On quasi-classical estimations of boron nanotubes ground-state parameters

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Abstract. The explicit expressions in term of B–B bond length are obtained for atomic sites coordinates and intersite distances in boron nanotubes of regular geometry. Using the charge and potential distributions in boron atom parameterized within initial quasi-classical approximation, the boron–boron pair potential curve is constructed. It leads to the boron–boron interatomic distance, binding energy, and relative vibration frequency equilibrium values which only slightly are deviated from averaged bond length in structural units of boron and boron-rich solids, dissociation energy, and oscillatory quantum of the diboron molecule, respectively. This curve together with obtained formulas should be useful for calculating of boron nanotubes geometrical and other ground-state parameters.

1. Introduction
As it is well known, variety of boron crystalline modifications and boron-rich solids mainly are constructed from the interconnected boron icosahedra [1]. The same short-range structure is characteristic for amorphous boron [2]. Then, most of B atoms usually are members of regular atomic triangles. This circumstance leads to possibility of the new kind on boron-based materials in form of planar or rolled boron surfaces with triangular two-dimensional lattices.

Such geometries for finite Bₙ clusters experimentally can be estimated based on measurements of apparent ionization potentials and fragmentation patterns for collision-induced dissociation [3]. Theoretically nanostructural formation of boron clusters was proposed for the first time by Boustani [4]. According to local-spin-density calculations (including nonlocal corrections), most of structures were found to prefer planar or quasi-planar arrangements (the latter is generated from planar one by forcing the boron atoms out of plane, up and down, and in periodic fashion) and can be considered as fragments of a surface or as segments of a sphere.

Experimentally the atomic and electronic structures and chemical bonding of small boron clusters up to 20 atoms were probed by the photoelectron spectroscopy combined with appropriate quantum calculations. In particular, clusters B₅ and B₅ were investigated [5] using anion photoelectron spectroscopy. The global minimum of B₅⁻ was found to have a planar structure with a closed-shell ground-state. Excellent agreement was observed between ab initio detachment energies and experimental spectra, firmly establishing the ground-state-structures for both B₅⁻ and B₅. Hepta- and octa-coordinated boron atoms in molecular wheels B₆ and B₇ were observed and confirmed in [6]. It was also reported [7] about experimental and theoretical evidences that small boron clusters prefer planar structures and exhibit aromaticity and antiaromaticity according the Hückel rules. Aromatic
boron clusters possess more circular shapes, whereas antiaromatic ones are elongated. Thus, planar boron clusters can be considered as only series of molecules representing a new dimension of boron chemistry. Most of the small boron clusters $B_{n}$, $B_{n}$, and $B_{n}$ with $n = 2 - 15$ as individual species in the gas phase have been reviewed in [8]. It was emphasized that free small boron clusters were characterized using photoelectron spectroscopy and ab initio calculations, which established their planar or quasi-planar shapes. Experimentally quasi-planarity of the small boron clusters also were confirmed in [9,10].

Experimental investigations and computational simulations revealed [11] that boron clusters, which favour planar structures up to 18 atoms, prefer three-dimensional structures beginning at 20 atoms. Neutral cluster $B_{20}$ has found to have a double-ring tubular structure, even though the $B_{20}^{-}$ remains planar. As for the anion $B_{20}^{-}$ itself, the tubular structure was shown to be isoenergetic to two-dimensional structures, which were observed and confirmed by photoelectron spectroscopy. The twodimensional – three-dimensional transition observed at $B_{20}$ suggests that it may be considered as the embryo of the thinnest single-walled all-boron nanotubes. In [12], it was reported first synthesis of pure boron single-walled nanotubes by a chemical reaction over a catalyst with parallel, uniform-radius cylindrical pores. According to recent communication, the multi-walled boron nanotubes also have been synthesized (see reference in [13]).

A systematic theoretical study on $B_{n}$ clusters carried out applying first-principles quantum-mechanical methods to determine their geometric structures show that they are composed of two fundamental units: either of hexagonal or pentagonal pyramids [14]. The resulting quasi-planar and convex structures can be considered as fragments of planar surfaces and segments of nanotubes or hollow spheres, respectively [15,16]. According to the Hartree–Fock self-consistent-field geometry optimization performed in [17] using Slater-type orbitals basis set, fragment of the quasi-planar boron structure is more stable than its isomers in form of isolated unit cell of the real $\alpha$-rhombohedral boron crystal or predicted boron quasi-crystals. The nanotubular isomers composed of parallel-lying (staggered) atomic rings in turn are shown to be even more stable. As it was mentioned, both predicted quasi-planarity of boron clusters [18] and boron tubular forms [19] were confirmed experimentally.

Recently, density-functional-theory has been employed [20] to calculate the electronic and geometric structures, total and binding energies, harmonic frequencies, point symmetries, and highest-occupied-molecular-orbital – lowest-unoccupied-molecular-orbital gaps of small boron clusters $B_{n}$ ($n = 2 - 12$). The linear, planar, convex, quasi-planar, cage, and open-cage structures have been found. The first and second energy differences have been used to obtain most stable sizes of clusters. None of the lowest-energy-structures and their isomers is shown to have an inner atom. Later, the studies have been extended on $B_{n}$ clusters with $n = 13 - 20$ (see [21]). They are found to form additional diverse structural motifs, ultimately can yield distinct nanostructures. Within whole range of $n = 2 - 20$, almost all physical properties of $B_{n}$ clusters are size-dependent. In particular, vibration frequencies are increasing with size. The double-ring tubular form of $B_{20}$ cluster has found to have the highest binding energy per atom.

First-principles calculations reported in [22] also reveal that boron can form wide variety of metastable planar and tubular forms. The preferred planar structure is a buckled triangular lattice that breaks the threefold ground-state degeneracy of the flat triangular plane. When the plane is rolled into a tube, this degeneracy leads to a strong chirality dependence of the binding energy. The achiral $(n,0)$-tubes derive their structure from the flat triangular plane, while the achiral $(n,n)$-tubes arise from the buckling plane, and have large cohesion energies and different structure as a result. Density functional theory calculations carried out [23] to obtain geometric structure of boron sheets and nanotubes show that buckled boron sheet with certain buckling height is more stable than the flat sheet. But, boron nanotubes formed by rolling up of a boron sheet exhibit buckling surfaces if helicity allows for the formation of alternating up and down B-atoms rows in the surface. In all other cases, boron nanotubes exhibit only flat surfaces. Hence, all the $(n,0)$-tubes have to prefer buckled geometry, while not all $(n,n)$-tubes do same.
2. Methods

For analysis of the boron nanotubular structures and future purposeful designing devices based on nanotubular boron it is important to be able to predict reliably the sizes of nanotubes with given indexes. Here this task is solved for the mostly regular forms with equal B−B lengths, which exhibit flat surfaces. Namely, the quasi-classical B−B pair interatomic binding energy curve is constructed, and then the expressions of radii of the zigzag and armchair boron nanotubes in terms of B−B bond length are obtained considering geometries of such structures.

Previously, it had been demonstrated [24,25] that an atom can be considered as a quasi-classical electron system in sense of Maslov criterion and, on this basis, the quasi-classical approach to the construction of interatomic pair potentials had been elaborated. Within the initial quasi-classical approximation, using quadratic polynomial approximation for the electron screening factor standing in the effective atomic potential the binding energy \( E = E(d) \) between pair of the identical (e.g. boron) atoms was expressed as

\[
-4E(d) = \sum_{j=0}^{n-1} (n_+U_j + n_-U_j)(W(R_i, R_j, d) + W(R_{i+1}, R_{j+1}, d) - W(R_i, R_{j+1}, d) - W(R_{i+1}, R_j, d)) + 2A_0 \sum_{i=0}^{n-1} (A_i / d + B_i + C_i d) \theta(d - R_i) \theta(R_{i+1} - d) .
\]

Here \( d \) is the interatomic distance; \( n_+U, A_0, B_0, \) and \( C_0 \) are the known quasi-classical parameters of the electron-density and potential distributions in the interacting atoms; \( R_i \) is the radius of effective electron cloud affecting an electron of the \( i \)th subshell, while \( s \) is the total number of subshells in an atom. \( W(R_i, R_j, d) \) is a known algebraic function expressing dependence of two spheres’ intersection region volume upon their radii \( R_i \) and \( R_j \), and centre-to-centre distance \( d \); and \( \theta(d - R_i) \theta(R_{i+1} - d) \) is a Heaviside step-function. These parameters and electron cloud radii can be obtained by fitting quasi-classical electron energy levels and mean orbital radii of the electrons to their first-principles, e.g. Hartree–Fock, values.

As for the procedure of the determination of boron nanotubes radii, it is following.

If \( d_{(n,0)} \) is the B−B bonds lengths in a zigzag \((n,0)\) nanotube (figure 1), the height of the equilateral triangle built up from the boron atoms in vertexes equals to \( \delta_{(n,0)} = \sqrt{3} d_{(n,0)} / 2 \). On the other hand, the regular \( 2n \)-gon with sides of \( \delta_{(n,0)} \) is inscribed into the circle with radius coincident the tube radius \( r_{(n,0)} \). Consequently, \( r_{(n,0)} = \delta_{(n,0)} / 2 \sin \pi / 2n \) and

\[
r_{(n,0)} = \frac{\sqrt{3} d_{(n,0)}}{4 \sin \frac{\pi}{2n}} .
\]

Let \( d_{(n,n)} \) and \( r_{(n,n)} \), respectively, denote the B−B bond length and radius in an armchair \((n,n)\) nanotube (figure 2). It is clear that the regular \( n \)-gon with sides of \( d_{(n,n)} \) is inscribed into the circle with radius of \( r_{(n,n)} \). Consequently,

\[
r_{(n,n)} = \frac{d_{(n,n)}}{2 \sin \frac{\pi}{n}} .
\]

Nanotube index \( n = 1,2,3,... \) determines the number of atoms because the nanotube unit cell consists of \( 2n \) boron atoms. At \( n = 1 \) zigzag nanotube degenerate in zigzag atomic chain, while armchair nanotube degenerate in straight atomic chain. Correspondingly, formula obtained for \( r_{(n,n)} \) in general case, does not works; instead it should be assumed \( r_{(1,1)} = 0 \).
Now about the detailed regular geometries of the zigzag and armchair boron nanotubes, which we will describe using cylindrical coordinates \( \tilde{r} (\rho, \varphi, z) \) useful in tubular binding energy and electronic structure calculations.
Figure 3. Lattice constant of boron zigzag nanotube (black circles – B atoms, solid legs – B–B bonds).

Figure 4. Lattice constant of boron armchair nanotube (black circles – B atoms, solid legs – B–B bonds).

Constant of the zigzag \((n,0)\) nanotube one-dimensional lattice equals to \(d_{(n,0)}\) (figure 3). Its unit cell consists of two equidistant atomic rings in parallel planes perpendicular to the axis, each with \(n\) boron atoms. Evidently, cylindrical coordinate \(\rho\) for all atomic sites equals to tube radius:

\[
\rho = r_{(n,0)}.
\]  

As for the coordinates \(\varphi\) and \(z\), they equal to

\[
\varphi = \frac{(4k-3-(-1)^k)\pi}{2n},
\]

\[
z = \frac{ld_{(n,0)}}{2}.
\]

Here \(k = 1,2,3,\ldots,n\) and \(l = 0,\pm1,\pm2,\ldots\) number atomic sites in given plane and atomic planes, respectively.
If $d_{(n,n)}$ is the B–B bond length in an armchair $(n,n)$ nanotube, the side $\delta_{(n,n)}$ of the regular $2n$-gon inscribed into the circle with tube radius of $r_{(n,n)}$ is determined as $\delta_{(n,n)} = 2r_{(n,n)} \sin \pi/2n$. One-dimensional lattice constant of the armchair nanotube (figure 4) equals to the doubled leg of the right triangle with another leg of $\delta_{(n,n)}$ and hypotenuse of $d_{(n,n)}$, i.e., according to the Pythagorean theorem, $2\sqrt{d_{(n,n)}^2 - \delta_{(n,n)}^2} = \sqrt{4 - 1/\cos^2 \pi/2n} d_{(n,n)}$. Its unit cell also consists of two atomic rings in parallel planes perpendicular to the tube axis and, from its part, each ring consists of $n$ boron atoms. Coordinate $\rho$ for all atomic sites again equals to tube radius:

$$\rho_B = r_{(n,n)},$$

while the rest cylindrical coordinates equal to

$$\varphi = \frac{(4k - 3 - (-1)^k) \pi}{2n},$$

$$z = \sqrt{1 - \frac{1}{4 \cos^2 \frac{\pi}{2n}}} l d_{(n,n)},$$

where again $k = 1,2,3,\ldots,n$ and $l = 0,\pm 1,\pm 2,\ldots$.

On the basis of above obtained relations, it was found the squared distances between arbitrary atomic site $\vec{r}(\rho,\varphi,z)$ and site $\vec{r}_0(\rho,0,0)$ of the so-called central atom with $l = 0$ and $k = 1$, i.e., with $\varphi = 0$ and $z = 0$, $(\vec{r} - \vec{r}_0)^2 = 4 \rho^2 \sin^2 \varphi/2 + z^2$, in zigzag

$$\left(\frac{\rho_B}{d_{(n,n)}}\right)^2 = \frac{3 \sin^2 \frac{(4k - 3 - (-1)^k) \pi}{4n}}{4 \sin^2 \frac{\pi}{2n}} + \frac{l^2}{4},$$

and armchair tubes

$$\left(\frac{\rho_B}{d_{(n,n)}}\right)^2 = \frac{\sin^2 \frac{(4k - 3 - (-1)^k) \pi}{4n}}{\sin^2 \frac{\pi}{n}} + \left(1 - \frac{1}{4 \cos^2 \frac{\pi}{2n}}\right) l^2.$$

### 3. Results and discussion

Using quasi-classical B–B interatomic pair potential and based on above given description of the boron nanotubes’ geometry it is possible to calculate easily their ground state parameters, like the equilibrium bond length, equilibrium binding energy per atom, zero-point vibration frequencies etc. By them the absolute and relative stabilities of regular boron nanotubes can be estimated.

Thereto the quasi-classical B–B binding energy $E = E(d)$ in dependence on interatomic distance $d$ seems to be useful. Part of its parameters, like the coefficients of harmonic and anharmonic terms $c \approx 0.12$ au and $g \approx 4.0$ au in the corresponding interatomic potential $U(d)$, which in the vicinity of equilibrium distance $d = d_0$ is approximated by the function $U(d_0) + c(d - d_0)^2 - g(d - d_0)^3$, and atomic core charge of $A_0 \approx 3.151$ (which is near the boron atom valence of 3) were successfully applied to interpret isotopic composition effect on boron structural [26] and melting parameters [27], respectively. Analysis of the corresponding binding energy curve (1) (converted from potential energy one using virial theorem for system total energy) based on the parameters obtained equating quasi-classical electron energy levels and mean orbital radii of the electrons with their Hartree–Fock values (table 1) leads to the equilibrium B–B distance of 3.37 au (1.78 Å), binding energy at that distance of...
0.103 au (2.80 eV), and relative vibration frequency of 0.00480 au (0.131 eV). These values slightly, only by few percents are deviated from the averaged experimental B–B bond length in main structural units of boron and boron-rich compounds – icosahedra of 3.40 au (1.80 Å), dissociation energy of 0.099 au (2.69 eV), and oscillatory quantum of 0.00479 au (0.130 eV) of diboron molecule B₂, respectively.

**Table 1.** Quasi-classical parameters of the electron-density and potential distributions in B atom.

|   | R₁, au | A₁, au | −B₁, au | C₁, au | −n₁, au | U₁, au |
|---|--------|--------|---------|--------|---------|--------|
| 0 | 0      | 3.151  | 2.078   | 0.3864 | 0.03982 | 0.6342 |
| 1 | 2.317  | 1.351  | 0.523   | 0.0509 | 0.00213 | 0.0332 |
| 2 | 4.964  | 0.333  | 0.113   | 0.0096 | 0.00028 | 0.0005 |
| 3 | 5.890  |        |         |        |         |        |

**Table 2.** Tabulated boron–boron binding energy function.

| d, au | E(d), au |
|-------|----------|
| 3.20  | 0.101408 |
| 3.21  | 0.101656 |
| 3.22  | 0.101887 |
| 3.23  | 0.102100 |
| 3.24  | 0.102297 |
| 3.25  | 0.102478 |
| 3.26  | 0.102642 |
| 3.27  | 0.102791 |
| 3.28  | 0.102925 |
| 3.29  | 0.103043 |
| 3.30  | 0.103147 |
| 3.31  | 0.103236 |
| 3.32  | 0.103311 |
| 3.33  | 0.103372 |
| 3.34  | 0.103420 |
| 3.35  | 0.103454 |
| 3.36  | 0.103475 |
| 3.37  | 0.103483 |
| 3.38  | 0.103479 |
| 3.39  | 0.103462 |
| 3.40  | 0.103433 |
| 3.41  | 0.103393 |
| 3.42  | 0.103341 |
| 3.43  | 0.103278 |
| 3.44  | 0.103203 |
| 3.45  | 0.103118 |
| 3.46  | 0.103023 |
| 3.47  | 0.102917 |
| 3.48  | 0.102802 |
| 3.49  | 0.102677 |
| 3.50  | 0.102542 |
The binding energy curve obtained in initial quasi-classical approximation for interacting boron atoms are expressed by a piece-wise analytical function. Evidently, for numerical calculations the tabulated form would be more appropriate. Here such form (in atomic units) is given (table 2) over the range from \( a = 3.20 \) up to \( 3.50 \) au (i.e. in the vicinity of equilibrium interatomic distance of \( 3.37 \) au) with step of argument of \( 0.01 \) au, what seems sufficient to provide accurate energy computations.

On basis of above obtained formulas, sizes of the small single-walled B-nanotubes were estimated (table 3) assuming bond lengths as \( d_{\infty} = 1.78 \) Å, what is the equilibrium interatomic distance value according to the quasi-classical B–B pair potential. Actually, \( d_{(n,0)} \) and \( d_{(n,n)} \) depend on \( n \); and their exact values can not be determined geometrically. In general, this task requires solving of the physical problem of the binding energy maximization for given nanotubular structure with respect B–B bond length. But, these dependences evidently have to be weak and in all cases in satisfactiry approximation \( d_{(n,0)} \) and \( d_{(n,n)} \) can be substituted by the mentioned value of \( 1.78 \) Å.

### Table 3. Estimated radii of small-sized boron zigzag and armchair nanotubes.

| \((n,0)\) or \((n,n)\) | \(r_{(n,0)}\) or \(r_{(n,n)}\), Å |
|-----------------|-----------------|
| (1,1)           | 0.00            |
| (1,0)           | 0.77            |
| (2,2)           | 0.89            |
| (3,3)           | 1.03            |
| (2,0)           | 1.09            |
| (4,4)           | 1.26            |
| (5,5)           | 1.51            |
| (3,0)           | 1.54            |
| (6,6)           | 1.78            |
| (4,0)           | 2.01            |
| (7,7)           | 2.05            |
| (8,8)           | 2.33            |
| (5,0)           | 2.49            |
| (9,9)           | 2.60            |
| (10,10)         | 2.88            |
| (6,0)           | 2.98            |
| (11,11)         | 3.16            |
| (12,12)         | 3.44            |
| (7,0)           | 3.46            |

Analogously, one can estimate molar binding energy of a boron nanotube. On the one hand, any constituent boron atom has 6 nearest neighbours. On the other hand, binding energy between pair of boron atoms is about \( 2.80 \) eV. So, taking into account interaction only between nearest neighbours the tube binding energy per atom may be calculated as \( 2.80 \) eV \( \times 6 / 2 = 8.40 \) eV. Of course, it is the estimation: actually binding energy should depend on the tube index.

### 4. Summary

Thus, using the electron-density and potential distributions in a boron atom parameterized within the initial quasi-classical approximation, it is possible to tabulate boron–boron pair binding energy curve, which leads to the boron–boron equilibrium interatomic distance, equilibrium binding energy, and relative vibration frequency values only slightly deviated from averaged bond length in structural units of boron and boron-rich solids, dissociation energy, and oscillatory quantum of the diboron molecule, respectively. On this basis, the B–B bond length and molar binding energy in a boron nanotube are
predicted to be about 1.78 Å and 8.40 eV, respectively. Besides, the explicit expressions in term of B–B bond length are found for the flat zigzag and armchair boron nanotubes radii, atomic sites coordinates and intersite distances. There are made numerical estimations for the mostly small-sized boron nanotubes.

The proposed B–B binding energy curve together with obtained explicit formulas describing tubular geometries should be useful for calculating not only geometrical, but also other ground-state parameters of the boron nanotubes. From their part, these results can serve as a relevant basis for further investigations of the boron nanotubes electron structure.

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