

***Ab initio* many-body calculations of static dipole polarizabilities of linear carbon chains and chainlike boron clusters**

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In this paper we report a theoretical study of the static dipole polarizability of two one-dimensional structures: (a) linear carbon chains C_n ($n=2-10$) and (b) ladderlike planar boron chains B_n ($n=4-14$). The polarizabilities of these chains are calculated both at the Hartree-Fock and the correlated levels by applying accurate *ab initio* quantum-chemical methods. Methods such as restricted Hartree Fock, multiconfiguration self-consistent field, multireference configuration interaction, Møller-Plesset second-order perturbation theory, and coupled-cluster singles, doubles, and triples levels of theory were employed. Results obtained from *ab initio* wave-function-based methods are compared with the ones obtained from the density-functional theory. For the clusters studied, directionally averaged polarizability per atom for both the systems is seen to increase with the chain size.

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I. INTRODUCTION

The role that atomic and molecular clusters will play in future nanotechnologies is indisputable.^{1,2} The experimental progress in this field has been breathtaking, and novel applications have been found in areas such as molecular transport and optoelectronics.¹⁻³ However, theoretical research in this area can also play a very important role in that, by undertaking calculations on clusters of different types, it can help the experimentalists in identifying different structures for investigation. *Ab initio* calculations on structural and electronic properties of atomic clusters are frequently performed, and the results are put to test in the experiments.⁴ One such property of clusters is their electric-dipole polarizability whose experimental and theoretical determination is an area of intense research.¹ The measurements of dipole polarizability are frequently used by experimentalists to characterize the nature of atomic and molecular species.¹ It describes the response of the electron cloud of the given molecular system to the presence of a dc electric field, and thus is easily amenable to experiment. Since the static polarizabilities are the zero-frequency limits of the corresponding dynamic quantities, they also provide information about the response of the system to off-resonant ac fields. Most of the theoretical calculations of both the structural and electronic properties such as static polarizabilities of atomic clusters are performed within the framework of density-functional theory (DFT). Despite the fact that DFT has enjoyed indisputable success in solid-state physics and quantum chemistry as a computationally cheap routine tool for large-scale investigations, the drawback is that results depend highly on the chosen functional, and cannot be improved in a systematic way. Wave-function-based *ab initio* quantum-chemical techniques on the other hand are free from this flaw, and provide a large

array of methods of different accuracy and computational cost. Moreover, the prediction of reliable values of dipole polarizabilities and hyperpolarizabilities by rigorous quantum-chemical methods has made significant contributions, and added new vigor, to the search for optical materials.^{3,4} Thus, in order to obtain reliable estimates for dipole polarizabilities, and also to cross check the DFT-based results, it is worthwhile to investigate the electron-correlation effects in a systematic way by using quantum-chemical many-body techniques. In this work, we present fully size-consistent *ab initio* calculations to the static dipole polarizability of linear carbon clusters C_n ($n=2-10$) and chainlike boron clusters B_{2n} ($n=2-7$), of increasing size. The reason behind our focus on one-dimensional structures is that quantum confinement due to reduced dimensions, combined with the possible delocalization of the electrons along the backbone, can lead to enhanced linear and nonlinear susceptibilities of these structures, as compared to their three-dimensional counterparts. In the present study, the electron-correlation effects have been taken into account by various size-consistent methods: multireference configuration interaction, second-order Møller-Plesset perturbation theory, coupled-cluster singles and doubles (CCSD), and coupled-cluster singles and doubles with the perturbative treatment of the triples [CCSD(T)]. All earlier calculations on these systems, with the exception of B_4 , were performed within the framework of DFT, with which we compare our results. Next, we briefly review the state of the art of research on these two types of clusters.

Carbon clusters have been the subject of research for decades as possible key materials for future nanotechnologies.² For the smaller systems, up to and including those containing nine atoms, linear neutral, positively and negatively charged clusters are generated and detected in experiments.⁵ The

structures and energetics of linear carbon clusters are well studied by employing coupled-cluster approaches.^{6–8} Recently, we studied the ground state of an infinite carbon chain at the *ab initio* level using various many-body approaches including CCSD(T).⁹ Lou and Nordlunder have investigated the influence of an electric field on the energetic stability of linear carbon chains.¹⁰ Recently Fuentealba¹¹ has calculated the static dipole polarizabilities of carbon chains using density functionals of the hybrid type in combination with the finite-field method. He showed that dipole polarizabilities are an important quantity for the identification of clusters with different numbers of atoms and even for the separation of isomers. Here we compare our many-body-methods-based polarizabilities with those computed by Fuentealba¹¹ using the DFT approaches.

Boron is a trivalent element with the valence shell configuration s^2p^1 . Although compared to carbon, the valence shell of boron is electron deficient, and it still exhibits sp^2 hybridization with strong directional chemical bonds.¹² In composite materials, for small content, boron tends to form a linear chain, while as its content increases it can form structures ranging from two to three dimensional.¹² As far as isolated clusters containing boron are concerned, experimentally, they have been studied by Anderson and co-workers,¹³ and by La Placa *et al.*¹⁴ In addition, Chopra *et al.*¹⁵ and Lee *et al.*¹⁶ have experimentally synthesized boron-nitrogen nanotubes and cage-like boron-nitrogen structures. Several authors have also reported theoretical calculations on the boron clusters.^{17–30} Boustani *et al.*²¹ have shown theoretically that, similar to carbon, boron has a strong potential to form stable nanotubular structures. Boustani recently studied small cationic²² and neutral boron²³ clusters and obtained structures that are fundamentally different from crystal subunits of the well-known α - and β - rhombohedral phases of boron, which consist mainly of B_{12} icosahedra. Boustani and Quandt classified the boron clusters into four topological groups: convex and spherical,²⁴ quasiplanar,²⁵ and nanotubular.²⁶ The quasiplanar and convex structures can be considered as fragments of planar surfaces, and as segments of hollow spheres, respectively. The main focus of their theoretical work has been to ascertain the structures of larger boron clusters in terms of a small number of building blocks.^{27,28} However, recently Sabra and Boustani²⁸ studied the ground-state energetics of ladderlike quasi-one-dimensional clusters of boron by quantum-chemical methods. They concluded that such structures are not the lowest in energy. However, because of the proximity of the structures' energy to that of the true ground-state geometries, they can be regarded as metastable states.²⁸ Thus, with some experimental manipulation, it may be possible to realize such structures in laboratory. Keeping this possibility in mind, we decided to compute the static polarizabilities of ladderlike quasi-one-dimensional structures of boron by *ab initio* many-body methods. In addition to the quantum-chemical calculations, we also perform the DFT-based calculations of static dipole polarizabilities of these clusters using the same basis set, so as to understand the influence of electron-correlation effects on the polarizabilities of these systems. Recently, Reis and co-workers computed the static dipole polarizabil-

ities of rhombic B_4 using various quantum-chemical methods,²⁹ and several other boron clusters B_n ($n=3-8,10$) within the framework of DFT, employing a variety of exchange-correlation functionals.³⁰ However, unlike the quasi-one-dimensional geometries considered by us, Reis *et al.*³⁰ performed these calculations on the ground-state geometries of boron clusters optimized earlier by Boustani.²⁷ We compare our many-body static polarizabilities of various boron clusters to those reported by Reis *et al.*^{29,30} in order to understand the influence of the cluster structures on their static polarizabilities.

The remainder of the paper is organized as follows. In Sec. II, the applied methods and computational details are briefly described. The results are then presented and discussed in Sec. III. Finally, our conclusions are presented in Sec. IV.

II. METHODS AND COMPUTATIONAL DETAILS

For the closed-shell clusters, first the polarizabilities are calculated using the restricted Hartree-Fock (RHF) method, and thereafter the electron-correlation effects are included via the Møller-Plesset second-order perturbation theory (MP2), and the coupled-cluster techniques. For the open-shell clusters, the calculations are initiated by the multireference self-consistent-field (MRSCF) method, while the electron-correlation effects are taken into account by the multireference configuration-interaction (MRCI) method. In order to calculate static dipole polarizability first we performed calculations without an external electric field, and then we added an external electric field of strength 0.001 a.u. along the x , y , and z axes separately. Stability of the results with respect to the value of the field was carefully examined by performing some calculations for various other values of the field strength. However, when we perform high-level correlated calculations, the expectation value of the dipole moment is not directly available. Therefore, to calculate the static dipole polarizabilities, we have adopted a finite-difference formula in which the diagonal polarizability tensor elements are obtained through the second derivative of the total energy with respect to the external electric field. The field-dependent total energy is used in the following finite-difference formula:

$$\alpha_{jj} = - \left[\frac{\partial^2 E(\epsilon_j)}{\partial \epsilon_j^2} \right]_{\epsilon=0} = - \lim_{\epsilon_j \rightarrow 0} \frac{E(\epsilon_j) + E(-\epsilon_j) - 2E(0)}{\epsilon_j^2} \\ = \lim_{\epsilon_j \rightarrow 0} 2 \frac{E(0) - E(\epsilon_j)}{\epsilon_j^2},$$

where $E(\epsilon_j)$ is total energy with respect to field $\epsilon_j=0.001$ a.u. and $E(0)$ is total energy without field. This equation holds only for centrosymmetric systems.

For the linear carbon chain, assuming the z axis is the chain direction, we calculated the parallel (α_{zz}) and perpendicular (α_{xx}) components of the static dipole polarizability. Our calculations are performed using the geometry reported by Watts and Bartlett.⁸ Since the ground state of an even

number of carbon atoms is a triplet and an odd number of carbon atoms is a singlet we calculated the static dipole polarizabilities of an even number of carbon atoms, i.e., C₄, C₆, C₈, and C₁₀ for its ground state by the MRSCF and the MRCI methods, whereas for an odd number of carbon atoms, i.e., C₃, C₅, C₇, and C₉, we calculated them by using the RHF, MP2, CCSD, and the CCSD(T) methods. All calculations were performed with the MOLPRO molecular-orbital *ab initio* program package³¹ by employing Sadlej basis sets³² which were especially constructed for the calculation of dipole polarizabilities.

For the chainlike boron clusters we assumed that the boron atoms were lying in the *xy* plane, with the chain direction along the *x* axis. We first optimized the geometry of each cluster, i.e., B₄, B₆, B₈, B₁₀, B₁₂, and B₁₄, for its ground state at the B3LYP/6-31+G(*d*) level of approximation by using the GAUSSIAN98 program.³³ The ground state is singlet for B₄, B₁₀, B₁₂, and B₁₄ and triplet for B₆ and B₈. Then we calculated the parallel (α_{xx}), transverse (α_{yy}), and perpendicular (α_{zz}) components of the static dipole polarizabilities with standard polarized valence double-zeta (VDZ) basis sets at the Hartree-Fock and correlated levels, e.g., MRCI, MP2, CCSD, and CCSD(T) by employing the MOLPRO molecular-orbital *ab initio* program package.³¹ Although the basis set we used in chainlike boron clusters is a rather small basis set, a larger set would have been computationally too expensive when we prolong the chain. It has been shown further in Ref. 30 that using the larger triple-zeta basis set aug-cc-pVTZ does not have a large effect on the calculated polarizabilities for the cluster B₄. Therefore, for these clusters the chosen basis set should be sufficient.

III. RESULTS AND DISCUSSIONS

A. Linear carbon clusters

The calculated Cartesian components of static dipole polarizabilities and average polarizabilities $\alpha_{av} = (\alpha_{zz} + 2\alpha_{xx})/3$ for linear carbon clusters are presented in Table I. Figure 1 presents our calculated polarizabilities per atom, plotted as a function of the number of atoms in the chain (*N*). Additionally, for the sake of comparison, in the same figure we have also plotted the DFT-based results of Fuentealba.¹¹ It is not possible for us to compare our results to experiment because of the absence of any polarizability data on the carbon chains. From Fig. 1 it is obvious that the parallel component of the static dipole polarizability per atom, α_{zz}/N , increases roughly linearly from C₂ to C₁₀, whereas perpendicular components α_{xx}/N and α_{yy}/N are essentially constant as a function of *N*. As far as the comparison of our results with the DFT results of Fuentealba¹¹ is concerned, the agreement is generally very good on all components of polarizabilities except for the case of *N*=2. For *N*=2, however, Fuentealba¹¹ reports an anomalously large value of α_{xx} (and hence α_{xx}/N), making it disagree with his values of α_{xx}/N computed for higher values of *N*. From Fig. 1 it is also clear that the directionally averaged polarizability per atom α_{av}/N also shows an overall increase as a function of the chain length. Since polarizability is an extensive quan-

TABLE I. Linear carbon clusters: Static dipole polarizabilities (in a.u.) calculated with the Sadlej basis set (Ref. 32).

Atoms	Methods	$\alpha_{xx} = \alpha_{yy}$	α_{zz}	α_{av}
C ₂	MRSCF	28.00	25.22	27.07
	MRCI	24.57	25.24	24.79
	DFT/B3LYP ^a	100.00	33.90	78.00
C ₃	RHF	24.72	51.16	33.53
	MP2	24.46	51.68	33.53
	CCSD(T)	24.82	52.66	34.10
	DFT/B3LYP ^a	25.30	50.50	33.70
C ₄	MRSCF	29.86	91.88	50.54
	MRCI	29.71	92.38	50.60
	DFT/B3LYP ^a	32.10	93.70	52.60
C ₅	RHF	35.42	145.74	72.19
	MP2	35.38	149.74	73.50
	CCSD(T)	35.50	149.88	73.63
	DFT/B3LYP ^a	36.20	142.90	71.70
C ₆	MRSCF	40.81	219.88	100.50
	MRCI	40.45	220.40	100.44
	DFT/B3LYP ^a	42.80	214.70	100.00
C ₇	RHF	46.54	303.50	132.19
	MP2	46.22	314.80	135.75
	CCSD(T)	46.74	312.30	135.26
	DFT/B3LYP ^a	47.00	285.80	127.00
C ₈	MRSCF	51.82	464.78	189.47
	MRCI	51.34	462.11	188.26
	DFT/B3LYP ^a	52.60	403.00	169.00
C ₉	RHF	57.58	537.12	217.43
	MP2	57.20	555.04	223.15
	CCSD(T)	57.64	551.54	222.27
C ₁₀	MRSCF	62.85	777.51	301.07
	MRCI	62.29	776.39	300.32

^aTaken from Ref. 11.

tity, therefore, for very large numbers of atoms in the chain ($N \rightarrow \infty$), α_{av}/N should approach its bulk value. However, from our results it is obvious that for *N*=10, α_{av}/N is still increasing as a function of *N*, exclusively because of the increase in the parallel component α_{xx}/N . One can understand the increase in α_{xx}/N as a function of *N* on intuitive grounds based upon the behavior of π electrons. π electrons (of which the carbon chain has two per atom), compared to σ electrons, are highly delocalized along the chain direction. Therefore, it will take much larger cluster sizes before their response to an external field approaches that for the bulk.

The other somewhat surprising aspect of our results for the carbon chains is the generally excellent agreement obtained between the DFT values and the many-body values of the static polarizabilities. This means that for the static polarizabilities of carbon chains, DFT is able to describe the electron-correlation effects quite well. It is also rather interesting to note that the MP2 method provides a theoretical description of these clusters quite close to that obtained with the CCSD(T) method. A similar effect was observed by Maroulis³⁴ in the polarizability calculations of a system composed of two water molecules.

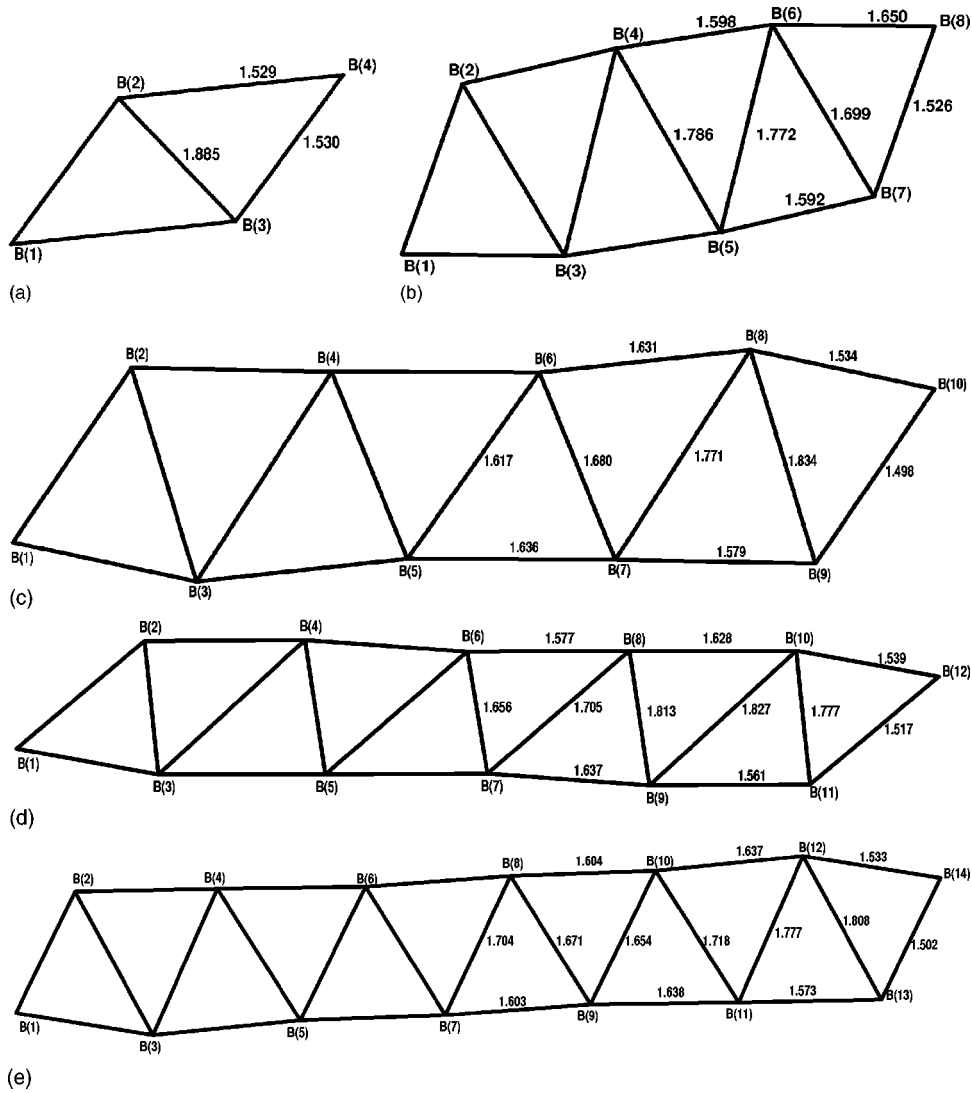


FIG. 1. The static dipole polarizability per atom of linear carbon clusters. The lines have been plotted to guide the eyes.

B. Chain-like boron clusters

Earlier Sabra and Boustani²⁸ had shown that strictly one-dimensional chains of boron are unstable. They demonstrated that boron prefers to form a zigzag ladderlike quasi-one-dimensional structure.²⁸ Therefore, in the present work we have concentrated on the identical structures of boron B_{2n} ($n=2-7$), which, as shown in Fig. 1, can be obtained by adding boron dimers to B_4 , which has a parallelogram structure. First we optimized the ground-state geometry of each of these clusters by employing the B3LYP/6-31+ $G(d)$ method, and these optimized geometries are given in Fig. 1. From optimization we found that the system is completely centrosymmetric. The optimized geometries of each cluster are comparable to those obtained by Boustani²⁷ who optimized the structures of elemental, convex and quasiplanar boron clusters B_n ($n=2-14$) at the RHF level with the 3-21 G basis set.

Results of our calculation on longitudinal (α_{xx}), transverse (α_{yy}), perpendicular (α_{zz}), and directionally averaged polarizabilities $\alpha_{av} = (\alpha_{xx} + \alpha_{yy} + \alpha_{zz})/3$ at the Hartree-Fock

and correlated levels, as well as at the DFT level, are presented in Table II. The polarizabilities per atom based upon this data are plotted as a function of the number of atoms in the cluster in Fig. 2. An inspection of the table and the figure reveals the following trends: (i) The longitudinal static dipole polarizability per atom α_{xx}/N increases almost linearly with N , and the component α_{yy}/N shows a gradual decrease, while α_{zz}/N exhibits saturation. (ii) For the triplet ground-state clusters B_6 and B_8 , the polarizabilities computed by the MRSCF and the MRCI methods are in almost complete agreement indicating that the MRSCF method has already captured the most important correlation effects. (iii) For the remaining clusters whose ground states are singlet, the inclusion of electron-correlation effects leads to a reduction of the α_{xx} component, while the other components are rather unaffected. For example, the CCSD(T) value of α_{av} for B_{14} is about 6% smaller compared to its RHF value. (iv) Similar to the case of carbon chains, for all boron clusters considered here, generally there is very good agreement between the polarizabilities computed by the best wave-function methods

TABLE II. Chainlike boron clusters: Static dipole polarizabilities (in a.u.) calculated with the VDZ basis set.

Atoms	Methods	α_{xx}	α_{yy}	α_{zz}	α_{av}
B ₄	RHF	82.72	65.54	27.30	58.52
	MP2	66.34	57.28	27.30	50.31
	CCSD(T)	69.88	58.98	27.12	51.99
	DFT/B3LYP	74.60	61.60	29.20	55.13
B ₆	MRSCF	145.45	92.86	40.78	93.03
	MRCI	144.64	92.16	40.28	92.36
	DFT/B3LYP	145.51	91.15	40.39	92.35
B ₈	MRSCF	210.72	101.93	62.73	125.12
	MRCI	211.28	101.17	61.54	124.66
	DFT/B3LYP	229.05	102.40	60.51	130.65
B ₁₀	RHF	361.86	121.24	97.00	193.37
	MP2	362.08	120.86	63.54	182.16
	CCSD(T)	345.70	118.90	79.82	181.47
	DFT/B3LYP	350.20	118.00	88.40	185.53
B ₁₂	RHF	527.32	153.60	77.90	252.94
	MP2	445.82	129.52	76.04	217.12
	CCSD(T)	469.70	140.06	76.58	228.78
	DFT/B3LYP	505.80	142.20	76.80	241.60
B ₁₄	RHF	698.90	160.16	115.36	324.81
	MP2	680.52	152.68	75.92	303.04
	CCSD(T)	664.48	155.08	97.66	305.74
	DFT/B3LYP	683.80	155.20	104.00	314.33

[MRCI and CCSD(T)], and the ones computed using the DFT/B3LYP approach. Thus, in this case also, DFT is able to account for the electron-correlation effects quite well.

Since there are no experimental results for the static dipole polarizabilities for the ladderlike structures of boron, we compare our results to the theoretical results obtained by other authors.^{29,30} First considering the case of rhombic B₄, for the average static dipole polarizability α_{av} , we obtained 51.99 a.u. with the CCSD(T) approach while Reis and Papadopoulos²⁹ reported a CCSD(T) value of 60.00 a.u. for the same quantity. The α_{xx} and α_{yy} values from our calculations cannot be directly compared to those reported by Reis and Papadopoulos²⁹ because of the different orientations of the x and the y axes in their calculations. However, for α_{zz} , whose values can be compared directly, Reis and Papadopoulos²⁹ reported the value of 39.5 a.u., while we obtained 27.12 a.u. for the same quantity. Although the optimized geometries, as well as the basis set used by Reis and Papadopoulos²⁹ were somewhat different from ours, we still believe that those factors cannot explain the difference of ≈ 12 a.u. in the values of α_{zz} . However, clearly it is this disagreement—the reasons behind which are not clear to us—which is primarily responsible for the disagreement in the values of α_{av} observed between our results and those of Reis and Papadopoulos.²⁹

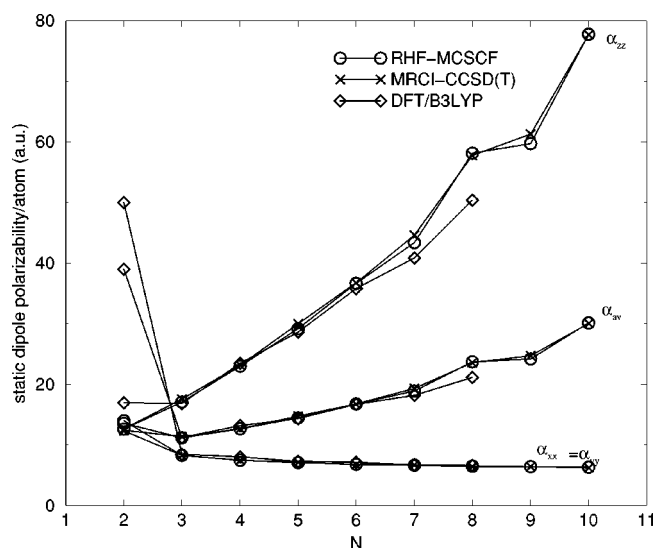


FIG. 2. The static dipole polarizability per atom of chainlike boron clusters. The lines have been plotted to guide the eyes.

Besides B₄, there are no theoretical results on the larger ladderlike clusters of boron. However, in another paper, Reis *et al.*³⁰ reported DFT-based calculations of the static polarizabilities of convex and quasiplanar B_n ($n=3-10$) clusters whose geometries were optimized earlier by Boustani.²⁷ Therefore, in order to understand the effect of the geometric structure on the polarizabilities of boron clusters, we compare our results on B₆, B₈, and B₁₀, with the corresponding isomers studied by Reis *et al.*³⁰ For B₆ Reis *et al.*³⁰ considered a benzenelike hexagonal geometry with D_{2h} symmetry, and computed the value $\alpha_{av}=101.3$ a.u. For B₈ also Reis *et al.*³⁰ considered a ringlike structure with D_{7h} symmetry and reported $\alpha_{av}=114.6$ a.u. Finally, for B₁₀ they considered a quasiplanar structure with C_{2h} symmetry and calculated $\alpha_{av}=143.7$ a.u.³⁰ These can be compared with our DFT values of α_{av} of the ladderlike B₆, B₈, and B₁₀ which were obtained to be 92.35 a.u., 130.65 a.u., and 185.53 a.u., respectively. From the comparison it is clear that although the polarizability of the benzenelike B₆ is larger than that of the ladderlike B₆, for clusters containing larger number of atoms (B₈ and B₁₀) quasi-one-dimensional ladderlike structures are more polarizable than the planar structures. Although no theoretical results on α_{av} for the planar structures of B₁₂ and B₁₄ are available, it is clear that even for those clusters ladderlike structures will be obtained to be more polarizable. The fact that for a larger number of atoms, ladderlike boron chains will be more polarizable than quasiplanar isomeric structures of boron can be understood based upon intuitive arguments. As Sabra and Boustani²⁸ showed by explicit calculations, with increasing size, the π -electron population of these ladderlike chains increases. Since the π electrons are quite delocalized along the chain direction, their response to the electric fields directed along the chain direction will be quite large leading to the large values of α_{xx} obtained in our calculations. The fact that α_{xx} increases quite rapidly with the increasing number of atoms also confirms this hypoth-

esis. Although the quasiplanar structure of boron also has π electrons due to the sp^2 hybridization, their response to the external field is distributed in two directions due to their two-dimensional character, leading to smaller polarizabilities. Therefore, it is the combined effect of π electrons and the reduced dimensionality which makes the ladderlike chains of boron more polarizable than their quasiplanar counterparts.

IV. CONCLUSIONS AND FUTURE DIRECTIONS

In conclusion, we have reported a systematic *ab initio* study of the static dipole polarizability of the linear carbon chains and the ladderlike boron chains employing Hartree-Fock, many-body, and DFT-based approaches. For closed-shell clusters the polarizabilities computed by the RHF method were generally within 5%–6% agreement with the ones computed by the CCSD(T) method. Similarly for the open-shell clusters the MRSCF polarizabilities were found to be in very good agreement with the ones computed by the MRCI method. Additionally, DFT-based results on the polarizabilities were found to be in very good agreement with the ones computed by the many-body methods. This suggests the possibility that by employing computationally less expensive approaches such as RHF, MRSCF, DFT, etc. one can perform

similar calculations on even larger and more complex clusters, and obtain reasonable results on static polarizability. We believe that such a line of investigation should be pursued in future calculations.

Our results demonstrate that in both the systems the component of the polarizability along the chain direction, as well as the average polarizability, increase with the chain size. This is fully consistent with presence of delocalized π electrons in these one-dimensional clusters. Thus, both types of clusters should be useful in nonlinear optical applications as well. Of late, the molecular-transport properties of carbon chains have been of much interest to physicists,³⁵ because of the presence of delocalized π electrons in them. However, our polarizability calculations point to the presence of delocalized π electrons also in the ladderlike boron clusters, thus rendering them possibly useful in molecular-transport-based applications. First-principles studies of the excited states and the transport properties of such clusters will be the subject of future investigations.

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