

***Ab initio* many-body calculations on infinite carbon and boron-nitrogen chains**

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In this paper we report first-principles calculations on the ground-state electronic structure of two infinite one-dimensional systems: (a) a chain of carbon atoms and (b) a chain of alternating boron and nitrogen atoms. Meanfield results were obtained using the restricted Hartree-Fock approach, while the many-body effects were taken into account by second-order Møller-Plesset perturbation theory and the coupled-cluster approach. The calculations were performed using 6-31G\*\* basis sets, including the *d*-type polarization functions. Both at the Hartree-Fock (HF) and the correlated levels, we find that the infinite carbon chain exhibits bond alternation with alternating single and triple bonds, while the boron-nitrogen chain exhibits equidistant bonds. In addition, we also performed density-functional-theory-based local-density-approximation (LDA) calculations on the infinite carbon chain using the same basis set. Our LDA results, in contradiction to our HF and correlated results, predict a very small bond alternation. Based upon our LDA results for the carbon chain, which are in agreement with an earlier LDA calculation [E.J. Bylaska, J.H. Weare, and R. Kawai, *Phys. Rev. B* **58**, R7488 (1998)], we conclude that the LDA significantly underestimates Peierls distortion. This emphasizes that the inclusion of many-particle effects is very important for the correct description of Peierls distortion in one-dimensional systems.

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**I. INTRODUCTION**

Carbon occurs in several allotropic forms depending upon the nature of its interatomic bonding. In diamond, it exhibits  $sp^3$  hybridization resulting in a three-dimensional (3D) structure. In its graphite form, it exhibits  $sp^2$  hybridization, resulting in a layered structure. While in the carbyne form, the carbon atoms exhibit  $sp$  hybridization consistent with a predominantly 1D, chainlike, character.<sup>1</sup> Although, truly infinite isolated single chains of carbon atoms do not exist in nature, however, there are several experimental examples of the tendency of carbon atoms to form 1D or quasi-1D structures. Lagow *et al.*<sup>2</sup> demonstrated that linear chains containing up to 28 atoms can be stabilized by adding nonreactive terminal groups. There is strong experimental evidence to suggest that carbon chains and rings are also precursors to the formation of more complicated structures such as fullerenes and nanotubes.<sup>3-5</sup> In addition, atom-resolved scanning-tunneling microscopy experiments, on the (100) surface of  $\beta$ -SiC indicate the formation of carbon atomic chains.<sup>6</sup> Similarly, simulations performed on tetrahedral amorphous carbon surfaces also indicate the formation of rings and chains.<sup>7</sup> Additionally, for the carbon cluster anions  $C_n^-$  there is sufficient experimental evidence to indicate the existence of chains for  $n \leq 10$ , and rings for the larger structures.<sup>8</sup>

From a theoretical point of view as well carbon chains and rings have elicited a large amount of interest.<sup>9-24</sup> Let us assume an infinitely long carbon chain (C chain hereafter), with the conjugation direction along the *x* axis. If the chain

were to have equal bond distance (cumulenic character with exclusively double bonds), then it will exhibit metallic character with the occupied band structure consisting of: (a) a core band composed of *1s* orbitals (b) a valence  $\sigma$  band consisting mainly of  $sp$  hybrids, and (c) two half-filled degenerate  $\pi$  bands at the Fermi level composed of  $\pi_y$  and  $\pi_z$  orbitals.<sup>16,19,22,23</sup> Therefore, the question arises whether such a chain will undergo a Peierls-type distortion to become an insulator with bond alternation along the chain (acetylenic character with alternating single and triple bonds). For a finite ring of carbon atoms the same question reads: will it exhibit aromatic (equal bonds) or antiaromatic (bond alternated) behavior?<sup>9-11,15</sup> Carbon rings containing  $4N$  atoms ( $N$  is an integer) undergo bond alternation due to first-order Jahn-Teller (JT) distortion.<sup>9-11,15,25</sup> However, the answer for a ring containing  $4N+2$  atoms is not straightforward because, if it undergoes bond alternation, it can only be due to a second-order JT effect.<sup>9-11,26</sup> Perhaps it is due to this uncertainty as to whether the infinite linear C chain ( $C_{4N+2}$  ring, with large  $N$ ) will undergo Peierls distortion (second-order JT effect) that has led to numerous theoretical studies of these systems.<sup>9-24,27</sup> First-principles calculations of the infinite C chain fall in two categories, namely, the Hartree-Fock<sup>21-24</sup> (HF) and the density-functional-theory (DFT) calculations.<sup>10,11,16,18,19</sup> *Ab initio* HF calculations invariably predict an infinite C chain with bond alternation to be energetically more stable as compared to the equidistant configuration.<sup>21-24</sup> However, HF calculations generally have a tendency to overestimate bond alternation, which was also evident in our previous studies on *trans*-polyacetylene.<sup>28,29</sup> It

is only the subsequent treatment of electron-correlation effects that brings the bond-alternation in such systems closer to the experimental reality.<sup>28</sup> Therefore, one would expect that the DFT-based approaches, which do include electron-correlation effects in an approximate manner, would provide an unambiguous picture. However, this is not the case. Whereas the local-density-approximation (LDA) results of Springborg and co-workers<sup>16,18,19</sup> place the bond alternation in the range  $0.1 \text{ \AA} \leq \delta \leq 0.2 \text{ \AA}$  ( $\delta = r_{\text{single}} - r_{\text{triple}}$ ), the recent LDA study of Bylaska *et al.*<sup>11</sup> predicts only a very small value  $\delta < 0.04 \text{ \AA}$  for the infinite chain. Keeping in view these conflicting results obtained for the bond alternation from the DFT calculations, and the fact that HF results tend to overestimate  $\delta$ , we believe that a systematic study of the influence of electron-correlation effects on the bond alternation in the infinite C chain is in order. Therefore, we decided to apply our *ab initio* wave-function-based many-body methodology used earlier to study a number of conjugated polymers,<sup>28,30-32</sup> to the problem of the infinite C chain as well. In addition, to put our correlated results in proper perspective, we also performed LDA calculations on the C chain using the same basis set that was used for the HF and the subsequent many-body calculations. These LDA calculations were performed using the CRYSTAL98 program.<sup>33</sup> Indeed our many-body calculations predict  $\delta \approx 0.15 \text{ \AA}$  close to the findings of Springborg and co-workers<sup>16,18,19</sup> but in complete disagreement with those of Bylaska *et al.*<sup>11</sup> However, our LDA calculations performed with the CRYSTAL98 code<sup>33</sup> predict a very small bond alternation of  $\delta \approx 0.04 \text{ \AA}$ , in excellent agreement with the LDA value of  $\delta \approx 0.036 \text{ \AA}$  reported by Bylaska *et al.*<sup>11</sup>

Another useful concept to quantify the tendency towards bond alternation is the condensation energy defined as the difference in energy/atom of the equidistant configuration and the bond alternating configuration. Our best value of the condensation energy, obtained at the many-body level using the coupled-cluster approach, is 18.4 milliHartree/atom. This value is much larger than 0.13 milliHartree/atom predicted by our LDA calculations and also the LDA value of 0.09 milliHartree/atom, reported by Bylaska *et al.*<sup>11</sup> Thus our many-body calculations indicate a much stronger tendency for the infinite carbon chain to undergo Peierls distortion as compared to the LDA calculations.

In addition to the infinite C chain, in this paper we also study an infinite chain composed of boron and nitrogen atoms (BN chain, hereafter). If we consider a two-atom unit cell, the carbon and the BN chains are isoelectronic. Thus if the two chains exhibit different behavior, it will be entirely due to the differences in the nature of bonding caused by different atomic species. As a matter of fact, starting from well-known carbon-based materials, the prospect of obtaining novel material by performing alternate boron and nitrogen substitution, has fascinated experimentalists and theoreticians alike.<sup>30,34-39,41</sup> Of course, cubic and hexagonal BN, which are the counterparts of diamond and graphite, respectively, are well-known materials. In our own earlier work,<sup>30</sup> as also in the works of Armstrong and co-workers,<sup>34</sup> the BN analogs of *trans*-polyacetylene and polyethylene were investigated theoretically. BN analogs of fullerene-like cages and

nanotubes have been studied theoretically by several authors.<sup>36,37,39</sup> Experimentally, the BN nanotubes were first synthesized by Chopra *et al.*,<sup>38</sup> while recently, multiwall BN nanotubes, as well as fullerene-like BN cages, have been synthesized by Lee *et al.*,<sup>40</sup> in a catalyst-free manner, using the laser-ablation technique. Additionally, Côté *et al.*<sup>41</sup> calculated the optical properties of the BN analogs of photoluminescent conjugated polymers poly(para-phenylene) and poly(para-phenylenevinylene). However, to the best of our knowledge, the infinite isolated BN chain has not been studied theoretically so far. Therefore, in light of the current interest in novel BN compounds structurally similar to carbon-based compounds, a parallel study of the infinite BN chain is desirable. Indeed, we find that the infinite BN chain has properties different than the infinite C chain in that it does not exhibit bond alternation. This result is similar to our earlier result where we found that the BN analog of *trans*-polyacetylene does not exhibit bond alternation.<sup>30</sup>

The remainder of this 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. APPLIED METHODS AND COMPUTATIONAL DETAILS

For the linear infinite C chain we chose a unit cell consisting of two carbon atoms, while for the BN chain a corresponding unit cell consisting of one boron atom and one nitrogen atom was considered. For both systems HF calculations were performed first to obtain the results at the mean-field level. For the dimerized C chain, as well as for the BN chain, the HF calculations were performed in the infinite system limit using both the Bloch-orbital-based electronic-structure program CRYSTAL,<sup>33,44</sup> as well as our own Wannier-function-based program WANNIER.<sup>29</sup> Both these programs use the linear combination of atomic-orbital approach based on Gaussian-type basis functions. However, for the equidistant C chain, we encountered convergence difficulties with the CRYSTAL program when diffuse basis functions were used. Therefore, for the metallic C chain, we obtained HF results by performing finite-cluster calculations using clusters of increasing size, and by ensuring that the convergence with respect to the cluster size was achieved. To further check the accuracy of the finite-cluster approach, the finite-cluster HF calculations were also repeated for the case of insulating chains for which the infinite system HF results (CRYSTAL and WANNIER) were available, and excellent agreement between the two sets of results was obtained.

As mentioned earlier, for the purpose of comparison with other approaches, we also performed LDA calculations on the infinite C chain to study its bond-alternation properties. These LDA calculations were performed with the CRYSTAL98 program,<sup>33</sup> employing the same 6-31G\*\* basis set as was used in the HF and the subsequent many-body calculations. Both in the HF and the LDA calculations performed with the

Bloch-orbital-based CRYSTAL program,<sup>33,44</sup> particular attention was paid to the convergence of total energies with respect to the number of  $\mathbf{k}$  points used in the Brillouin-zone (BZ) integration. The number of  $\mathbf{k}$  points was increased until the total energy/cell had converged at least up to  $1.0 \times 10^{-6}$  Hartrees. We noticed that using 30  $\mathbf{k}$  points in the irreducible part of the BZ was sufficient to achieve aforesaid convergence both for HF and the LDA calculations performed with the CRYSTAL program.<sup>33,44</sup> Moreover, the excellent agreement observed among the HF energies/cell computed using the CRYSTAL program, our own WANNIER program,<sup>29</sup> and the finite-cluster-based HF calculations, leaves no doubt that the convergence in energies has been achieved.

The many-body calculations beyond HF were performed only within the finite-cluster model. However, since the correlation effects are highly localized in real space, convergence with respect to the cluster size is rarely a problem here. Moreover, in our earlier calculations on the infinite LiH chain,<sup>31</sup> and the bulk LiH,<sup>42</sup> we had carefully compared the correlated calculations performed simultaneously on the infinite system and its finite cluster, and found excellent agreement between the two sets of results. The issue of the convergence of the present set of results with respect to the cluster size is very important, and, therefore, will be discussed again in Sec. III.

In order to perform the correlated calculations, three different many-body approaches, viz., second-order Møller-Plesset perturbation theory (MP2), coupled-cluster singles and doubles (CCSD), and coupled-cluster singles and doubles with perturbative treatment of the triples [CCSD(T)] were used. All the finite-cluster-based calculations, both at the HF and the correlated level, were performed with the MOLPRO molecular orbital *ab initio* program package.<sup>43</sup> In order to minimize the boundary effects associated with the finite clusters, we extracted the energy per unit cell from the finite-cluster calculations by computing the total energy differences between the clusters containing  $n$ , and  $n+1$  unit cells, with as large a value of  $n$  as feasible. In view of the typical accuracy of the periodic HF codes, i.e., 1 milliHartree per atom, we consider the results to be converged with respect to  $n$ , when the (total/correlation) energy per unit cell is stable within this accuracy. The undimerized C chain, which consists of C atoms connected by double bonds, was terminated with two H atoms on each end, and the energy/cell was computed using the expression

$$E = \lim_{n \rightarrow \infty} \Delta E_n = \lim_{n \rightarrow \infty} [E(C_{2n+2}H_4) - E(C_{2n}H_4)]. \quad (1)$$

The insulating C chain, consisting of alternating single and triplet bonds, was terminated with a single CH bond, leading to the formula

$$E = \lim_{n \rightarrow \infty} \Delta E_n = \lim_{n \rightarrow \infty} [E(C_{2n+2}H_2) - E(C_{2n}H_2)]. \quad (2)$$

As far as the BN chain is concerned, its bonding pattern is not obvious. Therefore, several end-termination schemes to saturate the dangling bonds were explored. These included

TABLE I. Total energy  $E_{tot}$  (Hartree), cohesive energy  $\Delta E_{coh}$  (eV) per unit (C-C) and bond lengths ( $\text{\AA}$ ) for the undimerized structure of the infinite carbon chain. Cohesive energies were computed with respect to separated atoms.

Method	$E_{tot}$	$\Delta E_{coh}$	$r_{double}$
Finite cluster SCF	-75.5644	5.733	1.251
MP2	-75.7847	10.327	1.268
CCSD	-75.7813	9.570	1.267
CCSD(T)	-75.7996	10.052	1.272

terminating the chains with: (a) one H atom on each end, (b) two H atoms on each end, and (c) unequal number of H atoms on the two ends. However, converged energies per cell were found to be quite insensitive to the end geometry of the chain. Therefore, in close analogy with the undimerized C chain, we finally settled with terminating the BN chain with two H atoms on each end, and the expression

$$E = \lim_{n \rightarrow \infty} \Delta E_n = \lim_{n \rightarrow \infty} [E(\{BN\}_{n+1}H_4) - E(\{BN\}_nH_4)] \quad (3)$$

was used to compute its energy per unit cell. As discussed in the following section, the HF energy/cell of the BN chain obtained by this method is in excellent agreement with the ones obtained from the infinite-chain calculations performed with the CRYSTAL and WANNIER programs. Therefore, we believe that the aforesaid termination scheme, which effectively models a BN chain as composed of double bonds, is a sound one.

### III. RESULTS AND DISCUSSIONS

Calculations on both the systems were performed with 6-31G\*\* basis sets. For the HF calculations on the infinite insulating chains, we had to increase the outermost  $p$ -type exponents of the original basis sets because of the linear-dependence-related problems. This led to 0.29871 for carbon (original 0.16871), 0.16675 for boron (original 0.12675), and 0.29203 for nitrogen (original 0.21203). The outermost  $s$ -type exponents of the original basis set were left unaltered. The  $d$ -type exponents used for each atom were: 0.8 for carbon, 0.6 for boron, and 0.8 also for nitrogen. These  $d$  exponents were preferred over the original  $d$ -type exponents available from the MOLPRO library,<sup>43</sup> because they led to lower total energies. For the correlated calculations, we used the original basis set to compute the energy/cell and the correlation energy was computed by subtracting from it the HF energy/cell obtained by finite-cluster calculations done also with the original basis set. In this manner, we ensured that no spurious contributions to the correlation energy were obtained because of the use of two different basis sets during these calculations. Next we discuss the results obtained for the two systems in detail.

#### A. Carbon chain

Our final results for the equidistant and dimerized C chains, employing the wave-function-based approaches [HF,

TABLE II. Total energy  $E_{tot}$  (Hartree), cohesive energy  $\Delta E_{coh}$  (eV) per unit (C-C) and bond lengths ( $\text{\AA}$ ) for the dimerized structure of the infinite carbon chain. Cohesive energies were computed with respect to separated atoms.

Method	$E_{tot}$	$\Delta E_{coh}$	$r_{single}$	$r_{triple}$
WANNIER SCF	-75.5807	6.176	1.367	1.173
CRYSTAL SCF	-75.5798	6.150	1.369	1.173
Finite cluster SCF	-75.5810	6.184	1.360	1.174
MP2	-75.8232 <sup>a</sup>	11.375	1.337	1.217
CCSD	-75.8220 <sup>a</sup>	10.678	1.362	1.197
CCSD(T)	-75.8364 <sup>a</sup>	11.053	1.358	1.207

<sup>a</sup>Correlation contributions added to CRYSTAL SCF energies.

MP2, CCSD, CCSD(T)], are presented in Tables I and II, respectively. Results of our LDA calculations performed with CRYSTAL98 program,<sup>33</sup> along with the comparison of our results with those of other authors, are presented in Table III. As mentioned earlier we experienced convergence difficulties with the CRYSTAL program for the undimerized chain, so HF results for that system were obtained by the finite-cluster approach only. Moreover, all the correlated calculations were also done in a finite-cluster model. Therefore, it is important for us to demonstrate the convergence of all the finite-cluster-based results for both the undimerized and the dimerized C chain as a function of the cluster size.

Total HF energy/cell as a function of the number of unit cells  $n$  in the cluster is plotted in Fig. 1, and it is clear that the convergence with respect to the cluster size has been achieved both for the dimerized and undimerized chains, at least, to the milliHartree level. Table I also presents the total energy/cell for the undimerized chain including contributions of the electron-correlation effects, while the corresponding data for the dimerized chain is presented in Table II. The convergence of the correlation energy/cell computed by the CCSD(T) method for both types of chains, with respect to

the cluster size, is presented in Fig. 2. It is clear from these figures that the energies for the dimerized chain converge very rapidly, consistent with our intuitive picture of localized electrons in such systems. The convergence in the undimerized chain, although comparatively slower, has also been achieved, at least, to the milliHartree level.

The optimized geometries reported in this work were obtained by the usual procedure of first performing several total energy calculations for various geometry parameters, and then fitting the results by a least-squares procedure to polynomials of suitable degrees. The fact that the finite-cluster results at the HF level agree fully with those obtained by the CRYSTAL and WANNIER programs gives us added confidence in their correctness. It is clear that the dimerized structure is energetically much more stable as compared to the metallic one, at all levels of calculations [SCF, MP2, CCSD, CCSD(T)]. At the HF level we obtained a percentage bond alternation  $\delta(\%)=14.5\%$  [where  $\delta(\%)=(\delta/r_{av})\times 100$ , with  $r_{av}=(r_{single}+r_{triple})/2$ ], and at the CCSD(T) level of correlation it reduces to 11.8%. The condensation energy, defined earlier as the difference in the total energy/atom between the optimized undimerized and the dimerized C chains, at various levels of correlation treatments, is obtained to be  $E_{cond}^{HF}=8.8$  milliHartrees,  $E_{cond}^{MP2}=19.25$  milliHartrees,  $E_{cond}^{CCSD}=20.35$  milliHartrees, and  $E_{cond}^{CCSD(T)}=18.4$  milliHartrees. Thus, based on the CCSD(T) approach, which is the most sophisticated correlation approach that we have used in these calculations, our final result for the condensation energy of an infinite C chain of 18.4 milliHartrees/atom. As reported in Table III, the value of condensation energy obtained from our LDA calculations performed with CRYSTAL98 program<sup>33</sup> was 0.13 milliHartrees/atom, which is very close to the LDA value of 0.09 milliHartrees/atom reported by Bylaska *et al.*,<sup>11</sup> and much smaller than our many-body results based upon the CCSD(T) method.

The summary of our many-body and LDA results, along with those obtained by other authors is presented in Table III.

TABLE III. Infinite carbon chain: comparison of the present results with those of other authors. The percentage bond alternation  $\delta(\%)=(\delta/r_{av})\times 100$ , where  $\delta=r_{single}-r_{triple}$ , and  $r_{av}=(r_{single}+r_{triple})/2$ .

Author	Method	$r_{single}$ ( $\text{\AA}$ )	$r_{triple}$ ( $\text{\AA}$ )	$\delta(\%)$	$E_{cond}$ (mHartrees/atom)
This work	RHF	1.360	1.174	14.5	7.80
This work	CCSD(T)	1.358	1.207	11.8	18.40
This work	LDA	1.286	1.246	1.6	0.13
Bylaska <i>et al.</i> <sup>11</sup>	LDA	1.288 <sup>a</sup>	1.252 <sup>a</sup>	2.9 <sup>b</sup>	0.09 <sup>b</sup>
Eriksson <i>et al.</i> <sup>16</sup>	LDA	1.376	1.296	6.0	
Springborg <i>et al.</i> <sup>18</sup>	LDA	1.503	1.259	18.0	
Springborg <sup>19</sup>	LDA	1.439	1.249	14.1	
Karpfen <sup>22</sup>	RHF	1.363	1.198	12.9	
Kertész <i>et al.</i> <sup>23</sup>	RHF	1.145 <sup>c</sup>	1.405 <sup>c</sup>	20.4	
Kertész <i>et al.</i> <sup>24</sup>	UHF	1.335	1.185	11.9	
Teramae <i>et al.</i> <sup>21</sup>	RHF	1.339	1.166	14.1	

<sup>a</sup>Calculated from the average bond distance of 1.270  $\text{\AA}$  and  $\delta=2.9\%$ .

<sup>b</sup>Upper limit (Ref. 11).

<sup>c</sup>Calculated from the average bond distance of 1.275  $\text{\AA}$  and  $\delta=20.4\%$ .



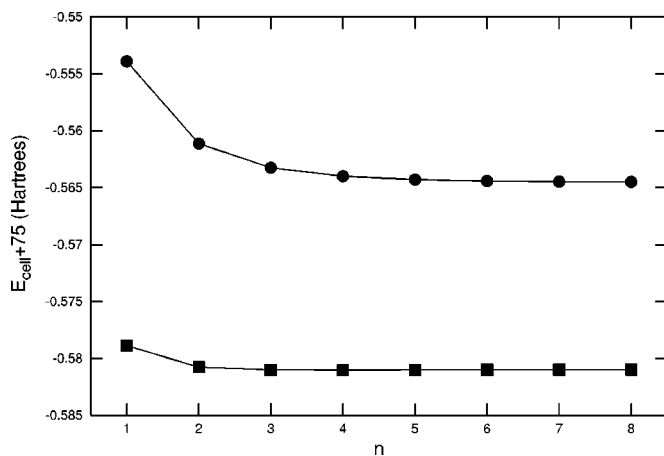


FIG. 1. Total HF energy per unit cell for both the undimerized (circles) and dimerized (squares) carbon chains computed by the finite-cluster approach [cf. Eqs. (1) and (2)], plotted as a function of the number of unit cells  $n$ . Two carbon atoms were assumed per unit cell. The bond distances in these calculations correspond to the optimized geometries reported in Tables I and II.

It is clear from the table that the results obtained by various authors on the optimized geometry parameters of the C chain vary quite a bit, however, almost all of them report the bond alternation to be more than 10%. The exceptions to this result are (a) our own LDA calculation [ $\delta(\%)=1.6$ ], (b) LDA calculations of Eriksson *et al.*<sup>16</sup> [ $\delta(\%)=6.0$ ], and (c) LDA calculations of Bylaska *et al.*<sup>11</sup> [ $\delta(\%)=2.9$ ]. Thus these recent LDA results, which predict rather small bond alternation for the C chain, are in contradiction with the older LDA calculations,<sup>18,19</sup> as well with our many-body results. We believe that one should expect a rather small bond alternation from the LDA-based calculations, because the homogeneous-electron-gas approximation therein leads preferentially to a metallic ground state. At this point, we would like to mention that recently Torelli and Mitas<sup>9</sup> performed

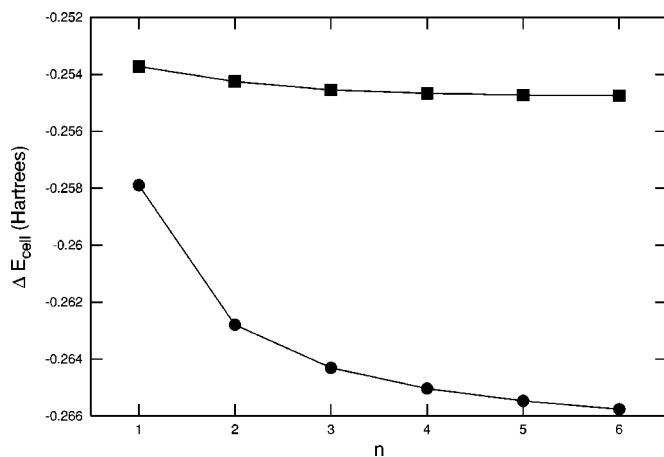


FIG. 2. Correlation energy per unit cell computed by the CCSD(T) approach both for undimerized (circles) and dimerized (squares) finite carbon chains, plotted as a function of the number of unit cells  $n$  in the finite cluster. For the undimerized chain  $r_{double} = 1.26$  Å, and for the dimerized chain  $r_{single} = 1.37$  Å, and  $r_{triple} = 1.175$  Å.

TABLE IV. Total energy  $E_{tot}$  (Hartree), cohesive energy  $\Delta E_{coh}$  (eV) per unit (BN) and B-N bond length  $r_{BN}$  (Å) of the infinite boron-nitrogen chain. Cohesive energies were computed with respect to separated atoms.

Method	$E_{tot}$	$\Delta E_{coh}$	$r_{BN}$
WANNIER SCF	-79.1801	7.5845	1.287
CRYSTAL SCF	-79.1794	7.5656	1.288
Finite cluster SCF	-79.1773	7.5076	1.287
MP2	-79.3968 <sup>a</sup>	11.9478	1.300
CCSD	-79.4017 <sup>a</sup>	11.4723	1.299
CCSD(T)	-79.4113 <sup>a</sup>	11.7204	1.301

<sup>a</sup>Correlation contributions added to CRYSTAL SCF energies.

calculations on the optimized ground-state geometries of  $C_{4N+2}$  rings using a quantum Monte Carlo method and their results for the bond alternation for the  $C_{18}$  and  $C_{22}$  rings were 7%. Although, our final CCSD(T) result of 11.8% bond alternation for the infinite C chain is more than that obtained by Torelli and Mitas<sup>9</sup> for the large C rings, yet we believe that qualitative trends indicated by most of the calculations suggest a significant bond alternation in the infinite C chains. In this context we would like to mention that for the finite ring systems containing  $4N+2$  carbon atoms, the Hückel theory predicts that the bond alternation due to the second-order Jahn-Teller distortion will increase with increasing  $N$ , eventually coalescing with the value corresponding to the Peierls distortion, for  $N \rightarrow \infty$ .<sup>45</sup> Discounting the basis-set effects, in our opinion, our value of bond alternation of 11.8% for the infinite C chain, as compared to 7% reported by Torelli and Mitas<sup>9</sup> for the  $C_{22}$  rings, is indicative that the aforesaid Hückel result is valid even when the many-body effects have been included.

Other authors have not reported the value of the condensation energies obtained in their calculations. But, based on the trends visible from the calculations on bond alternation, we believe that it is safe to assume that the condensation energy for the infinite C chain is in excess of 10 milliHartrees/atom. Thus for condensation energy, our many-body results, as well that of the Torelli and Mitas<sup>9</sup> for the finite rings, are quite different from our LDA results of 0.14 milliHartree/atom, and 0.1 milliHartree/atom reported by Bylaska *et al.*<sup>11</sup>

## B. BN chain

As mentioned earlier, in nature there appears to be a one-to-one correspondence between several structures of carbon and BN allotropes, such as diamond vs cubic BN, graphite vs hexagonal BN, and carbon nanotubes vs BN nanotubes etc. Therefore, it will be natural to assume that a BN chain, similar to a carbon chain, will also have a strictly linear geometry exhibiting  $sp$ -type hybridization with,  $180^\circ$  bond angles. However, this being the first theoretical study of this system, we decided to be careful with this assumption. Therefore, in our calculations, along with the linear geometry, we also explored the energetics of various zigzag structures of the BN chain. However, we found that in all cases the zigzag struc-

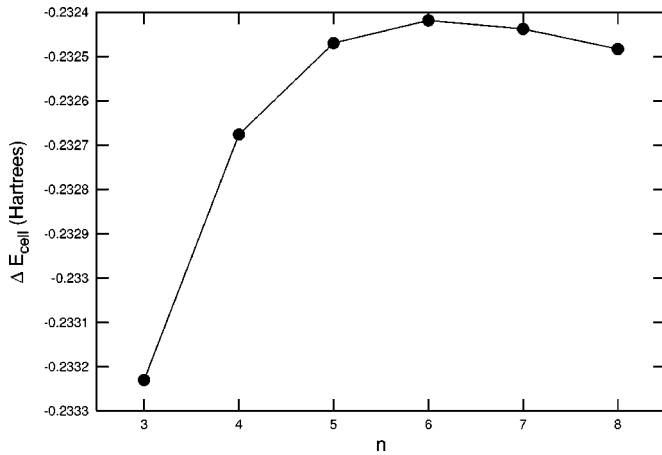


FIG. 3. Correlation energy per unit cell of finite boron-nitrogen chains computed by the CCSD(T) approach, plotted as a function of the number of unit cells  $n$  in the finite cluster. The bond distance was taken to be  $r_{\text{BN}} = 1.301 \text{ \AA}$ .

ture led to higher energies compared to the linear one, leading us to the conclusion that if the BN chains exist, similar to the C chains, they will have a linear structure. Table IV presents the results of our calculations for the BN chain both at the HF and the correlated levels. Since we obtained perfect agreement on the HF energy/cell for the BN chain from WANNIER, CRYSTAL, and finite-cluster-based approaches, we are again very confident of the correctness of our correlated studies performed on finite BN clusters saturated with hydrogens on the ends. To further confirm this point, in Fig. 3 we present the variation of the correlation energy/cell of BN chain, as a function of the number of unit cells in the cluster. It is obvious from the figure that satisfactory convergence in correlation energy has been achieved. At the CCSD(T) level we obtain a cohesive energy of 11.72 eV/cell, which is somewhat greater than the value of 11.05 eV/cell obtained for the dimerized C chain. This means that from an energetic point of view, the BN chain should at least be as stable as an isolated C chain, and, therefore, the probability of finding linear  $sp$ -type hybridized structures composed of BN units should be as high as that of the C units.

The other remarkable aspect of the BN chain, as compared to the C chain, is that it does not exhibit any bond alternation. This result is identical to our earlier theoretical study on polyiminoborane, which is the BN substituted analog of *trans*-polyacetylene.<sup>30</sup> In contrast to *trans*-polyacetylene that exhibits a bond alternation close to 0.1  $\text{\AA}$ , in case of polyiminoborane we obtained optimized geometries with equidistant BN atoms.<sup>30</sup> Of course, the Peierls theorem<sup>46</sup> does not apply to BN chain or polyiminoborane, because these systems are insulators even without bond alternation.<sup>47</sup> However, the absence of bond alternation in BN compounds can be understood from a different line of reasoning as well. BN systems, being heteronuclear in nature, have significant ionic contributions to bonding as opposed to the purely covalent carbon-based materials. Therefore, in BN systems in addition to the covalent interactions, electrostatic attraction between the B and N sites will also exist because of a degree of ionicity. It is this electrostatic

interaction due to ionicity in the BN systems that, in our opinion, leads to equal bond lengths. The optimized BN distance at the CCSD(T) level was obtained to be 1.3  $\text{\AA}$ , which is slightly more than the optimized average bond distance of 1.28  $\text{\AA}$  obtained for the infinite C chain. For the linear chain, our optimized BN distance of 1.3  $\text{\AA}$  should be compared to the in-plane BN distance of 1.45  $\text{\AA}$  in the hexagonal BN, and the BN distance of 1.57  $\text{\AA}$  observed in the cubic BN. The significant difference in these three BN distances is consistent with the fact that the BN chain, hexagonal BN and the cubic BN originate from very different bonding schemes based on  $sp$ ,  $sp^2$ , and  $sp^3$  hybridizations, respectively.

#### IV. CONCLUSIONS

In conclusion, we have presented an *ab initio* study of the ground-state properties of the infinite carbon and boron-nitrogen chains. The influence of electron-correlation effects was included by several approaches including the coupled-cluster method accounting for up to triple excitation operators. As far as the carbon chain is concerned, all our many-body calculations predict a dimerized ground state, consistent with the phenomenon of Peierls distortion. Thus our calculations on the infinite C chain based upon many-body methods, such as, the coupled-cluster approach, are in agreement with the Monte Carlo calculations of Torelli and Mitas<sup>9</sup> performed on carbon rings, which also revealed a strong tendency of these systems to exhibit bond alternation in the infinite chain limit. We also performed a parallel LDA calculation on the infinite C chain, which predicted very weak dimerization, in excellent quantitative agreement with the recent LDA results of Bylaska *et al.*<sup>11</sup> This, in our opinion, establishes in most unambiguous manner that LDA underestimates Peierls distortion in one-dimensional systems, and that powerful many-body methods, such as, the coupled-cluster approach, are essential for the correct description of the broken-symmetry ground state.

In addition, we also presented first principles correlated calculations on the ground state of an infinite boron-nitrogen chain. Based upon our calculations we conclude that the boron-nitrogen chain has a higher cohesive energy/cell as compared to the carbon chain, thus making BN-based 1D structures energetically at least as favorable as the carbon-based ones. Of course, it is a difficult task to synthesize isolated infinite atomic chains. However, similar to the case of carbon, it should certainly be possible to test in the laboratory whether finite one-dimensional clusters based on BN units exist. Along the same lines, it will also be worthwhile to theoretically optimize the geometries of the ground states of various BN-based finite clusters. In addition to the ground state, theoretical studies of their optically excited states will also be useful because they, in conjunction with photoabsorption-based experiments, can be used to characterize various clusters. We will investigate the electronic structure of BN clusters in a future publication.

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