



Planar Clusters of Identical Atoms in Equilibrium: 1. Diatomic Model Approach

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Abstract: Diatomic model, when is utilized to describe clusters of identical atoms, takes into account bonding only between neighboring pairs of atoms. According to the diatomic model, isomers of wrapped forms, e.g. built from nanotubular and/or fullerene-like structural fragments, have to be more stable energetically than their planar counterparts because planar clusters contain more peripheral atoms with dangling bonds and, correspondingly, lesser atoms with saturated bonds. At the same time, mentioned difference in coordination numbers between central and peripheral atoms leads to the bonds polarity in planar clusters. Introducing corrections related to the electrostatic forces reveals that small planar clusters can be more stable than their wrapped isomers. It is the Paper 1 of two, which provides a general theoretical frame for studying the planar clusters of identical atoms. The Paper 2 will be devoted to the numerical realization for all-boron planar clusters.

Keywords: Atomic Clusters, Planar Structure, Diatomic Model, Binding Energy, Bonds Polarity

1. Introduction

Boron case shows that small (quasi)planar clusters of identical atoms can be more stable than their structural isomers in the form of surfaces of nanotubes, fullerenes, or true three-dimensional structures – see our recent studies on planar boron clusters [1, 2], as well as Reviews on boron nanostructures in general [3 – 6].

In the Presentation [7], aims of the research in the field of elemental clusters, which are developing, simulating, modeling, and predicting novel structures, to build pre-selected, uniform nanostructured materials with specific properties, were formulated for case of boron. According to Boustani et al., boron cluster-structures can be classified into four groups: (quasi)planar, tubular, convex, and spherical clusters. Transition of (quasi)planar surfaces into tubules or cages may be pictured by rolling these surfaces into cylinders or spheres, respectively. And the closure of boron (quasi)planar surfaces into tubules or cages goes through an energy barrier path.

Combined experimental studies and computational simulations revealed [8] that boron clusters, which favor (quasi)planar structures up to 18 atoms, prefer tubular

structures beginning at 20 atoms. Using global optimization methods, it was found that the B₂₀ neutral cluster has a double-ring tubular structure with diameter of ~5.2 Å. For the B₂₀[–] anion, the tubular structure was shown to be almost isoenergetic to (quasi)planar structures, which were observed and confirmed by photoelectron spectroscopy. The structural transition observed at B₂₀ suggests that it may be considered as the embryo of the thinnest single-walled boron nanotubes.

High-level *ab initio* MO (molecular orbital) methods were employed [9] to determine the relative stability among four neutral B₂₀ and anionic B₂₀[–] isomers, particularly, the double-ring tubular isomer versus three low-lying planar isomers. These results also suggest that the planar-to-tubular structural transition starts at B₂₀ for neutral clusters but should occur beyond the size of B₂₀[–] for anion clusters.

In order to elaborate a direct experimental method available for structural determination of boron clusters, photoelectron spectroscopy of size-selected cluster anions was combined with quantum calculations to probe the atomic and electronic structures and chemical bonding of small boron clusters up to 20 atoms and shown [10] that small boron clusters prefer (quasi)planar structures. It was found that for neutral boron clusters the (quasi)planar-to-tubular structural transition

occurs at B_{20} , which possesses a double-ring structure, even though the B_{20}^- anion remains (quasi)planar.

Using *ab initio* QC (quantum-chemical) and DFT (density-functional-theory) methods, it was investigated the structural transition from (quasi)planar boron clusters into double- and triple-ring systems [11]. The first structural transition occurs at B_{19} and B_{20} clusters, while the second transition is expected between B_{52} and B_{54} clusters.

A mass spectrometric study of boron cluster anions B_n^- , $n = 7 - 55$, produced by laser vaporization from two different types of boron-containing sample rods – boron-rich boride and pure boron – was reported in [12]. In mass spectra recorded from the boride sample, a repeating intensity pattern of boron cluster anions having local maxima at $(B_{13}^-)(B_{12})_{0,2,3}$ as well as at B_{26}^- was observed. Similar phenomena were not observed with a pure boron sample. These facts were attributed to the structural differences between two materials, in particular, $(B_{12})(B_{12})_{12}$ super-icosahedral structure characteristic of the crystalline boron-rich borides.

Recently, it was experimentally detected [13] the highly stable quasi-planar boron cluster B_{36} of hexagonal shape, but with the central hexagonal hole.

Thus, it is expected that small clusters of identical atoms should have a (quasi)planar structure. But when the number of atoms constituting cluster exceeds a certain critical value (in case of boron $n \sim 20$), cluster has to transform into a nanotubular structure.

Of course, the relative concentrations of clusters with different numbers of atoms and their isomers are influenced by the kinematics of the producing of a substance in a clustered state. However, the key determining factor will still be their relative stability that quantitatively is expressed by the binding energy per atom. At fixed number of atoms in the cluster, isomers with symmetrical shapes and no “holes” in their structure, i.e. with the maximal number of interatomic bonds, would be more stable. Therefore, the key problem in the study of atomic clusters is the determining of their binding energy per atom.

This paper is the first part of the study carried out in order to solve theoretically above mentioned problem. Here, based on the diatomic model, a general scheme for calculation of the binding energy per atom for planar clusters of identical atoms is proposed. In the next part of the study, the developed scheme will be numerically realized for boron clusters.

2. Binding Energy in Diatomic Model

The saturation property of interatomic bonding serves for the basis of old diatomic model's [14] applicability to atomic structures, including clusters. Within this model, the binding energy of a structure equals to the sum of energies of the constituent chemical bonds between pairs of atoms.

The microscopic theory of thermal expansion of solids based on the diatomic model and its generalization to the three-dimensional periodical structures allows correct estimation of the order of magnitude of the thermal expansion

coefficient for many crystalline substances [15].

It should also be noted that despite its utmost simplicity, the diatomic model is still successfully used to calculate various anharmonic effects in solids [16].

We successfully used diatomic model to explain isotopic effect on boron lattices [17 – 19].

According to the diatomic model, a real, i.e., quasi-planar, cluster X_n built of $n \geq 2$ identical X-atoms located from each other at certain distances is modeled by the perfectly planar cluster, in which the lengths of all the X–X bonds are equal. Denote this single structural parameter of the model by d_0 . Suppose that the index i numbers the constituent atoms, $i = 1, \dots, n$, and C_i are their coordination numbers, respectively.

Let index k_i enumerates the nearest neighboring atoms of the i -atom, $k_i = 1, \dots, C_i$. Suppose that E_{ik_i} is the energy of binding between i - and k_i -atoms. Then, the cluster binding energy per atom would be

$$E = \frac{1}{2n} \sum_{i=1}^n \sum_{k_i=1}^{C_i} E_{ik_i}.$$

Here, the factor $\frac{1}{2}$ is introduced due to the fact that at the double summation the binding energies between any pair of neighboring atoms are counted twice.

In the standard diatomic model, binding energies between each pair of adjacent atoms are equal, $E_{ik_i} \equiv E_0$, and it turns out that

$$E \approx \frac{E_0}{2n} \sum_{i=1}^n C_i.$$

However, differences in the coordination number of constituent atoms of a cluster – a finite structure of atoms – lead to the redistribution of the outer valence shell electron charge and as a result to the different binding energies E_{ik_i} of diatomic pairs.

3. Polarity of Bonding in Clusters

If outer shell of an isolated X-atom contains ν electrons, outer shell valence charge of X-atom equals to

$$q = -e\nu$$

(e is the elementary charge). As for total shared electron charge, it would be of

$$Q = -en\nu.$$

Within the diatomic model of bonding, it is obvious to assume that this charge between atoms is divided in proportion to their coordination numbers:

$$q_i = -\frac{en\nu C_i}{\sum_{j=1}^n C_j}.$$

Corresponding changes in atomic charges are:

$$q_i - q = Z_i e = e v \left(1 - \frac{n C_i}{\sum_{j=1}^{j=n} C_j} \right).$$

It means the inducing of non-zero effective static atomic charges with charge numbers of

$$Z_i = v \left(1 - \frac{n C_i}{\sum_{j=1}^{j=n} C_j} \right),$$

respectively.

Consequently, the binding energy correction per atom related to the polarity of interatomic bonds is:

$$E_1 = - \frac{e^2}{8\pi\epsilon_0 n d_0} \sum_{i=1}^{i=n} \sum_{k_i=1}^{k_i=C_i} Z_i Z_{k_i}.$$

(ϵ_0 is the electrical constant).

4. Equilibrium Binding Energy Per Atom and Equilibrium Bond Length

We have obtained cluster equilibrium binding energy per atom in the diatomic approach:

$$E \approx E_0 + E_1 = \frac{1}{2n} \left(E_0 \sum_{i=1}^{i=n} C_i - \frac{e^2}{4\pi\epsilon_0 d_0} \sum_{i=1}^{i=n} \sum_{k_i=1}^{k_i=C_i} Z_i Z_{k_i} \right).$$

One should emphasize that here for the bond length stands d_0 , the value initially introduced in the diatomic model.

The equilibrium bond length d accounting for bonds polarity should be determined by the minimization of the system potential energy:

$$U(d) = \frac{1}{2n} \left(-E_0 + \frac{M\omega^2(d-d_0)^2}{4} \right) \sum_{i=1}^{i=n} C_i + \frac{e^2}{8\pi\epsilon_0 n d} \sum_{i=1}^{i=n} \sum_{k_i=1}^{k_i=C_i} Z_i Z_{k_i},$$

where M denotes mass of the atom. Consequently, $M/2$ is the reduced mass of the diatomic system. As for ω , it is the cyclic frequency of relative vibrations of bonded pair of atoms near the bond length value of d_0 .

Equilibrium bond length, which minimizes (maximizes) potential (binding) energy, is determined from the equation $U'(d) = -E'(d) = 0$:

$$M\omega^2(d-d_0) \sum_{i=1}^{i=n} C_i - \frac{e^2}{2\pi\epsilon_0 d^2} \sum_{i=1}^{i=n} \sum_{k_i=1}^{k_i=C_i} Z_i Z_{k_i} = 0.$$

Deviation d from d_0 is expected to be too small. Thus, in the good approximation:

$$d \approx d_0 + \frac{e^2 \sum_{i=1}^{i=n} \sum_{k_i=1}^{k_i=C_i} Z_i Z_{k_i}}{2\pi\epsilon_0 M \omega^2 d_0^2 \sum_{i=1}^{i=n} C_i}.$$

5. Conclusions

Since clusters are open two-dimensional structures, constituent atoms are divided into two parts. These are “central” atoms with higher coordination numbers and “peripheral” ones with reduced coordination numbers. For this reason, the average coordination number of atoms in a planar cluster is lower than in its isomers with closed two-dimensional structures – nanotubes and fullerenes.

The fact that nanotube and fullerene are obtained by the folding the corresponding fragments of the planar atomic sheet into a cylinder or a sphere, respectively, is followed by decreasing in the relative concentration of peripheral atoms. In nanotubes of finite length, peripheral atoms are only at their ends, while in fullerenes there are no peripheral atoms.

The number of bonds between atomic pairs in the cluster, and hence binding energy per atom, increases with the growth in the average coordination number of constituting atoms. This means that in the diatomic model, in general, planar clusters should be less stable than their nanotubular or fullerene-like counterparts with the same number of atoms. The contrasting behavior is expected in the case of small clusters because of significance of polarity-correction to the binding energy per atom.

Within the frames of diatomic model, the further refinement of the binding energy can be achieved by rejecting the equality between all the bond lengths. The differences in equilibrium interatomic distances will lead to the transformation of perfectly planar cluster into a quasi-planar structure.

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