

RESEARCH ARTICLE

Nanoclusters Binding Energy in Diatomic Model

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Abstract

There is proposed the general formulation of the diatomic model to calculate nanoclusters binding energy, the key value determining their relative

stabilities and, consequently, concentrations in forming processes. The simple special case of practical interest, when all the bond lengths can be assumed to be almost equal each to other, is considered in details.

Key Words: *Nanocluster; Diatomic model; Chemical bond; Binding energy*

Introduction

The binding energy per chemical formula unit of any clustered form of substance serves for most important factor determining relative stabilities and, consequently, relative concentrations of clusters with different numbers of atoms created during a formation process. It is why the key problem in the theoretical study of clusters is the calculation of their binding energies.

This issue can be quite correctly addressed within the old diatomic model [1] of bounded atomic structures, including clusters. It is based on the interatomic bonding saturation property. In the initial approximation, when the binding energy of a structure is expressed as the sum of energies of pair interactions between neighboring atoms, microscopic theory of expansion and its generalization to periodical structures allows quite correct estimation of the thermal expansion coefficient for crystalline substances [2]. Despite its simplicity, the diatomic model

successfully used to calculate other anharmonic effects in solids as well [3].

To the best our knowledge, there exists no literature on calculating clusters binding energy within diatomic model, unless our previously developed diatomic-type models for small all-boron (quasi) planar clusters to estimate their relative stabilities [4-7] and dipole moments [8,9]. These results have been summarized in the mini-review [10].

Here we significantly improve this approach by introducing the most general formulation of the diatomic model to calculate binding energy for a nanocluster of any structure.

General formulation

Within the frames of diatomic model, the binding energy $E^{(b)}$ of a nanocluster - a finite system of bounded atoms - is represented by the sum of energies of chemical bonds between nearest neighboring atoms in the corresponding structure.

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Let i index,

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

numbers different types of chemical bonds presented in the cluster under the consideration. Then, n denotes their total number. Introduce chemical bond lengths (distances between nuclei of nearest neighboring atoms) r_i and energies $U_i(r_i)$. In general, $U_i(r_i)$ are the sums of energies of valence interaction $U_i^{(v)}(r_i)$ between pair of atoms isolated from the rest of structure (*i.e.*, in the diatomic state) and additional electrostatic interaction $U_i^{(e)}(r_i)$ arising in result of valence electron charge redistribution, when initially isolated and electrically neutral atoms associate in the bounded system:

$$U_i(r_i) = U_i^{(v)}(r_i) + U_i^{(e)}(r_i) \quad (2)$$

Figure 1 shows the schematic view of interatomic pair potentials. At small interatomic distances, $r_i \rightarrow 0$, potential $U_i^{(v)}(r_i)$ is positive and tends to infinity, $U_i^{(v)} \rightarrow \infty$, while at large distances, $r_i \rightarrow \infty$, it is negative and tends to zero, $U_i^{(v)} \rightarrow 0$. At the point r_{0i} , interatomic pair potential reaches its minimum value $-U_{0i}$. Parameter r_{0i} is the bond length in the corresponding diatomic molecule. As for the parameter U_{0i} , it equals to the diatomic molecule binding (or dissociation) energy, when relative interatomic vibrations ground-state energy $E^{(gs)}$ is neglected.

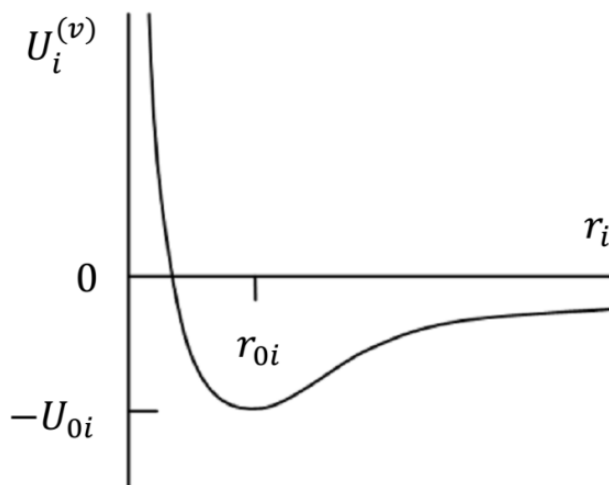


Figure 1) Schematic view of interatomic pair potential

Assuming that relative deviation of bond length r_i in the multi-atomic structure from its equilibrium value r_{0i} in the diatomic molecule is small, one can approximate $U_i^{(v)}(r_i)$ by the quadratic function of the $(r_i - r_{0i})$ difference (linear term absents as the function derivative vanishes at its minimum point):

$$U_i^{(v)}(r_i) \approx -U_{0i} + \frac{M_i \omega_i^2 (r_i - r_{0i})^2}{2} \quad (3)$$

where ω_i is the cyclic frequency of relative interatomic vibrations determining the ground-state vibrational energy

$$E_i^{(gs)} = \frac{\hbar \omega_i}{2} \quad (4)$$

and M_i is the reduced mass of the pair of atoms with masses m_{1i} and m_{2i} , respectively:

$$\frac{1}{M_i} = \frac{1}{m_{1i}} + \frac{1}{m_{2i}} \quad (5)$$

By introducing effective charge numbers Z_{1i} and Z_{2i} corresponding the static electric charges localized on pair of nearest neighboring atoms, electrostatic correction to the bond energy (in Gauss units) is expressed as

$$U_i^{(e)}(r_i) = \frac{Z_{1i} Z_{2i} e^2}{r_i} \approx E_{0i} \left(1 - \frac{r_i - r_{0i}}{r_{0i}} \right) \quad (6)$$

Here constant

$$E_{0i} = \frac{e^2 Z_{1i} Z_{2i}}{r_{0i}} \quad (7)$$

denotes the electrostatic energy in diatomic molecule at equilibrium bond length of $r_i = r_{0i}$. Above applied approximation takes into account only linear term $\sim (r_i - r_{0i})$. There is no need to retain quadratic term as well, like the valence energy case, because the electrostatic energy itself is a relatively small correction to the valence energy.

Chemical bond energy is minus sum of energies of corresponding interatomic pair interaction and ground-state vibrations energies. Thus, if a cluster contains N_i bonds of i -type its binding energy can be written as

$$E^{(b)}(r_1, r_2, r_3, \dots, r_n) = -\sum_{i=1}^n N_i (U_i(r_i) + E_i^{(gs)}) \approx -\sum_{i=1}^n N_i \left(U_{0i} - E_{0i} - \frac{\hbar \omega_i}{2} \right) - \sum_{i=1}^n \frac{N_i M_i \omega_i^2 (r_i - r_{0i})^2}{2} + \sum_{i=1}^n \frac{N_i E_{0i} (r_i - r_{0i})}{r_{0i}} \quad (8)$$

Symmetry of the structure leads to C_j constraints—relations to be satisfied by bond lengths r_i :

$$C_j(r_1, r_2, r_3, \dots, r_n) = 0 \quad (9)$$

$$j = 0, 1, 2, \dots, m \quad (10)$$

Here j index numbers the constrain, while m is their total number. Evidently, number of variables should exceed number of conditions to be fulfilled by them: $n > m$.

In general, to find equilibrium bond lengths in the structure and corresponding binding energy of the cluster one has to maximize $E^{(b)}$ against variables $r_1, r_2, r_3, \dots, r_n$ at given constrains $C_j = 0$.

Thus, our model is developed based on four key approximations:

(1) Binding energy of a cluster of atoms is expressed as the sum of energies of pair interactions between neighboring in its structure atoms.

(2) Assuming that relative deviations of bond lengths in the cluster multi-atomic structure from their equilibrium values in corresponding diatomic molecules are small, the bond energies are approximated by quadratic functions of bond lengths changes in cluster.

(3) Electrostatic corrections to the bond energies are expressed through effective charge numbers corresponding to the static electric charges localized on pairs of nearest neighboring atoms.

(4) Energies of relative interatomic vibrations in a cluster are approximated by ground-state vibrational energies of corresponding diatomic molecules.

Here we have constructed only a theoretical frame for calculations and do not aim conducting numerical calculations themselves. Choosing the physical systems of practical interests, preparing the corresponding input data, writing the computer code, conducting numerical calculations, and finally checking their effective-

ness in this way—all these need the writing of separate articles and then are tasks for our future works.

At current stage, expected effectiveness of the diatomic approach for practical applications can be evaluated only qualitatively—by an analogy. As stated above, despite first-glance simplicity even in its first approximation the diatomic model has been successfully used to calculate anharmonic effects in solids and, in particular, allowed quite correct estimation of the thermal expansion coefficient for crystals.

Special case of identical bonds

Let consider the simplest (but of practical interest) special case, when all the bond lengths can be assumed to be almost equal each to other:

$$r_1 = r_2 = r_3 = \dots = r_n \equiv r \quad (11)$$

It means that there are no constrains ($j = 0$) and other characteristics of valence bonding are equal as well:

$$r_{01} = r_{02} = r_{03} = \dots = r_{0n} \equiv r_0 \quad (12)$$

$$U_{01} = U_{02} = U_{03} = \dots = U_{0n} \equiv U_0 \quad (13)$$

$$\omega_1 = \omega_2 = \omega_3 = \dots = \omega_n \equiv \omega \quad (14)$$

$$M_1 = M_2 = M_3 = \dots = M_n \equiv M \quad (15)$$

However, characteristics E_{0i} (or Z_{1i} and Z_{2i}) of electrostatic bonding remain different.

Maximizing of the corresponding binding energy

$$E^{(b)}(r) = \left(U_0 - \frac{\hbar\omega}{2} \right) \sum_{i=1}^{i=n} N_i - \frac{M\omega^2(r-r_0)^2}{2} \sum_{i=1}^{i=n} N_i + \frac{r-r_0}{r_0} \sum_{i=1}^{i=n} N_i E_{0i} \quad (16)$$

leads to the equation

$$\frac{dE^{(b)}(r)}{dr} = -M\omega^2(r-r_0) \sum_{i=1}^{i=n} N_i + \frac{1}{r_0} \sum_{i=1}^{i=n} N_i E_{0i} = 0 \quad (17)$$

from which the equilibrium bond lengths and corresponding binding energy are

$$r = r_0 + \frac{\sum_{i=1}^{i=n} N_i E_{0i}}{M\omega^2 r_0 \sum_{i=1}^{i=n} N_i} = r_0 + \frac{e^2 \sum_{i=1}^{i=n} N_i Z_{1i} Z_{2i}}{M\omega^2 r_0^2 \sum_{i=1}^{i=n} N_i} \quad (18)$$

and

$$E^{(b)}(r) = \left(U_0 - \frac{\hbar\omega}{2} \right) \sum_{i=1}^{i=n} N_i + \frac{\left(\sum_{i=1}^{i=n} N_i E_{0i} \right)^2}{2M\omega^2 r_0^2 \sum_{i=1}^{i=n} N_i} =$$

$$\left(U_0 - \frac{\hbar\omega}{2} \right) \sum_{i=1}^{i=n} N_i + \frac{e^4 \left(\sum_{i=1}^{i=n} N_i Z_{1i} Z_{2i} \right)^2}{2M\omega^2 r_0^2 \sum_{i=1}^{i=n} N_i} \quad (19)$$

respectively.

Concluding remarks

In summary, it is developed a diatomic model based general formalism to obtain binding energy and other characteristics of clusters theoretically, with acceptable accuracy. There is demonstrated its simplification for case of practical interest, when all the bond lengths can be considered as equal. Obtained relations would be useful for characterizing and development of the processes of nano clustered materials formation.

In principle, the proposed model is suitable not only for atomic clusters of any size, but any form of condensed matter as well. However, for infinite systems of atoms, it will be necessary to specify periodic (crystals) or chaotic (liquids or disordered solids) lattices of atoms. Another problem arising for condensed matter and large -or even medium-sized clusters is associated with too large numbers of equations, which

must be solved to find the equilibrium lengths and energies of chemical bonds, and constraints to be satisfied by these lengths.

Application of the method will be appropriate for small-sized, *i.e.*, nanoclusters, in which the numbers of central and peripheral atoms are comparable. The study of nanoclusters is preferable not only because of the relative simplicity of calculations, but mainly for effective accounting the static atomic charges arising from the valence electron density redistribution between central and peripheral atoms, which is characteristic of nanoclusters.

Thus, proposed diatomic approach would be especially different and distinct from others to quantify the nanoclusters physical properties related to valence electron density redistribution between constituent atoms (such as bonds energy, length, polarity, etc).

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