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Letter

Theoretical Investigation of the Interfacial Properties of Boron Nitride

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Abstract: Hybrid systems of boron-nitride nanotubes (BNNTs) and biological compounds are well-suited for abroad range of applications. First-principles methods are used to characterize the interface of these hybrid systems. Previous work has shown that the sensing capabilities of pristine BNNT are limited by long-ranged interactions. In this study, the surfaces of pristine and functionalized BNNTs are investigated. The surfaces of the functionalized BNNTs give new properties to the tubes, which may enhance their sensing capabilities, while retaining their stability and chemical inertness. The calculated elastic properties exhibit anisotropic mechanical properties that surpass graphene in the armchair direction. For the calculations 2D and 3D, Au6, Au10, Au12, Au14 and Au16 clusters were selected. Their properties were analyzed in a free-standing configuration and on a substrate of h-BN.

Keywords: Nanomaterials; Boron-nitride; DFT; Elastic properties; Stability.

Introduction

Nanomaterials have been the subject of research since the 1960s however, since the discovery and synthesis of C60 the field has come center stage [1]. Researchers are predicting new materials, discovering new methods of synthesis and finding novel applications on a daily basis. A prime example of the rapid rate of research and publication in the nanomaterials realm is graphene. In 2013, it was shown that there were about 9000 articles published since the original experimental announcement in 2004 [2, 3]. With this speed of innovation, studies investigating the risks of these new materials to our health and environment are falling behind [4]. The discoveries started with zero-dimensional materials, followed by one-dimensional and then rounded out with two-dimensional materials. The dimensionality of nano-materials describes not the atoms, but the directions in which electron can travel. Fullerenes, clusters or nanoparticles are molecular, which leads to the localization of electrons within the structure, when the materials are in an isolated environment. Another way to picture this is by looking at the number of directions that the material can be modeled with an infinite amount of images or periodic boundaries. A three dimensional material would not be considered a nanomaterial but would be a “traditional” bulk materials and would not have any dimension in the sub-micron range. There has been a funding push by the US government, that was initiated in 2011 for developing such nano-materials [5]. This project is a multi-agency initiative designed to accelerate the discovery, manufacture and application of advanced materials. The project has invested over 250 million dollars into R&D, which has spurred many aspects of materials design, one of which is the prediction of materials [5].

A powerful tool that has enabled this initiative is the growth of computation power. A fundamental component to material prediction is electronic structure theory. It is the foundation of this dissertation and it has led to a large fraction of publications in materials research [6]. Many other materials methods (molecular dynamics, coarse-grain methods, and etc.) have grown alongside electronic structure theory. The theoretical foundation was discovered back in the 1920's with the work of Paul Dirac and Erwin Schrödinger. They were awarded the Nobel Prize in 1933 "for the discovery of new productive forms of atomic theory". Schrödinger greatest work was on the, now named, non-relativistic Schrödinger Equation [7]. Dirac has a similar, but relativistic equation, also named after the discoverer, the Dirac Equation [8]. Both of these equations are wave-equations that, within the correct framework, accurately describe tiny particles (electrons).

Theoretical Investigations

There have been numerous studies investigating the interactions between biological molecules with carbon-based materials [9]. Similar studies have been done with boron-nitride materials [10]. All these studies limited their scope to pristine materials, whose interactions are all long-ranged vdW interactions and π−π stacking for aromatic molecules. Other materials of interest include noble metal clusters [11], other nanotubes and monolayers [12], 2-D layered transition-metal dichalcogenides, transition metal oxides, and others [1]. In most cases, either the inherent defects of the materials can be used or the surface can be modified to enable stronger interactions to occur. These modifications range from binding more sensitive molecules on the surface through π−π stacking or through permanent chemical bonds [13, 14]. The covalent modifications will alter the structural and electronic properties of the nanomaterials, while the non-covalent maintain the intrinsic properties of the materials. Carbon based nano-materials have been heavily investigated over the past decades for fundamental re-search, industrial production and potential applications. For graphene the most effective approach, so far, has been with graphene oxide. The modified material has found a number of uses in the biological community. Boron-nitride materials have also seen its share of modifications to enhance its properties for applications [14]. There are theoretical investigation studying the peptide-nanomaterial interface. Researchers are also interested in the interaction due to the potential to grow nanomaterials using peptides [15]. Some of the topologies that have been investigated as substrates for these applications include nanotubes, nanowires, nanoparticles, nanorods and two-dimensional (2-D) sheets [11]. Boron nitride nanotubes, one of the emerging nanomaterials, have a morphology similar to carbon NTs (CNTs). Boron nitride nanotubes are recognized as viable candidates for conjugation with biomolecules, showing a strong affinity toward proteins in larger scale interactions. Hilder et. al. [16] have studied periodic cell membranes with boron-nitride nanosheets through different interaction schemes.

Methodology

In 1900, physicist encountered a problem now known as the "ultraviolet catastrophe". The classical theory, Rayleigh-Jeans law predicted low wavelength behavior of blackbody radiation correctly but the short wavelengths drastically diverged from the experimental observations. This problem was being tackled by an individual who is now known as the “founder” of quantum physics. In his solution to the problem, Max Planck was the first to quantize electro-magnetic energy. He achieved this by following the statistical work of the second-law of thermodynamics. The law was previously published by Boltzmann, which received a large deal of skepticism from the community. Planck’s newly derived black-body radiation law postulated that electro-magnetic energy was quantized in the following manner indicated by eq. (1).

$$E = h\nu \tag{1}$$

In the above equation, *h* is Planck’s constant and *v* is the frequency of radiation, where *v* takes on discrete values. At the time Planck proposed this novel solution, he, along with the community, were skeptical of the radical consequences. After two decades of experiments by others in the laboratory, it earned him the Nobel Prize in Physics in 1918. Since that law was proposed, skepticism has trailed almost every idea in quantum physics. Many times, theory and experiments conflicted during the evolution of quantum mechanics and when they agreed it was typically perceived with a similar trepidation. The Hamiltonian of a many body problem with Columbic interactions expands as eq. (2).

$$H_e = \sum_i \frac{1}{2}\nabla_i^2 + \sum_{i,A}\frac{Z_A}{r_{iA}} + \sum_{i<j}\frac{1}{r_{ij}} + \sum_{B<A}\frac{Z_A Z_B}{R_{AB}} + \sum_A \frac{1}{2M_A}\nabla_A^2 \tag{2}$$

In the above equation, *i* and *j* are indices representing the electrons, A and B represent the nuclei, r_{ij} is the distance between particle x and y (*i* and *j* are electrons and A and B are nuclei), and M_A is the mass of nucleus A.

Pseudopotentials serve three important functions. They allow for a lower cutoff energy for a plane-wave basis set, they reduce the number of electrons in the calculation and they allow for the addition of relativistic effects within a non-relativistic framework. The pseudopotential approximation is implemented by splitting the core and valance states and replacing the core electrons with a weaker potential (pseudopotential). This in turn will generate pseudo-wave function as seen in Figure 1. The number of nodes is in the wave-function is reduced, decreasing the cost need to represent the core electrons. Density functional theory allows the N-electron wave function to be replaced with a simpler 3-D electron density. This greatly reduces the cost and effort required needed to calculate systems. The pedagogical beginnings of density functional theory is introduced through the statistical models introduced by Llewellyn Thomas in 1927 and a year later by Enrico Fermi.

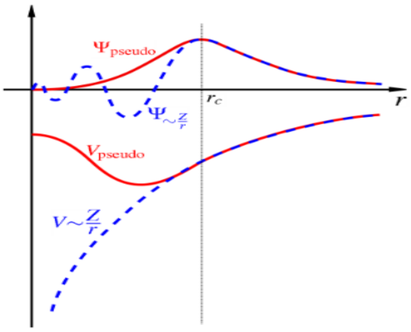

Figure 1: The real wave-function (blue) and the pseudopotential (red) in the potential of a nucleus (*Z*/*r*). The wave-functions will match at a point r_c. The smooth of behavior near the center of the nucleus reduces the needed cutoff energy for the plane-wave basis set. The image taken from Wikipedia [17].

Boron Nitride

In Boron nitride nanotubes were predicted in 1994 and then synthesized in 1995. Its 2-D analogue, monolayer hexagonal boron-nitride, was first predicted in 2006 and then synthesized in 2009. Boron-nitride is analogous to graphene and carbon nanotube in structure. All of the atoms are sp2 bonded and they share the same number of electrons per atomic pair (C-C with four each and B-N with three and five electrons). Due to the difference in nuclei, the B-N bonds are more ionic, which leads to stronger interlayer properties, this may lead to difficulties in exfoliation. The difference in atoms types leads to a variation in the distributions of chiralities observed. Carbon nanotubes have an equal probability of forming all three variations of nanotubes (arm-chair, chiral and zig-zag) when grown. Boron-nitride, however is predominately zig-zag. Another artifact of the ionicity is that boron-nitride nanotubes tend to be multi-walled, resulting in the hybridization of the σ and π states of the inner and outer tubes [9]. Both boron-nitride nanotubes and monolayers are wide band gap semiconductors with a band gap around 5-6 eV. The properties of boron-nitride nanotubes are almost independent of chirality. There are two differences between the zig-zag and armchair nanotubes. First, that the zig-zag boron nitride nanotube's band gap decreases as the radius decreases and the arm-chair BNNTs have an indirect band gap. In Figures 2 and 3, the band gap for both zig-zag (n, 0) and armchair (n, n) nanotubes are shown, chiral nanotube band gaps always fall in between these two extremes [18]. A sheet of boron nitride has a direct band gap, at the K k-point, of 4.67 eV, as shown in Figure 2 and published previously by Guo and Lin in 2005 [18]. Experiments have shown that the band gap of monolayer h-BN is around 6 eV, with recent findings narrowing the value to 6.17 eV [16]. Boron-nitride is known for its excellent chemical inertness and thermal stability [16]. However, these properties change when with smaller boron-nitride nanotubes [18]. It has been shown with small molecules, water, ammonia and formic acid, that chemical bonds will form with polar molecules. Indeed, boron-nitride nanomaterials have been always expecting to do crucial roles.

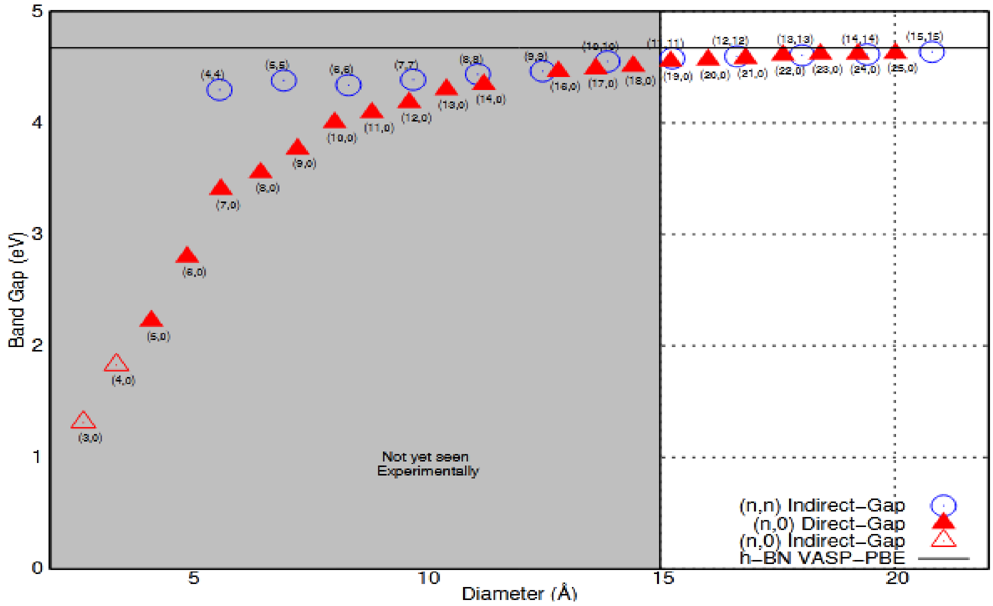

Figure 2: The band gap of selected zig-zag (n, 0) and armchair (n, n) nanotubes. The gray area covers nanotubes sizes that have not yet been observed. The smallest sized that has been observed has a radius of around7.5 Å. The arm-chair nanotubes all have indirect gaps and the most of zig-zag nanotubes and h-BN have a direct gap 3.4.

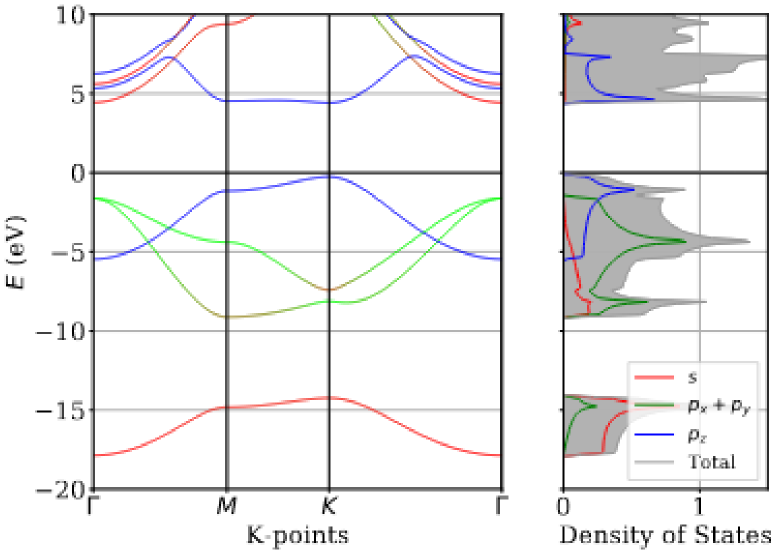

Figure 3: The band structures and projected density of states (PDOS) and total density of states (TDOS) of the unit cell of h-BN, where *s* (blue), in-plane p_x and p_y (green), out-of-plane p_z (blue) and total (grey) are shown.

Results and Discussion

To gain a better understanding of the nature of the bonding in this 2-D material, calculations of the Bader charges were performed. Figure 4 (Right panel) shows a charge of 0.9e (i.e. loss of 2.1e) associated with the B atoms.

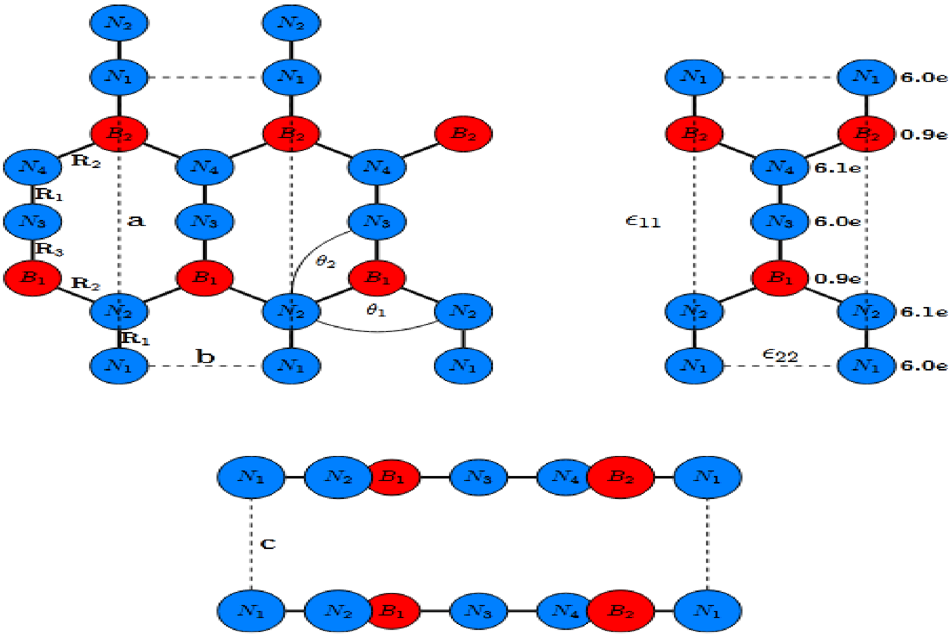

Figure 4: The structure of BN2 (Top left). The unit cell consisting of two B atoms (red) and four N atoms (blue) is outlined with the dashed (–) lines. The lattice parameters, bond lengths and bond angles together with Bader charges on each atom are also listed. Directions for the applied strain 11 and 22 are shown. The AA stacked bilayer structure (bottom) is shown with the interlayer distance (c) of 3.17 Å.

The calculated band structure and density of states find the BN2 electronic properties to be metallic with the states around the Fermi level are dominated by the in-plane *p*-orbitals as shown in Figure 5. These in-plane orbitals are mainly associated with N1 and N3 atoms with smaller contributions from N2, N4 and B atoms.

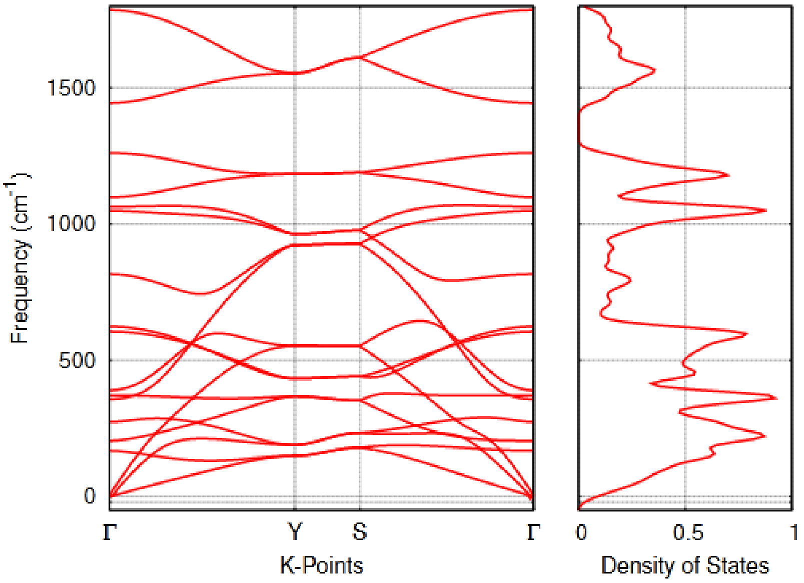

Figure 5: The calculated band structure and density of states of the BN2.

Conclusion

For electronic structure calculations, the optimization problem needs to be taken to a grander scale. In the past modeling elements, e.g., cutoff energies and k-point meshes, were optimized to make problems tractable, now this a trivial aspect of simulations. While these series and meshes cannot be set to infinity, they can be set to default values that capture the relevant physics associated with the given problem. The difficulties now lay in the determining the parameter space, how many permutations of a structure should be investigated and what rules can we apply to limit this space. Previously researchers only had the capabilities to look at a few select materials at a time. State-of-the-art calculations are oriented around discovery a material for a problem instead by searching hundreds if not thousands of potential candidates. We must integrate each computational tool that we have at our disposal to solve problems on a multi-scale level, from all electron calculations to continuum mechanics to the laboratory bench. Researchers are building work flows that allow for high-throughput calculations. This requires a substantial amount of automation that must be done with care and thought. In this dissertation, the ground work for a general understanding of the chemistry and physics for boron-nitride was gained. A few data points were filled in and disseminated to the public. We have only looked in to a handful of vectors for amino acids and gold to interact with pristine boron-nitride. The potential chemistry that can occur that have not been included are limitless. For the physiological setting there are countless other molecules that can interact and potentially degrade the desired properties of the structures. The inclusion of water can potentially change the chemistry that are possible.

Disclosure Statement

The author(s) did not report any potential conflict of interest.

References

1. Kroto HW, Heath JR, O'Brien SC, Curl RF, Smalley RE. C60: Buckminsterfullerene. Nature. 1985;318:162-3.
2. Tallentire J. The new "Gold Rush": graphene's research renaissance. Graphene. 2022:135-62.
3. Novoselov KS, Geim AK, Morozov SV, Jiang DE, Zhang Y, Dubonos SV, Grigorieva IV, Firsov AA. Electric field effect in atomically thin carbon films. Science. 2004;306:666-9.

4. Xia T, Li N, Nel AE. Potential health impact of nanoparticles. Annual Review of Public Health. 2009;30:137-50.
5. White A. The materials genome initiative: one year on. MRS Bulletin. 2012;37:715-6.
6. Haunschild R, Barth A, Marx W. Evolution of DFT studies in view of a scientometric perspective. Journal of Cheminformatics. 2016;8:1-2.
7. Schrödinger E. An undulatory theory of the mechanics of atoms and molecules. Physical Review. 1926;28:1049-70.
8. Dirac PA. Note on exchange phenomena in the Thomas atom. Mathematical Proceedings of the Cambridge Philosophical Society. 1930;26:376-85.
9. Zhong X, Mukhopadhyay S, Gowtham S, Pandey R, Karna SP. Applicability of carbon and boron nitride nanotubes as biosensors: effect of biomolecular adsorption on the transport properties of carbon and boron nitride nanotubes. Applied Physics Letters. 2013;102:133705.
10. Singla P, Riyaz M, Singhal S, Goel N. Theoretical study of adsorption of amino acids on graphene and BN sheet in gas and aqueous phase with empirical DFT dispersion correction. Physical Chemistry Chemical Physics. 2016;18:5597-604.
11. Xie HJ, Lei QF, Fang WJ. Intermolecular interactions between gold clusters and selected amino acids cysteine and glycine: a DFT study. Journal of Molecular Modeling. 2012;18:645-52.
12. Waters K, Pandey R, Karna SP. Amino acid analogue-conjugated BN nanomaterials in a solvated phase: first principles study of topology-dependent interactions with a monolayer and a (5, 0) nanotube. ACS Omega. 2017;2:76-83.
13. Lee CH, Zhang D, Yap YK. Functionalization, dispersion, and cutting of boron nitride nanotubes in water. The Journal of Physical Chemistry C. 2012;116:1798-804.
14. Sainsbury T, Satti A, May P, Wang Z, McGovern I, Gun'ko YK, Coleman J. Oxygen radical functionalization of boron nitride nanosheets. Journal of the American Chemical Society. 2012;134:18758-71.
15. Slocik JM, Naik RR. Probing peptide–nanomaterial interactions. Chemical Society Reviews. 2010;39:3454-63.
16. Hilder TA, Gaston N. Interaction of boron nitride nanosheets with model cell membranes. ChemPhysChem. 2016;17:1573-8.
17. Pseudopotential from Wikipdia. https://en.wikipedia.org/wiki/Pseudopotential.
18. Guo GY, Lin JC. Systematic ab initio study of the optical properties of BN nanotubes. Physical Review B. 2005;71:165402.

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