

# Energy relations between small and large unit cell boron–nitrogen polymer analogues of spiral graphite and nanoneedle structures

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**Abstract** Based on a comparison of nuclear charges combined with a convexity property of Hamiltonians, and employing nuclear charge transformations representing a limited case of the Universal Molecule Model, simple electronic energy relations are obtained for the unit cells of polymeric boron–nitrogen analogues of carbon-based nanoneedles and spiral graphite structures.

**Keywords** Unit cell relations · Universal molecule model · Spiral graphite · Nanoneedles

## 1 Introduction

Some novel all-carbon structures, themselves structural elements of spiral graphite as well as various nanoneedles [1, 2] (very thin nanotubes with inaccessible interior) have suggested the viability of analogous structures where carbon atom pairs are replaced by the isoelectronic boron–nitrogen pair [3–5]. Several such structures have been found theoretically and the fact that they are isoelectronic with the corresponding all-carbon species allows the use of some relations restricted for isoelectronic families. One such relation, based on nuclear charge variations, is useful for obtaining electronic energy bounds for one molecule by a linear combination of the energies of a pair of related molecules.

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Several of these relations are based on models where some of the discrete quantities, for example nuclear charge values, are allowed to vary continuously. In the extreme model of the “Universal Molecule” [6], not only the nuclear coordinates, but all parameters of molecules are considered as formal real variables, including the number of electrons, the number of nuclei, and nuclear charges which may take any non-negative values, specifically, zero. This “Universal Molecule” model allows formal transformations between real molecules. For example, as the nuclear charges of ammonia, 7, 1, 1, 1, continuously change to 8, 1, 1, 0, for intermediate values the model does not correspond to any real chemical object, but at the final integer values reality returns, essentially, turning ammonia into a distorted form of water. Some of the common properties and also some of the interrelations between real molecules can be studied within this framework, for example, by establishing connections with the fictitious “Universal Molecule”, and using these relations and the Universal Molecule as an intermediary and reference to establish new, direct relations between real molecules.

In this contribution we are going to be concerned with a specific problem, exploiting the fundamental ideas of the Universal Molecule approach: by nuclear charge variations, we are going to show that simple relations are applicable between the electronic energies of small unit cell and some larger unit cell polymers which are the boron–nitrogen analogues of some carbon-based nanostructures, specifically, nano-needles and components of spiral graphite.

## 2 Nuclear charge variation and the electronic energy

Here we describe only the fundamental idea behind the nuclear charge variation approach; for more detail and special applications the reader may consult the original references [7–18]. Reference [19] discusses an early application to the unit cell problem within a biopolymer context.

Consider the  $w$  nuclear charges of a molecule as the components of a  $w$ -dimensional nuclear charge vector  $\mathbf{z}$ , also the Cartesian coordinates of the nuclei as the components of the 3D position vectors  $R_i$ , whereas the components of these position vectors are collected into the  $3w$ -dimensional vector  $\mathbf{R}$  describing the nuclear arrangement. With these notations, the electronic Hamiltonian of the molecule can be written as

$$H_e(\mathbf{R}, \mathbf{z}) = -1/2 \sum_{i=1}^k \Delta_i - \sum_{i=1}^k \sum_{j=1}^w z_j / |R_i - R_j| + \sum_{i < i'}^k 1 / |R_i - R_{i'}| \quad (1)$$

The electronic energy expectation value is then given as

$$E_e = \langle \psi_e | H_e | \psi_e \rangle \quad (2)$$

where  $\Psi_e$  is the electronic wavefunction of the molecule.

Let us assume that there are three isoelectronic molecules,  $M$ ,  $M^{(1)}$ , and  $M^{(2)}$  in their electronic ground states, and for their nuclear charge vectors  $\mathbf{z}$ ,  $\mathbf{z}^{(1)}$ , and  $\mathbf{z}^{(2)}$ ,

respectively, the following convexity relation holds:

$$\mathbf{z} = \alpha \mathbf{z}^{(1)} + (1 - \alpha) \mathbf{z}^{(2)}, \quad (3)$$

where

$$0 \leq \alpha \leq 1. \quad (4)$$

In addition, these three molecules are arranged and potentially distorted so that they do have a common nuclear geometry, where the ordering of nuclei in the nuclear charge vectors also specifies which nuclei of molecules  $M^{(1)}$ , and  $M^{(2)}$  are taking identical relative locations with any given nucleus of molecule  $M$ . For example, taking the ammonia–water pair discussed above, we may consider a distorted water molecule where the O–H bond lengths and the H–O–H bond angle are the same as the N–H bond lengths and the H–N–H bond angle in ammonia.

Exploiting the fact that the electronic Hamiltonian is linear in the nuclear charges, and also applying the variational theorem when replacing the wavefunction of molecule  $M$  with the actual wavefunctions of molecules  $M^{(1)}$ , and  $M^{(2)}$ , the following series of relations can be written:

$$H_e = \alpha H_e^{(1)} + (1 - \alpha) H_e^{(2)} \quad (5)$$

$$E_e = \langle \psi_e | H_e | \psi_e \rangle = \alpha \langle \psi_e | H_e^{(1)} | \psi_e \rangle + (1 - \alpha) \langle \psi_e | H_e^{(2)} | \psi_e \rangle \quad (6)$$

$$\begin{aligned} & \alpha \langle \psi_e | H_e^{(1)} | \psi_e \rangle + (1 - \alpha) \langle \psi_e | H_e^{(2)} | \psi_e \rangle \\ & \geq \alpha \langle \psi_e^{(1)} | H_e^{(1)} | \psi_e^{(1)} \rangle + (1 - \alpha) \langle \psi_e^{(2)} | H_e^{(2)} | \psi_e^{(2)} \rangle = \alpha E_e^{(1)} + (1 - \alpha) E_e^{(2)} \end{aligned} \quad (7)$$

that is,

$$E_e \geq \alpha E_e^{(1)} + (1 - \alpha) E_e^{(2)} \quad (8)$$

The above result, an energy relation between molecules based on changes in the nuclear charges, have been used in a variety of simple applications [7–19].

### 3 Nuclear charge transformation between unit cells of different sizes and bounds for the electronic energy

One of the motivating aspects of applying nuclear charge convexity relations to various larger molecules is the possibility to obtain energy bounds for polymers of large unit cells in terms of other polymers of smaller unit cells. Whereas large unit cell polymers represent notoriously difficult computational challenges, in some special cases of nuclear charge combinations one can provide shortcuts to reliable energy bounds and

additional estimates based on the much simpler computations of polymers of smaller unit cells.

The fact that the neutral C–C atom pair is isoelectronic with the neutral B–N atom pair also implies that their nuclear charges fulfill the simple condition that for the diatomic fragments C–C, B–N, and N–B their respective nuclear charge vectors (written as row vectors) fulfill the convexity relation

$$\mathbf{z} = \alpha \mathbf{z}^{(1)} + (1 - \alpha) \mathbf{z}^{(2)}, \quad (9)$$

with

$$\alpha = 0.5, \quad (10)$$

where

$$\mathbf{z} = (6, 6), \quad (11)$$

$$\mathbf{z}^{(1)} = (5, 7), \quad (12)$$

$$\mathbf{z}^{(2)} = (7, 5). \quad (13)$$

One should also note that if for some other choices for selecting roles of the same three fragments in the convexity relation (9) the two nuclear charge vectors on the right-hand side of Eq. 9 are identical, then the left-hand side vector will also become the same. Hence, as long as C–C pairs are not combined with B–N or N–B pairs on the right-hand side, all convex combinations lead to one of the above three fragments on the left-hand side of the equation. In particular, no fractions of integers will result, and the formal “interpolated” molecules (entities often appearing in connection with the Universal Molecule model) will always have viable, actual integer-charge nuclei.

As an actual example, we are going to consider three polymers, I–III, composed from the above three atom pairs (in fact, the second and third atom pairs are identical, except for the reversed roles the B and N atoms play). Whereas these polymers of the example all have relatively small unit cells, they serve as a valid illustration of the method, which is the most useful if the relative sizes of the two smaller unit cell polymers relate to each other as relative primes, and the size of the largest unit cell is a multiple of both of these relative primes. The simplest is the situation if the small sizes actually relate to each others as primes and the size of the large unit cell is the product of the other two sizes.

Polymers I and II are regarded as the two, small unit cell polymers for which it is relatively easy to obtain reliable energy results, whereas the third polymer, of the largest unit cell, is assumed to present computational challenges.

The unit cells are as follows:

Polymer I  
 C B N C N B  
 C N B C B N  
 Polymer II  
 C N B C N B C B N  
 C B N C B N C N B  
 Polymer III  
 C C C C N B C B N C N B C C C C C C  
 C C C C B N C N B C B N C C C C C C

The unit cell of polymer I has to be repeated three times to make a chain segment as long as the unit cell of polymer III, whereas the unit cell of polymer II has to be repeated twice to make a chain segment as long as the unit cell of polymer III. Clearly, in this example, the length of the unit cell of polymer III is the product of the length of the other two unit cells.

Indeed, for a fulfillment of the isoelectronic condition, we need a three unit cell fragment of polymer I, and a two unit cell fragment of polymer II in order to make them comparable with the unit cell of polymer III.

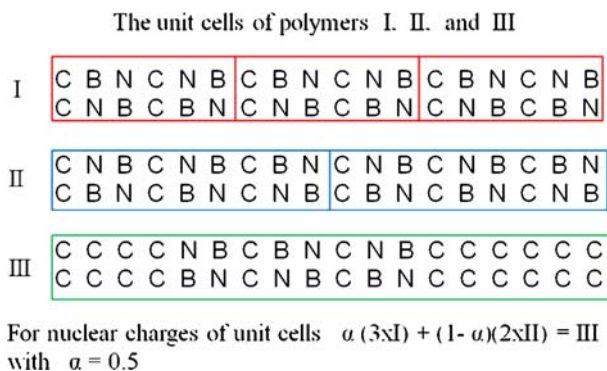
After some inspection we can conclude that for these fragments the nuclear charge vectors  $\mathbf{z}(\text{I})$ ,  $\mathbf{z}(\text{II})$ , and  $\mathbf{z}(\text{III})$  each has dimension 36, and they fulfill the convexity relation

$$\mathbf{z}(\text{III}) = \alpha \mathbf{z}(\text{I}) + (1 - \alpha) \mathbf{z}(\text{II}) \quad (14)$$

with

$$\alpha = 0.5 \quad (15)$$

This follows simply from the fact that the linear combination (14) can be broken down to nuclear pairs, and the combination will result only in such pairs which also occur in the two-dimensional relations (9)–(13). This fact is illustrated in Fig. 1.



**Fig. 1** Illustration of the relations between polymer segments of various unit cell lengths

As a consequence of the nuclear charge convexity relation, the electronic energy result for the lowest electronic states holds, and one obtains for the fragment energies that

$$E_e(\text{III}) \geq \alpha E_e(3\text{I}) + (1 - \alpha)E_e(2\text{II}) \quad (16)$$

Here I, II, and III symbolize the actual unit cells of the corresponding polymers.

Although energy is an extensive property, nevertheless, in polymers an additive treatment of unit cell energies requires further assurances for the inclusion of short range and long range interactions. Hence for real, finite length polymers, especially for ones containing only a relatively small number of unit cells, the following relations can serve only as an approximation:

$$E_e(3\text{I}) = 3E_e(\text{I}) \quad (17)$$

$$E_e(2\text{II}) = 2E_e(\text{II}), \quad (18)$$

and the same limitation applies to the overall relation involving unit cell energies:

$$E_e(\text{III}) \geq \alpha 3E_e(\text{I}) + (1 - \alpha)2E_e(\text{II}) \quad (19)$$

Nevertheless, the above relation (19) illustrates both the power and the insight that can be obtained by applying this limited version of the Universal Molecule model.

## 4 Summary

The actual result of the example is obtained essentially using only back-of-the-envelope type calculations. A simple inspection of the nuclear charges is sufficient to obtain energy bounds for a large unit cell polymer, using energy information corresponding to two, small unit cell polymers, where for the latter direct energy calculations are far more feasible. Employing this limited version of the Universal Molecule model, one can obtain information about a quantity that can be computed directly only with considerable effort, using only quantities requiring much less computational effort, and additionally only trivial nuclear charge computations.

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