

**Dipole polarizability of isovalent carbon and boron cages and fullerenes**

Rajendra R. Zope and Tunna Baruah

*Department of Physics, The University of Texas at El Paso, El Paso, Texas 79968, USA*

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Recent works have shown that the nonmetallic  $\alpha$ -boron cages and fullerenes have valence electronic structures that are identical to those of the corresponding carbon cages and fullerenes to which they are structurally related. By studying the first-order response of these systems ( $C_{60}$ ,  $B_{80}$ ,  $C_{240}$ , and  $B_{320}$  fullerenes and  $C_{24}$  and  $B_{32}$  cages) to an applied static electric field, we show that this similarity in valence electron structures results in an interesting relation between their dipole polarizabilities. The dipole polarizabilities of the  $\alpha$ -boron cages and fullerenes obtained by density functional calculations are simply proportional to the dipole polarizabilities of the related carbon cages and fullerenes.

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**I. INTRODUCTION**

In the last two years, a number of interesting studies on boron nanostructures have been reported.<sup>1–11</sup> Among these reports, a couple of very interesting studies by Tang and Ismail-Beigi<sup>8</sup> and Yang *et al.*<sup>10</sup> using the density functional calculations demonstrated the existence of a stable boron sheet consisting of triangular and hexagonal motifs.<sup>8,10</sup> The exact boron analog of graphene buckles when optimized and is less stable than the triangular sheet. The  $\alpha$ -boron sheet found by Tang and Ismail-Beigi<sup>8</sup> has *holes* (hollow hexagons) surrounded by hexagons with an additional interior boron atom at the centers of six-member rings (filled hexagons). Each filled hexagonal ring has three neighboring holes arranged in an alternate fashion. This arrangement results in isolation of the *holes* from each other. Tang and Ismail-Beigi<sup>8</sup> argued that the stability of the  $\alpha$ -boron sheet is due to an optimal balance of two-center and three-center bondings.<sup>8</sup> The  $\alpha$ -boron sheet can be rolled up to obtain nanotubes. The  $\alpha$ -boron nanotubes thus obtained are the most stable boron nanotubes so far.<sup>1,5</sup>

The carbon fullerenes are hollow cage structures in which each carbon atom is bonded to its three neighbors. They can be viewed as finite-closed three-dimensional graphene sheets. Inserting a pentagon in graphene introduces curvature in a flat graphene sheet. Using exactly 12 pentagons a closed carbon fullerene can be obtained from graphene. Likewise, hollow  $\alpha$ -boron fullerenes can be obtained by introducing pentagons into the planar  $\alpha$ -boron sheet. To obtain  $\alpha$ -boron fullerenes the pentagons should be introduced in place of holes. We have recently shown that the procedure to construct members of  $60n^2$  icosahedral carbon fullerene can also be used to generate a family of  $80n^2$  icosahedral  $\alpha$ -boron fullerenes.<sup>12</sup> This procedure consists of cutting equilateral triangles from  $\alpha$ -boron sheet and pasting them on to the 20 triangular faces of an icosahedron.

The  $B_{80}$  fullerene, the smallest member of  $80n^2$  icosahedral  $\alpha$ -boron fullerenes, was found to be particularly stable among a number of boron fullerenes in the size range of 20–100.<sup>2</sup> Earlier studies on hollow boron nanostructures have primarily focused on boron hydrides<sup>13,14</sup> and capped boron equivalent of carbon fullerenes.<sup>15,16</sup> The particular stability of  $B_{80}$  was later understood to be due to its compat-

ibility with  $\alpha$ -boron sheet. Larger members of  $80n^2$  icosahedral  $\alpha$ -boron fullerenes are energetically more stable than the  $B_{80}$  fullerene due to larger fraction of boron atoms in “ $\alpha$ -boron-sheet”-like environment.<sup>12</sup>

Starting from the  $\alpha$ -boron sheet, hollow structures of boron can also be obtained using 6 four-member rings instead of 12 pentagonal rings.<sup>17</sup> It can be shown that a  $32n^2$  class of energetically stable boron cages can be constructed starting from  $\alpha$ -boron sheet by introducing six four-member rings.<sup>18</sup> The hollow boron structure made closed using pentagons will be called fullerenes, and those made closed using four-member rings will be called cages throughout this work. Alternatively, the  $\alpha$ -boron cages and fullerenes can be constructed starting from their carbon cousins using a modified leapfrog-type algorithm.

The report of  $B_{80}$  fullerene received wide attention due to its structural similarity with the celebrated  $C_{60}$  fullerene. Apart from the structural similarity between them, these two fullerenes are isoelectronic, which results in similarity in their electronic properties.<sup>4</sup> Each member of  $80n^2$  icosahedral boron fullerene is structurally related to the corresponding member from  $60n^2$  carbon fullerene family. Also, for a given  $n$  the boron and the corresponding carbon fullerenes are isovalent; that is, they have same number of valence electrons. Our recent density functional calculations on  $B_{80}$ ,  $B_{320}$ ,  $B_{720}$ , and  $B_{1280}$  icosahedral fullerenes showed that the valence electronic structure of these fullerenes is *identical* to their partners  $C_{60}$ ,  $C_{240}$ ,  $C_{540}$ , and  $C_{960}$  from the carbon family. Such similarity in the electronic structure of  $\alpha$ -boron and carbon fullerenes and cages has also been noted by others.<sup>9,19</sup> The valence electrons in boron and carbon fullerenes occupy exactly same irreducible representations. Qualitative understanding of the similarities in valence electronic structure can be obtained by assuming that the valence electrons are freely moving in a spherical well provided by the ionic positions. While the two sets of fullerenes have same valence electronic structure, the energy differences between the eigenvalues are not the same. The electronic properties that are less sensitive to small differences in energy levels will be similar or related for the two sets of fullerenes. One such experimentally accessible property is the linear static dipole polarizability, which is a measure of response of electrons in the system to an applied electric field. The purpose of this Brief Report is to examine the relation between the dipole polar-

TABLE I. The number of  $s$ ,  $p$ , and  $d$  functions and the range of the exponents of the Gaussian functions used in the calculations.

Atom	$s$	$p$	$d$	Exponent
C	5	4	3	$7.72 \times 10^{-2} - 2.22 \times 10^4$
B	5	4	3	$5.48 \times 10^{-2} - 1.72 \times 10^4$

izabilities of boron and carbon fullerenes (and cages). Using density functional theory (DFT), we determine the dipole polarizabilities of a number of boron and carbon fullerenes (and cages). Our calculations show that (static dipole) polarizability of the boron fullerenes (cage) to a good approximation can be obtained from the polarizability of their carbon cousins.

## II. THEORY

When a fullerene cage is placed in a static electric field  $\vec{F}$ , the electrons in it redistribute in response to the field. This response is characterized by the polarizability of the molecule. The elements of the static dipole polarizability tensor are

$$\alpha_{ij} = - \frac{\partial^2 E}{\partial F_i \partial F_j}. \quad (1)$$

Here,  $E$  is the total molecular energy and  $F_i$  is the  $i$ th ( $x$ ,  $y$ , or  $z$ ) component of the electric field. Equation (1) is the coefficient of the second term in Taylor's expansion of total energy  $E$  in the presence of field,

$$E(F) = E_0 + \sum_i \left( \frac{\partial E}{\partial F_i} \right) F_i + \frac{1}{2} \sum_{ij} \left( \frac{\partial^2 E}{\partial F_i \partial F_j} \right) F_i F_j + \dots \quad (2)$$

## III. COMPUTATIONAL DETAILS

All calculations are performed within density functional theory as implemented in the NRLMOL code.<sup>20,21</sup> The implementation is based on linear combination of atomic orbital approach. The exchange-correlation effects were treated at generalized gradient level according to the Perdew-Burke-Ernzerof parametrization.<sup>22</sup> Large polarized Gaussian basis sets are used. The details of the basis set are summarized in Table I. A few salient points about the NRLMOL code are that the same set of primitive basis functions for an atom is used for all the contracted functions. The Table I also shows the range of the exponents (alpha) for the primitive Gaussians. The NRLMOL code uses a mesh, which is variational with respect to the accuracy of the integrals.<sup>20</sup> The geometry of structures is optimized using the LBFGS algorithm.

In order to construct the polarizability tensor, we apply an electric field of magnitude 0.01 Ryd/Bohr along various directions. The total energies are obtained self-consistently for

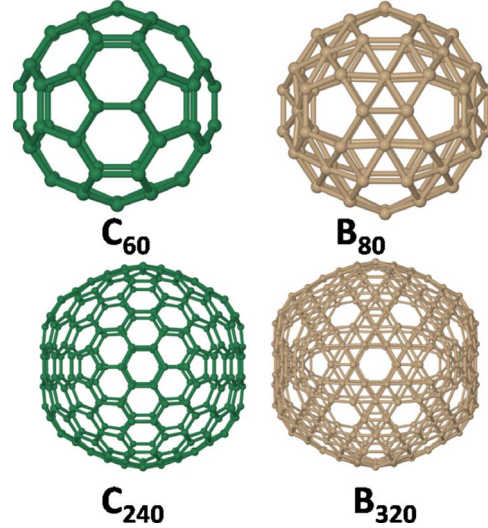


FIG. 1. (Color online) The structures of boron fullerenes from the  $80n^2$  series and their parent carbon fullerenes from  $60n^2$  series.

each field value using the tight convergence criteria of  $2.0E-8$  Ryd for total energies. The components of polarizability tensor are obtained by the finite difference of total energies of fullerenes in the presence of electric field. Since the application of the electric field breaks the symmetry the calculations have to be carried out using only the C1 symmetry. This adds to the computational expenses. Alternatively, applying a uniform field along a high-symmetry axis in some of the cages can reduce the computational effort. We have tried to reduce the computational efforts whenever possible. The mean polarizability is determined as an average of diagonal elements of the polarizability tensor. Alternatively, the polarizability can also be obtained by finite difference of induced dipole moments. The polarizability obtained from total energies and from dipole moments agrees within 1%.

## IV. RESULTS AND DISCUSSION

We have chosen three pairs of related carbon and boron cages to examine the similarities in their polarizabilities. We chose the first two members of the  $60n^2$  series of the carbon fullerenes, namely, C<sub>60</sub> and C<sub>240</sub>, and their boron cousins from the  $80n^2$  series, the B<sub>80</sub> and B<sub>320</sub> fullerenes. The next member from the boron fullerene family, B<sub>720</sub>, is too large to compute the polarizability using the all-electron approach taken here. The structures of the icosahedral C<sub>60</sub>, C<sub>240</sub>, and their boron derivatives B<sub>80</sub> and B<sub>320</sub> are shown in Fig. 1. Apart from these icosahedral cages, we have also calculated the polarizabilities of the C<sub>24</sub> cage and its boron counterpart B<sub>32</sub> cage whose structures are shown in Fig. 2. These cages are the first members of the infinite class of octahedral  $24n^2$  carbon cages and the  $32n^2$  boron derivatives and are made closed using 6 four-member rings (squares) instead of 12 pentagonal rings as in fullerenes.

The B<sub>80</sub> fullerene is vibrationally unstable in the icosahedral point-group symmetry.<sup>4,23</sup> It has  $T_h$  point-group symmetry. However, the energy gain upon symmetry lowering is very small. Its polarizability, the property of interest for this

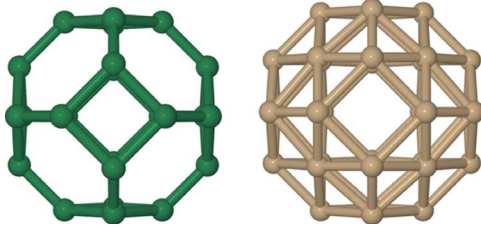


FIG. 2. (Color online) The optimized structures of the  $C_{24}$  (left) and  $B_{32}$  (right) cages.

work, changes negligibly upon symmetry lowering. Therefore we have performed the calculations described here maintaining the icosahedral symmetry. The  $C_{60}$  fullerene is isovalent with  $B_{80}$  fullerene. Similarly, the  $C_{240}$  is isovalent with  $B_{320}$ . The valence electronic structures of icosahedral  $C_{60}$  and  $B_{80}$  are same; that is, the valence electrons in two systems belong to same sets of irreducible representations. The energy ordering of orbitals is not necessarily same. Likewise, the valence electronic structures of  $C_{240}$  and  $B_{320}$  are same and also for  $C_{24}$  and  $B_{32}$ .<sup>12,17</sup> Therefore, the electronic distributions in these related (boron and carbon) clusters are similar although the sizes of the clusters are different. The valence electronic structure of the boron and carbon fullerenes is summarized in Table II.

The calculated values of the polarizabilities of the carbon and boron cages are presented in Table III along with the radii of these cages. We present the ratios of the carbon and related boron cage polarizabilities and also the ratio of polarizability to the cube of the radii. An inspection of the related carbon and boron cages shows that the radii of the carbon cage are 83% and 84% of its boron counterpart for icosahedral and octahedral cages, respectively. The larger radii of boron structures are due to the larger boron-boron bond lengths in comparison with carbon bond distances in carbon structures. The polarizability of a spherical charge distribution scales as cube of its radius. The boron cages have larger polarizability values compared to their carbon counterparts due to their larger sizes. We find that the average ratio of the polarizabilities of a pair of related carbon and boron cages is 0.55. This value is close to the cube of ratio of radii of carbon and boron fullerenes, which is 0.58. The deviation from this mean value is seen to arise for octahedral cages. This relation also shows that it is possible to predict the polarizability of a boron (carbon) cage from the polarizability values for another pair and its counterpart. The last value in Table III is a measure of polarizability per unit volume. For boron cages this value is consistently larger. It was earlier pointed out that for carbon fullerenes the value of  $\alpha/r^3$

TABLE III. The radii, static dipole polarizabilities ( $\alpha$ ), ratios of the polarizabilities of the carbon cage to its boron derivatives, and ratio of polarizability to the cube of the cage radius.  $\alpha_{vib}$  is the vibrational contribution to the polarizability.

Cage	Radius ( $\text{\AA}$ )	$\alpha$ ( $\text{\AA}^3$ )	Ratio $\alpha_C/\alpha_B$	$\alpha/r^3$	$\alpha_{vib}$ ( $\text{\AA}^3$ )
$C_{24}$	2.29	32	0.58	2.66	0.8
$B_{32}$	2.72	55		2.73	2.1
$C_{60}$	3.55	82	0.55	1.83	0.58
$B_{80}$	4.27	149		1.91	5.5
$C_{240}$	7.07	441	0.52	1.25	
$B_{320}$	8.47	844		1.39	

decreases as the size of the cage increases. The large value of  $\alpha/r^3$  for smaller fullerenes is mainly a quantum size effect.<sup>24</sup> The same effect is also evident for boron fullerenes and cages.

We have also calculated the contribution to the dipole polarizability due to the vibrational motion of the atoms of the cages (cf. Table III). The structures of the cages were not optimized in the presence of electric fields. As the earlier studies have shown that the bonding in these systems is predominantly covalent, the ionic (nuclear) contribution is determined within the double harmonic approximation according to the prescription described in Ref. 25. This requires first the calculation of all the vibrational modes for the cages. Since these calculations are expensive, we have performed them only for the smaller size cages, i.e., for  $C_{24}$ ,  $B_{32}$ ,  $C_{60}$ , and  $B_{80}$ . We find that the vibrational contribution to polarizability is  $2.1 \text{ \AA}^3$  for  $B_{32}$  and  $5.5 \text{ \AA}^3$  for  $B_{80}$ . The corresponding values for  $C_{24}$  and  $C_{60}$  are 0.8 and  $0.58 \text{ \AA}^3$ . Thus the lattice relaxation contribution is nearly 4% of the electronic polarizability for the boron cages, but for carbon cages the value shows more variations going from  $C_{24}$ (2.5%) to  $C_{60}$ (1%). These values also show that the electronic contribution is by far the most dominating factor in polarizability of these systems.

## V. CONCLUSION

In conclusion, we have studied the static dipole polarizabilities of a few pairs of related carbon cages and their boron derivatives. Our earlier calculations have shown that

TABLE II. The first two columns list the boron fullerene and its parent carbon fullerene. The valence electronic structures of boron fullerenes are presented in the last columns.

B fullerene	C fullerene	Valence electronic structure
$B_{32}$	$C_{24}$	$3a_{1g} 1a_{2u} 3e_g 1e_u 4t_{1u} 1t_{1g} 3t_{2u} 4t_{2g}$
$B_{80}$	$C_{60}$	$4h_u 7h_g 4g_u 4g_g 4t_{1u} 1t_{1g} 3a_g 4t_u 1t_{2g}$
$B_{320}$	$C_{240}$	$17h_u 23h_g 16g_u 16g_g 15t_{1u} 9t_{1g} 7a_g 1a_u 15t_{2u} 9t_{2g}$

the valence electron distributions of the carbon and boron cages, which are isovalent, are identical. In the present study we show that the ratios of the polarizabilities of related carbon and boron cages and fullerenes scale similarly. This study shows that the polarizability of boron fullerenes and cages can be derived to an excellent approximation from that of the polarizabilities of the related carbon fullerenes and

cages and that dipole polarizability is insensitive to details of the electronic structure.

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