-4$) clusters, forming the same kind of bonding and/or lone pair orbitals. Consequently, from this localization procedure we can conclude that $B_5H_5^{2-}$ and Si_5^{2-} as well as the mixed clusters, where one Si unit replaces a B−H molecular fragment, are adequately represented by similar bonding paradigms. This chemical bonding description is in total agreement with Osorio et al. findings,[34] using the AdNDP analysis.

Finally, taking into account that the compounds $B_5H_5^{2-}$ and Si_5^{2-} have been previously described as examples of systems with spherical aromaticity,[37,53] we have calculated values of nucleus independent chemical shifts (NICS) frequently used to assess aromaticity and antiaromaticity in a simple way. For the sequence $B_5H_5^{2-}$, $SiB_4H_4^{2-}$, $Si_2B_3H_3^{2-}$, $Si_3B_2H_2^{2-}$, $Si_4B_4H_4^{2-}$, and Si_5^{2-} we have found the NICS values −24.6, −24.1, −25.5, −32.7, −39.0, and −40.1, respectively. These quantities show that all of the studied systems present high aromaticity (in terms of NICS analysis), and this feature increases from $B_5H_5^{2-}$ to Si_5^{2-} clusters. This behavior is in agreement with the chemical compatibility of replacing a B−H unit by a silicon atom as discussed above.

V. CONCLUDING REMARKS

In this work we have used the recently proposed localization procedure based on the partitioning of the physical space into basins resulting from the topological analysis of ELF to describe the chemical bonding in the $Si_n(BH)_{5-n}^{2-}$ ($n = 0-5$) clusters. In contrast to the information obtained from the classical analysis of ELF, this procedure predicts similar bonding patterns for these clusters. This information is in total agreement with the fact that the consecutive isoelectronic substitution of a B−H unit by a Si atom along the transformation from $B_5H_5^{2-}$ to Si_5^{2-} does not affect the overall structure of the species. Our results enforce the previous explanations based on similar bonding patterns showed by both chemical compounds.

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Notes
The authors declare no competing financial interest.

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