Electronic and piezoelectric properties of BN nanotubes
from hybrid density functional method

H. J. Xiang,1,2 Z. Y. Chen,1,2 and Jinlong Yang1,2,3

1Hefei National Laboratory for Physical Sciences at Microscale,
University of Science and Technology of China,
Hefei, Anhui 230026, People’s Republic of China
2USTC Shanghai Institute for Advanced Studies,
University of Science and Technology of China,
Shanghai 201315, People’s Republic of China

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Abstract

The electronic and piezoelectric properties of the boron nitride (BN) nanotubes are investigated with the hybrid density functional (B3LYP) method. We first study bulk h-BN and BN sheet and find that the B3LYP band structure and energy gap are consistent with the GW results. The B3LYP band gap is larger than the LDA one by about 1.8 eV for both zigzag and armchair nanotubes with various radius. We give an alternative interpretation that the optical absorption lines at 4.45 eV might be due to the electron transition in small zigzag BN nanotubes. The piezoelectric constant from the B3LYP method for zigzag BN nanotubes are substantially larger than those in the PVDF polymer family, suggesting BN nanotubes as candidates for various nanoelectromechanical applications.

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Since their discovery in 1991, carbon nanotubes have attracted considerable interest worldwide because of their unusual properties and great potentials for technological applications. Simple p-band tight-binding model predicts that depending on the way of the rolling up the nanotube can be metallic or semiconducting or insulating.

Soon after the discovery of carbon nanotubes it became obvious that similar nanostructures could be formed by other elements and compounds which form layered structures bearing some resemblance to graphite. For example, hexagonal BN (h-BN) was predicted on the basis of theoretical calculations to be capable of forming nanotubes, a prediction which was later confirmed experimentally by the synthesis of such nanotubes. They are predicted to be semiconductors regardless of diameter, chirality, or the number of walls of the tube. This contrasts markedly with the heterogeneity of electronic properties of carbon nanotubes, and also makes pure BN nanotubes particularly useful for potential device applications. Furthermore, recent experiments indicated that BN nanotubes exhibit a stronger resistance to oxidation at high temperatures than carbon nanotubes. So as far as the optical and optoelectronic applications of nanotubes are concerned, BN nanotubes could be superior to carbon nanotubes. An important parameter for optical and optoelectronic applications is the optical band gap. Although all studies agree that BN nanotubes are semiconductors, however, the magnitude of the band gap of BN nanotubes and the band gap dependence on the chirality and radius are on debate in the literature. For example, Blase et al. showed that BN nanotubes are wide-gap semiconductors with a constant band gap of about 5.5 eV that is independent of the radius and helicity by carrying out local-density approximation (LDA) and quasiparticles calculations. A time-dependent localized-density-matrix calculation on BN nanotubes based on a semiempirical Hamiltonian indicated that the optical gap of BN nanotubes is independent of the chirality with a given tube diameter but dependent on both the tube length and the tube diameter. In contrast, two independent LDA calculations show that though the band gap of all the single-walled nanotubes with a diameter larger than 15 Å is independent of diameter and chirality, the band gap of the zigzag nanotubes with smaller diameters decreases strongly as the tube diameters decrease and that of the armchair nanotubes has only a weak diameter dependence. Experimentally, the measured band gap for BN nanotubes varies from 4.5 eV to 5.5 eV depending on the measurement method and the different synthesized BN nanotubes. Clearly, more theoretical studies employing reliable methods are needed to clarify the issue on the band gap of BN nanotubes.
It is well known that energy gaps between occupied and empty bands provided by LDA deviate much more from experimental values. One of the successful methodologies to correct the LDA band gap is using the GW approximation. The GW approximation takes account of dynamical screening effect of electrons within the random-phase approximation and has been applied to a wide range of semiconductors, and turned out to improve the band gap significantly to LDA. The quantum Monte Carlo (QMC) method has also been used to estimate excitation energies based on explicitly correlated wavefunctions. However, these calculations are computationally very demanding and only applicable to relatively small systems in spite of considerable progress made in developing more efficient computational algorithms. Recently, the B3LYP hybrid density functional method, which is well known in the study of thermochemistry of atoms and molecules, has been applied to some periodic systems. A recent study indicated that B3LYP reproduces observed band gaps reliably in a wide variety of materials, the B3LYP band gap is at least as accurate as that obtained with sophisticated correlated calculations or perturbation theories.

Recently, electric polarization, piezoelectricity, and pyroelectricity in BN nanotubes have attracted much interest. Using LDA calculation, Nakhmanson et al. showed that BN nanotubes are excellent piezoelectric systems with response values larger than those of piezoelectric polymers. However, previous studies on BeO and ZnO showed that the piezoelectric constants depend on the chosen functional: LDA always gives the largest absolute value for the piezoelectric constants, whereas the lowest absolute value is provided either by HF or B3LYP. So the question that how large the piezoelectric constants of BN nanotubes can be is opening. Here, in this work, we recalculate the piezoelectric constants in BN nanotubes using B3LYP functional.

In this paper, we study the electronic and piezoelectric properties for BN nanotubes using the B3LYP method. In the hybrid functional scheme the nonlocal Hartree-Fock (HF) approach is mixed into the energy functional of the GGA. Here, the Perdew-Wang gradient-corrected correlation energy, which was used in the original work of Becke, is replaced by Lee-Yang-Parr correlation energy. The calculations are carried out with the CRYSTAL package. The basis vectors for expanding the Kohn-Sham orbitals are linear combinations of atom-centered Gaussian basis sets. The all-electron basis sets adapted in the calculations are 6-21G* for B and N. The integration in reciprocal space has been carried out using a 1×1×16 Monkhorst-Pack k-point mesh to give well converged energy. We adopt
7, 7, 7, 7, and 14 as the integral tolerances to obtain high precision in monoatomic and bielectronic integrals. The total energy convergence threshold exponent is set as 9.

A single-walled BN nanotube is formed when a piece of hexagonal BN (h-BN) sheet is wrapped into a cylindrical form, the edges are seamlessly joined together and the ends of the cylinder closed. So to get the properties of BN nanotubes, as a first step, we start to study bulk h-BN and an isolated BN sheet. The crystalline structure of h-BN is hexagonal and has the $D_{6h}^4$. It consists of hexagonal graphite-like sheets but with an ABAB stacking with boron atoms in layer A found directly below nitrogen atoms in layer B. The experimental lattice parameters (a = 2.504 Å and c/a = 2.66) are used to perform all calculations. The isolated BN sheet is simulated by a two-dimensional (2D) hexagonal slab model with $a = 2.504$ Å. Fig. 1 shows the band structures for bulk h-BN and BN sheet. In addition, their LDA band structures are also shown in Fig. 1. We find that both B3LYP and LDA predict an indirect band gap between the bottom of the conduction band at the M point and the top of the valence band near K. The indirect and direct band gaps for bulk h-BN are shown in Table. I. The agreement between our B3LYP band gaps and previous GW values is very good. In fact, besides the band gap agreement, we find the B3LYP band structure also agrees well with the GW result: the difference between B3LYP result and LDA one is strongly dependent on the degree of orbital localization and that the overall corrections can not be reproduced by a rigid band shift of the conduction states with respect to the top of the valence states. For the isolated BN sheet, our results indicate that it is a direct gap at K semiconductor with an energy gap of 4.50 eV and 6.30 eV within LDA and B3LYP respectively. The good agreement between our B3LYP results and GW ones indicates that B3LYP describes very well the band gap and band structure for such systems composed by BN layers.

Now we turn to study BN nanotubes. First we fully optimized the zigzag BN(n,0) nanotubes with $n = 5 - 15$ and armchair BN(n,n) nanotubes with $n = 3 - 8$ using the B3LYP functional. The relaxed geometries for BN nanotubes are similar with previous LDA calculations. LDA is well known to predict good structural parameter but strongly underestimate the band gap for semiconductors. Here we discuss mainly the electronic properties obtained from the B3LYP calculations. We plot the band gap dependence upon radius of BN nanotubes in Fig. 2. First, the B3LYP band gap dependence is almost the same as previous LDA results: The energy gap of small zigzag BN nanotubes decreases
rapidly with the decrease of radius, in contrast, the energy gap armchair BN nanotubes has weak radius dependence. Secondly, the difference in the band gap between B3LYP band gap and LDA one is almost a constant (about 1.8 eV) for both zigzag and armchair nanotubes with various radius. Thirdly, For BN nanotubes with radius larger than 6 Å the B3LYP band gap is about 6.20 eV, agreed well with the B3LYP band gap for the isolated BN sheet. In a very recent study on BN nanotubes, three optical absorption lines were observed by means of optical absorption spectroscopy. The absorption line at 5.5 eV was attributed to the transitions between pairs of van Hove singularities in the one-dimensional density of states of BN single-wall nanotubes. The low energy line at 4.45 eV was considered to caused by the existence of a Frenkel exciton with a binding energy in the 1 eV range. From our calculation, the absorption line at 4.45 eV might also result from the transitions between pairs of van Hove singularities of BN nanotubes, such as BN(6,0) nanotube. Since B3LYP gives almost the same band structure for bulk h-BN as the GW quasiparticle one, it is expected that B3LYP would also give the accurate band structures for BN nanotubes. Thus we present the band structures for BN(5,5) and BN(6,0) nanotubes in Fig. 3. Both B3LYP and LDA results are shown. We can see that the difference between B3LYP band LDA band structures can’t be described by just raising the conduction band by the band gap difference. Not only the conduction bands are shifted upwards, but also the B3LYP valence bands below 3 eV with respect to the valence top differ significantly from the LDA counterpart: The most obvious difference is the B3LYP bands at about −15 eV below the valence top shift downwards 1.5 eV.

In the last decade, it has become possible to evaluate the components of the piezoelectric tensor and other dielectric properties such as the spontaneous polarization and the effective Born charges through a technique based on the evaluation of one Berry phase. The Berry-phase method can be employed to compute piezoelectric properties, which are directly related to polarization differences between strained and unstrained tubes. As most BN nanotubes synthesized experimentally are of zig-zag type, we only study the piezoelectric properties of zig-zag BN nanotubes. In the calculations, we model the isolated BN nanotubes with the supercell large enough to prevent the neighbour BN walls from interacting. However, since piezoelectric constants are well defined for three-dimensional systems and in order to better compare with previous LDA results, the calculated piezoelectric constants are normalized using the ratio between the volume of the supercell and that of the bundle.
of nanotubes assuming a close packed geometry with intertube equilibrium distance of 3.2 Å. For zig-zag BN nanotubes, the only surviving piezoelectric strain tensor component is $e_{33} = \delta P_3/\epsilon_3$, where $\epsilon_3 = c - c_0/c_0$ ($c$ is the lattice constant and $c_0$ is equilibrium values of $c$). The piezoelectric constant for different zigzag BN nanotubes are plotted in Fig. 4. If we assume that one BN pair contributes the same to $e_{33}$ for all zigzag BN nanotubes with various radius, $e_{33}$ should be approximately inversely proportional to the radius of the BN nanotube. It is indeed the case for $n > 5$, however, there is an abnormal small decrease of $e_{33}$ for BN(5,0) nanotube. We attribute the abnormal phenomenon to the strong $\sigma - \pi$ hybridization in BN(5,0) nanotube. Comparing with the LDA results obtained by Nakhman-son et al., the current B3LYP piezoelectric constants have similar magnitude. However, the LDA piezoelectric constants increase along with the decrease of the radius, in other words, BN(5,0) nanotube has the largest piezoelectric constant for all BN nanotubes studied. The discrepancy between our B3LYP and previous LDA results may result from the different functionals employed. As mentioned above, previous studies implied that piezoelectric constants for ZnO and BeO calculated using different Hamiltonians differ substantially. Here, we find that within both LDA and B3LYP, the piezoelectric constants for zig-zag BN nanotubes have similar magnitude, substantially larger than those (about 0.12 C/m$^2$) in the PVDF polymer family.

By employing the B3LYP functional, we examine the electronic and piezoelectric properties of BN nanotubes. The applicability of the B3LYP method in such BN systems is illustrated by the similarity between the B3LYP band structure of bulk h-BN and previous GW quasi-particle band structure. The current work supports previous LDA results that the energy gap of small zigzag BN nanotubes decreases rapidly with the decrease of radius, whereas, the energy gap of armchair BN nanotubes almost remains constant. The obtained B3LYP band gap is larger than the LDA one by almost constant (about 1.8 eV) for nanotubes with various chirality and radius. We give an alternative interpretation that the absorption lines at 4.45 eV might be due to the electron transition in small zigzag BN nanotubes. The piezoelectric constant within the B3LYP formalism for zigzag BN nanotubes are substantially larger than those in the PVDF polymer family, thus piezoelectric BN nanotubes hold promise for application in nanometer scale sensors and actuators.

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* Corresponding author. E-mail: jlyang@ustc.edu.cn

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TABLE I: Band gaps of bulk h-BN

|          | E\textsubscript{g} (eV) | B3LYP | Our LDA | Others’ LDA | GW     |
|----------|--------------------------|--------|---------|-------------|--------|
| direct   | 6.33                     | 4.48   | 4.46    | 6.47        |        |
| indirect | 6.06                     | 4.22   | 4.02    | 5.95        |        |

FIG. 1: (Color online) B3LYP and LDA band structures of (a) bulk h-BN and (b) an isolated BN sheet.
FIG. 2: B3LYP band gaps of BN($n, 0$) zigzag nanotubes with $n = 5 – 15$ and BN($n, n$) armchair nanotubes with $n = 3 – 8$. The radius refers to that of an unrelaxed BN nanotube. For comparison, previous LDA results are also reproduced here.

FIG. 3: (Color online) B3LYP and LDA band structures of (a) armchair BN(5,5) nanotube and (b) zig-zag BN(6,0) nanotube.
FIG. 4: Piezoelectric constant for zig-zag BN$(n, 0)$ nanotubes assembled in a bundle assuming a close packed geometry with intertube equilibrium distance of 3.2 Å.