

## ORIGINAL ARTICLE

# Effect of Static Atomic Charges on Small Elemental Clusters: Evidence from Boron

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## Abstract

Study examines the effect of static atomic charges on small elemental clusters relative stability. For this purpose equilibrium bonds length and specific (per atom) binding energy of all-boron neutral, anionic and cationic planar clusters  $B_n$  containing  $n \leq 15$  atoms are calculated in the frames of phenomenological diatomic molecular model imagining the cluster as a construction of pair interatomic chemical

bonds. In elemental clusters, which are finite structures of chemically identical but differently coordinated atoms, static charges of atoms are assumed to be proportional to their coordination numbers. Most symmetric clusters have revealed the non-monotonic dependencies of B-B length and specific binding energy on  $n$ , which seem to be related with differences in their structures. Obtained results provoke reconsidering the usual assumption that the equilibrium isomer of a cluster corresponds to its highest symmetry even at the significant static electrical charges localized on atomic sites.

**Key Words:** *Nanocluster; Atomic site charge; Binding energy; Diatomic model; Boron*

## Introduction

Crystals are known as finite space-periodic structures of bounded atoms. Frequently atoms in elemental crystals do not possess static electrical charges because of crystallographic equivalency of all the atomic sites. However, exceptions are crystals with complex unit cell, e.g., structural modifications of boron,

containing many atoms placed in several differently coordinated sites.

As for elemental clusters, which are the finite structures of identical atoms, charges localized on atoms in their bulk always differ from those for atoms placed on their surface again due to different coordination numbers of bulk and surface atomic sites, respectively. Actually, it

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is a nanoeffect most sharply revealed in small elemental clusters containing comparable numbers of atoms in their central part and periphery, where part of chemical bonds is dangled.

This work aims to consider theoretically - in diatomic molecular model imagining cluster as a construction of pair interatomic chemical bonds - the static atomic charges effect on elemental nanoclusters bonds length and specific (per atom) binding energy, consequently, their relative stability. Calculations are conducted for small all-boron neutral, anionic and cationic planar clusters  $B_n$  in most symmetric planar structures containing  $n \leq 15$  atoms.

Boron case is chosen because borophenes and other boron-rich 2D materials are of current academic and practical interests for unique complex of physical-chemical properties useful in technological applications - see some of last reviews [1-7]. At the lower number of atoms  $n$ , the all-boron clusters  $B_n$  prefer (quasi)planar structure and then can be considered [8,9] as building blocks for 2D boron materials.

## Method

Specific binding energy (binding energy per chemical formula unit) serves for key physical characteristic determining clusters relative stability and then affects relative concentrations of clusters with different sizes synthesized during a formation process. Clusters binding energy can be estimated in frames of the diatomic model based on the interatomic bonding saturation property. As for the all-boron small (quasi)planar clusters, to the best our knowledge there are no reports on their diatomic investigation unless our previous estimates of their relative stabilities [10-13] and also dipole moments [14,15]. Results obtained in this way

are summarized in reviews [16,17]. In [18], the binding energy problem was specially analyzed for  $B_{11}$ ,  $B_{12}$  and  $B_{13}$ , the three most abundant boron clusters.

In the phenomenological version of the diatomic model recently introduced [19] for nanoclusters, elemental clusters equilibrium bonds length and equilibrium binding energy  $E$  (in Gauss units) are

$$a = a_0 + \frac{2e^2Z}{\mu\omega^2a_0^2N} \quad (1)$$

and

$$E = \left(E_0 - \frac{\hbar\omega}{2}\right)N - \frac{e^2Z}{a_0} + \frac{e^4Z^2}{\mu\omega^2a_0^4N}, \quad (2)$$

respectively. Here  $a_0$ ,  $E_0$  and  $\omega$  are bond length in corresponding diatomic molecule, its binding (dissociation) energy and cyclic frequency of relative interatomic vibrations, while  $\mu$  stands for masses of the pair of identical atoms constituting the bond (molecule). And  $N$  is the total number of bonds in whole cluster. If index

$$i=1,2,3,\dots,k \quad (3)$$

numbers different types of chemical bonds presented in the cluster with  $k$  denoting their total number. And if  $N_i$  is the number of bonds of  $i$ -type, then

$$N = \sum_{i=1}^{i=k} N_i \quad (4)$$

As for the parameter  $Z$ , it is introduced by the formula

$$Z = \sum_{i=1}^{i=k} N_i Z_{i1} Z_{i2} \quad (5)$$

where  $Z_{i1}$  and  $Z_{i2}$  are static electric charge numbers of the pairs of atoms constituting  $i$ -type bonds. Atoms are identical, but their charge numbers can differ each from other when they are localized in structurally nonequivalent sites.

Above relations have been used [20] to find

bonds length and specific (per atom) binding energy for small  $n = 2-15$  boron planar clusters  $B_n$ . Calculations were based on semiempirical expressions

$$a[\text{\AA}] \approx 1.590 + \frac{0.2554 Z}{N} \quad (6)$$

and

$$E[\text{eV}] \approx 2.995 N - 9.053 Z + \frac{0.7273 Z^2}{N} \quad (7)$$

with numerical coefficients found from the experimental data available for diboron molecule  $B_2$ . Then, the specific binding energy for cluster of atoms is calculated as

$$\varepsilon = \frac{E}{n} \quad (8)$$

or

$$\varepsilon[\text{eV}] \approx \frac{2.995 N}{n} - \frac{9.053 Z}{n} + \frac{0.7273 Z^2}{N n} \quad (9)$$

Here, the first term,

$$\varepsilon_0 = \left( E_0 - \frac{\hbar\omega}{2} \right) \frac{N}{n},$$

corresponds to specific binding energy of clusters constituted from neutral boron atoms.

Below calculations are conducted by using formulas (6) and (9) containing the parameter  $Z$ . To know its values, we need the estimates of effective atomic charges in clusters under the consideration. They are found based on two assumptions: (1) Effective number of outer valence shell electrons localized on given atomic site is proportional to its coordination number; and (2) Every neutral boron atom

contains only 1 electron in outer valence shell ( $2p$ -state). Numerical values of summarizing them parameter  $Z$  for ground-state structures of boron planar clusters with  $n=2-15$  atoms in different charge states are shown below, in (Tables 1-3).

## Results

To evaluate the static atomic charges effect on elemental nanoclusters relative stability, equilibrium bonds length and specific binding energy are calculated for small (containing  $n=2-15$  atoms) all-boron planar clusters  $B_n$  in neutral, single-anionic and single-cationic charge states. Calculations are conducted only for ground state structural isomers, which are chosen based on criteria maximizing cluster binding energy:

- Maximum number of bonds.
- Highest possible symmetry.

Results obtained for planar clusters  $B_n^0$ ,  $B_n^+$  and  $B_n^-$  are presented in (Tables 1-3) respectively. Values obtained without taking into account atomic static electric charges are shown in parenthesis.

Revealed discrepancies between equilibrium bonds length and specific binding energies and those calculated with and without taking into account atomic static electric charges are visualized in (Figures 1-3) and (Figures 4-6) respectively.

TABLE 1

Equilibrium bonds length and specific binding energy of small neutral boron clusters  $B_n^0$  calculated with and without taking into account atomic static electric charges.







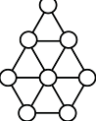
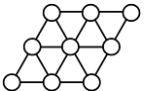
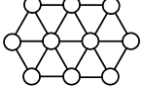
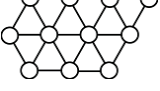
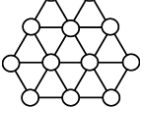
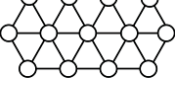
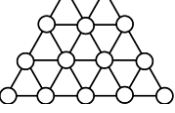
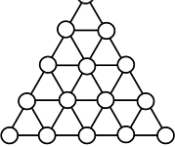
Structure	Cluster	Parameter $Z$	Bonds length $a$ ( $a_0$ ), Å	Specific binding energy $\varepsilon$ ( $\varepsilon_0$ ), eV
	$B_2^0$	0	1.59 (1.59)	1.48 (1.48)
	$B_3^0$	0	1.59 (1.59)	2.96 (2.96)
	$B_4^0$	-0.1200	1.58 (1.59)	3.97 (3.69)
	$B_5^0$	-0.2194	1.58 (1.59)	4.54 (4.14)
	$B_6^0$	-0.3333	1.58 (1.59)	4.94 (4.43)
	$B_7^0$	-0.4688	1.58 (1.59)	5.67 (5.07)
	$B_8^0$	-0.2857	1.59 (1.59)	5.50 (5.17)
	$B_9^0$	+0.2500	1.59 (1.59)	5.00 (5.25)
	$B_{10}^0$	-0.3850	1.59 (1.59)	5.96 (5.61)
	$B_{11}^0$	+0.0102	1.59 (1.59)	5.63 (5.64)
	$B_{12}^0$	+0.1875	1.59 (1.59)	5.77 (5.91)
	$B_{13}^0$	-0.5000	1.59 (1.59)	6.26 (5.91)
	$B_{14}^0$	+0.5625	1.60 (1.59)	5.55 (5.91)
	$B_{15}^0$	+0.7500	1.60 (1.59)	5.46 (5.91)

TABLE 2

Equilibrium bonds length and specific binding energy of small cationic boron clusters  $B_n^+$  calculated with and without taking into account atomic static electric charges.




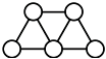
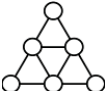
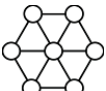
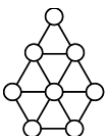

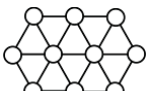
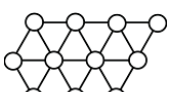
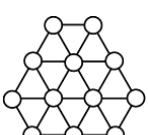
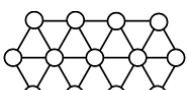
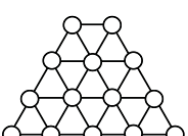
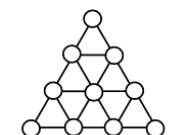



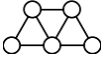
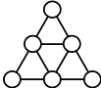
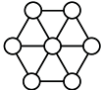
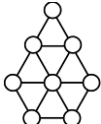
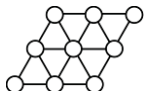
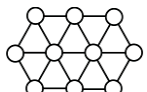
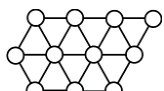
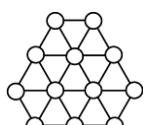
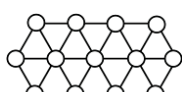
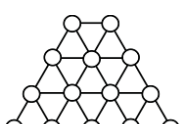
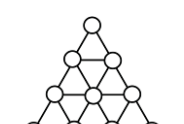
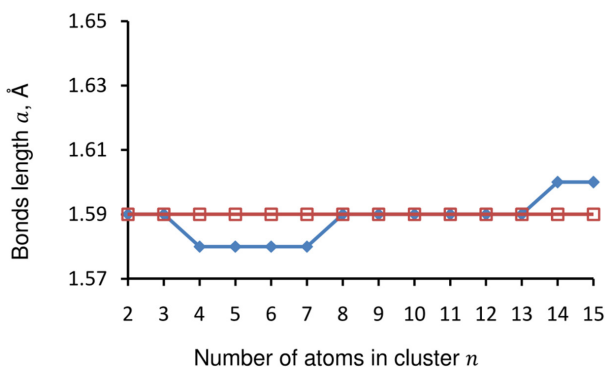
Structure	Cluster	Parameter $Z$	Bonds length $a$ ( $a_0$ ), Å	Specific binding energy $\epsilon$ ( $\epsilon_0$ ), eV
	$B_2^+$	+0.2500	1.65 (1.59)	0.37 (1.48)
	$B_3^+$	+0.3333	1.62 (1.59)	1.96 (2.96)
	$B_4^+$	+0.1700	1.60 (1.59)	3.31 (3.69)
	$B_5^+$	-0.0204	1.59 (1.59)	4.17 (4.14)
	$B_6^+$	-0.2593	1.58 (1.59)	4.82 (4.43)
	$B_7^+$	-0.3750	1.58 (1.59)	5.55 (5.07)
	$B_8^+$	-0.3125	1.58 (1.59)	5.53 (5.17)
	$B_9^+$	0	1.59 (1.59)	5.25 (5.25)
	$B_{10}^+$	-0.2465	1.59 (1.59)	5.84 (5.61)
	$B_{11}^+$	+0.2381	1.59 (1.59)	5.45 (5.64)
	$B_{12}^+$	-0.3125	1.59 (1.59)	6.15 (5.91)
	$B_{13}^+$	-0.1657	1.59 (1.59)	6.03 (5.91)
	$B_{14}^+$	+0.0590	1.59 (1.59)	5.87 (5.91)
	$B_{15}^+$	+0.4133	1.59 (1.59)	5.66 (5.91)

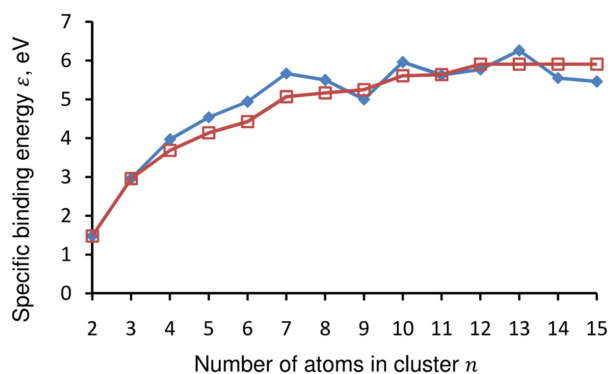
TABLE 3

Equilibrium bonds length and specific binding energy of small anionic boron clusters  $B_n^-$  calculated with and without taking into account atomic static electric charges.

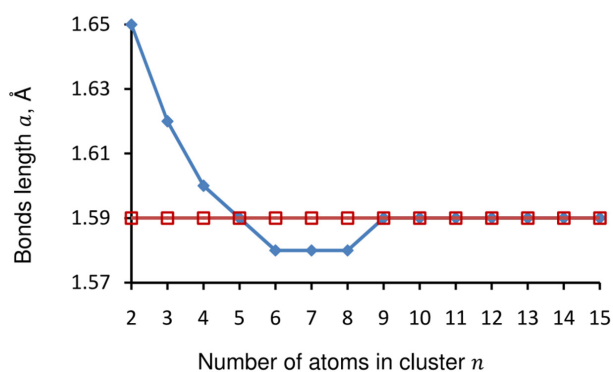
Structure	Cluster	Parameter $Z$	Bonds length $a$ ( $a_0$ ), Å	Specific binding energy $\varepsilon$ ( $\varepsilon_0$ ), eV
	$B_2^-$	+0.2500	1.65 (1.59)	0.37 (1.48)
	$B_3^-$	+0.3333	1.62 (1.59)	1.96 (2.96)
	$B_4^-$	+0.2500	1.60 (1.59)	3.13 (3.69)
	$B_5^-$	+0.2041	1.60 (1.59)	3.77 (4.14)
	$B_6^-$	+0.1852	1.60 (1.59)	4.15 (4.43)
	$B_7^-$	0	1.59 (1.59)	5.07 (5.07)
	$B_8^-$	+0.2589	1.60 (1.59)	4.88 (5.17)
	$B_9^-$	+1.0000	1.61 (1.59)	4.25 (5.25)
	$B_{10}^-$	+0.4127	1.60 (1.59)	5.24 (5.61)
	$B_{11}^-$	-0.7143	1.58 (1.59)	6.23 (5.64)
	$B_{12}^-$	+0.2461	1.59 (1.59)	5.72 (5.91)
	$B_{13}^-$	-0.2071	1.59 (1.59)	6.05 (5.91)
	$B_{14}^-$	+1.6151	1.61 (1.59)	4.87 (5.91)
	$B_{15}^-$	+1.4133	1.60 (1.59)	5.06 (5.91)



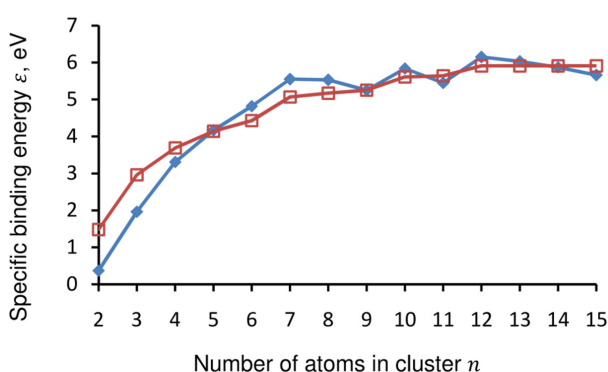
**Figure 1)** Bonds length in neutral boron clusters  $B_n^0$  in dependence on number of atoms calculated with ( $\blacklozenge$ ) and without ( $\square$ ) taking into account atomic static electric charges.



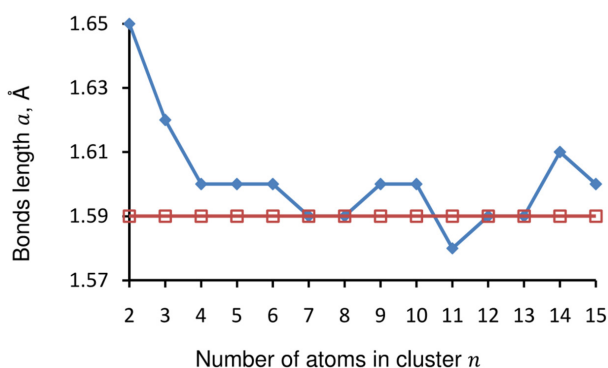
**Figure 4)** Specific binding energy of neutral boron clusters  $B_n^0$  in dependence on number of atoms calculated with ( $\blacklozenge$ ) and without ( $\square$ ) taking into account atomic static electric charges.



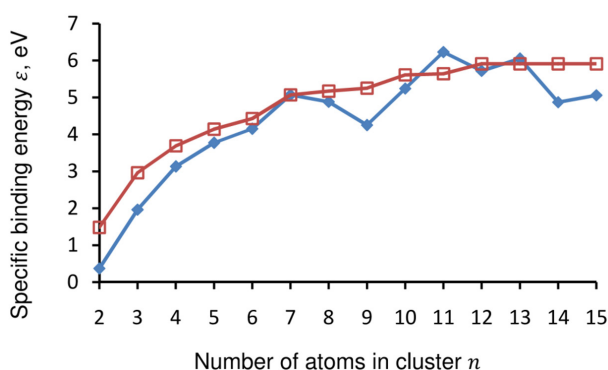
**Figure 2)** Bonds length in cationic boron clusters  $B_n^+$  in dependence on number of atoms calculated with ( $\blacklozenge$ ) and without ( $\square$ ) taking into account atomic static electric charges.



**Figure 5)** Specific binding energy of cationic boron clusters  $B_n^+$  in dependence on number of atoms calculated with ( $\blacklozenge$ ) and without ( $\square$ ) taking into account atomic static electric charges.



**Figure 3)** Bonds length in anionic boron clusters  $B_n^-$  in dependence on number of atoms calculated with ( $\blacklozenge$ ) and without ( $\square$ ) taking into account atomic static electric charges.



**Figure 6)** Specific binding energy of anionic boron clusters  $B_n^-$  in dependence on number of atoms calculated with ( $\blacklozenge$ ) and without ( $\square$ ) taking into account atomic static electric charges.



## Discussion

Thus, the equilibrium bonds length values in  $B_n^0$ ,  $B_n^+$  and  $B_n^-$  clusters found with taking into account atomic static electric charges are in the ranges of 1.58-1.60, 1.58-1.65 and 1.58-1.65 Å, respectively, while all the bonds length values found without taking into account atomic static electric charges are equal: 1.59 Å. As for the specific binding energy values in  $B_n^0$ ,  $B_n^+$  and  $B_n^-$  clusters found with taking into account atomic static electric charges, they are in the ranges of 1.48-6.20, 0.37-6.15 and 0.37-6.23 eV, respectively, while all the specific binding energy values found without taking into account atomic static electric charges are in the range of 1.48-5.91 eV.

Relatively palpable discrepancies between equilibrium bonds lengths and specific binding energies of ultra-small charged clusters with and without taking into account atomic static electric charges seem to be related to crudeness of the assumption that static atomic charges can be estimated on the basis of atomic sites coordination in the cluster structures even at too low number of constituent atoms. But, for moderate these relative deviations are smaller and, consequently, more credible. Signs of absolute deviations oscillate. That does not matter for bonds length. However, oscillation of the absolute deviations sign in case of specific binding energy point to the possibility of ground-state cluster isomers can be shaped differently depending on their charge states. This result provokes reconsidering assumption that equilibrium structure of a cluster corresponds

to its highest symmetry even at the significant static electrical charges localized on atomic sites.

## Conclusion

Identical atoms constituting elemental nanoclusters possess the different static electrical charges due to their different coordination in the structure with dangled bonds at its periphery. This nanosize effect is tested for boron small planar clusters applying the recently introduced version of diatomic model for clusters.

Equilibrium bonds length and specific (per atom) binding energy values for  $B_n^0$ ,  $B_n^+$  and  $B_n^-$  clusters ground-state structural isomers containing from 2 up to 15 boron atoms are calculated with and without taking into account atomic static electric charges. For ground-states are chosen structures with maximum possible number of bonds and highest possible symmetry to maximize cluster binding energy. There are detected changes in elemental nanoclusters equilibrium bonds length and specific binding energy values related to the non-zero static electrical charges localized on different atomic sites.

Specific binding energy deviation sign's oscillation with number of atoms in the cluster points to the possibility that ground-state cluster isomers can be shaped differently depending on their charge states. This result provokes reconsidering assumption that clusters ground-state structure corresponds to their highest symmetries even at the significant static electrical charges localized on their atomic sites.



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