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Structure and electronic properties of armchair boron nitride nanotubes

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Abstract

The structure and electronic properties of armchair boron nitride nanotubes have been investigated as a function of tube diameter using density functional theory. The length of each nanotube is kept constant. The structural parameters of the open end nanotube are studied. The variation in structural parameters is analyzed based on atomic charges of Mulliken and natural population analyses schemes. A topological analysis for charge density (ρ), and its second derivative ($\nabla^2\rho$) for bonds have been performed using atoms in molecules (AIM) theory. Finally, the analysis of the charge distribution and charge transfer processes have been studied using the NBO partitioning scheme, which helps us to understand the interactions inside the boron nitride nanotubes which are responsible for the stabilization of the armchair boron nitride nanotubes.

Keywords: Density functional theory; Boron nitride nanotubes; Topological properties; Mulliken population analysis; Natural population analysis; Atoms in molecules; Natural bond orbital

1. Introduction

Nanotubes have received much attention, since the discovery of carbon nanotubes in 1991 [1] and has opened up entirely new opportunities for the development of material science and engineering. One-dimensional nanostructure has become popular because of their importance in both the mesoscopic research and the development of nanodevices [2]. A carbon nanotube is a system that has many similarities with traditional crystal materials, because of the periodic lattice structures, but at the same time it can also be thought of as a molecular chain. A remarkable feature with respect to traditional solid state structures is the fact that carbon nanotubes like ordinary molecules deform under external forces and the electrical properties may change, in particular, the band gap may vary. Nanotubes with new shapes or compositions are prepared by drilling a hole in the anode and filling it with various materials. Abundant production of single wall nanotubes is achieved when the filling material is a mixture of graphite and cobalt [3]. The various mixtures of a metal with graphite were shown to produce nanotubes filled with the corresponding metal or carbides [4]. Finally the carbon network is partially substituted by boron and nitrogen either by using a mixture of boron and graphite and replacing the usual helium atmosphere by nitrogen [5] or by placing a hot pressed BN rod inside the drilled anode [6].

Similar to carbon nanotubes, boron nitride nanotubes (BN) represent an important class of nanotubes. Based upon similarities between carbon and BN-based materials, the existence of boron nitride nanotube was proposed [7]. The electronic structure of a single walled carbon nanotube can be either metallic or semiconductor [8]. Unlike carbon nanotube, boron nitride nanotube is a semiconductor [9] and hence this unique property helps in replacing carbon nanotubes in field effect nanotransistors, since the electric field is easily screened by metallic carbon nanotubes [10]. Electronic structure calculations indicate that, contrary to carbon nanotubes, they are constant band gap materials, which provide interesting possibilities for potential device

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applications [11]. Nanotubes with reduced number of layers including single-layer tubes are also formed with boron nitride [12].

BN nanotubes are considered to be a promising material for electronic industry, due to their structure and physical properties. The stability of this nanotube was first predicted based on tight binding [13] and first principles [14] calculations. This was first synthesized by Chopra et al. [15]. Recently Lee et al. [16] have fabricated single walled BN nanotubes in gram quantities. The mechanical, electronic, thermal and chemical properties of these materials suggest that BN nanotubes could be a useful component for many complex nano systems. Chang et al. [17] have predicted a giant thermal isotope effect for quasi one-dimensional boron nitride nanotubes, supporting predictions that low dimensional materials can have dramatic thermal isotope effects. The high thermal conductance of individual tubes or tubes in arrays might be exploited for thermal management applications, an issue of great current concern in electronics and power industries. Specifically boron nitride nanotubes could serve as electrically insulating yet highly thermally conducting wires, efficiently removing heat locally and piping it away via nanotube based phonon wave guides.

Boron nitride nanotubes are chemically inert, having a high temperature resistance to oxidation than carbon nanotubes and hence they are better candidates for composite materials. A recent theoretical study [18] has shown the existence of piezo electricity in boron nitride nanotubes due to the polar nature of the B–N chemical bond and the geometric phase involving quantum confinement effect. It is clear that BN nanotubes possess very interesting properties when compared with carbon nanotube and it is foreseen that this system will revolutionize some aspects of nanotube science and technology and thus opening a vast field of experimental and theoretical research. In actual practice, only the smallest carbon nanotubes are semiconducting and when the diameter increases, it regains the properties of graphite that is semi-metallic. Since BN nanotubes are found to be semiconductor irrespective of diameter, we have made an attempt to study the structural and electronic properties as a function of diameter.

Even though Hernandez et al. [19] have shown that the carbon nanotubes have a higher Young's modulus rather than any composite nanotubes, the structure of these new boron–nitrogen containing fullerenes and nanotubes have been studied and compared with that of carbon nanotubes [20]. In particular, it has been noted that BN–NT's have an almost constant band gap of 5.5 eV with respect to the geometric configuration of the tube, whereas the band gap of carbon nanotubes show a strong geometry dependence [14]. Ooi et al. [21] have calculated properties such as bulk modulus, cohesive energy and lattice constants to determine the relative predictive abilities of hexagonal boron nitride using density functional theory calculations. In fact, today BN structures are believed to lead to incredibly durable material that could have even better electronic qualities than carbon counterparts. Given the aforementioned studies on boron nitride nanotubes, the atomic and electronic structure studies on these boron nitride nanotubes are more complex and however is still lacking. The purpose of the present work is to understand the atomic structure of the BN nanotubes using density functional theory, which is a powerful method for structural analysis on an atomic scale. This study will give us a guidelines for designing the size of the tube, wall thickness, chirality, etc., for further synthesis of BN fullerene materials, which are expected to be the future nanoscale devices.

1.1. Computational details

Geometry optimizations were performed for a series of armchair boron nitride nanotubes by varying its diameter for (5, 5) to (10, 10) configurations. These structures were constructed from carbon nanotubes [22] by substitution of carbon with boron and nitrogen atoms. One end of the nanotube is saturated with hydrogen atoms and the other end is unsaturated. All the arm chair nanotubes have open ends on one side and are closed at the other side by hydrogen atoms. We have used the Austin Model 1 (AM1) semi-empirical method [23] as implemented in Gaussian 98 [24] to perform geometry optimizations within the restricted formalism on these structures. Single point calculations have been performed on these optimized structures to study the properties using B3LYP/6-31G* level of the density functional theory. These structures contain 100 (5×5), 120 (6×6), 140 (7×7), 160 (8×8), 180 (9×9) and 200 (10×10) equal number of boron and nitrogen atoms, which are shown in Fig. 1. In addition, 5×5 arm chair nanotube has been fully optimized using B3LYP/6-31G* level of the density functional theory. The length of the armchair nanotubes are kept constant. The electrophilicity of these armchair nanotubes is measured using the electronegativity index ω

$$\omega = \mu^2/2\eta$$

where μ and η are the chemical potential and chemical hardness. These values have been calculated using the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energies calculated using Hartree–Fock theory with 6-31G* basis set, since the orbital energies calculated by this level of theory is more meaningful and accurate than the DFT method. A topological analysis for charge density (ρ), its second derivative ($\nabla^2\rho$) for bonds and ellipticity have been performed using Bader's Atoms in molecules [25] (AIM) theory. The properties were evaluated using Morphy98 [26]. Analysis of the charge distribution and charge transfer processes were performed using the NBO partitioning scheme [27]. The natural charges calculated from the NBO analysis were shown to be significantly reliable. The second order perturbation energies, $E^{(2)}$ donor $\rightarrow$ acceptor, were calculated at the same level of theory.