Electronic Properties of Holey 2D Materials

2017 School of Science Summer Research Proposal

Greg Stewart

Abstract

Ever since the seminal calculations on graphene decades ago[1], and the breakthrough experiments which showed that electrons behave as massless Dirac fermions in graphene[2], the material has attracted widespread interest, along with other two dimensional materials as they have incredible potential for use in wide ranging electronic devices. This would not be possible without studying the intrinsic properties of such materials, starting with graphene and other carbon nano materials like carbon nanotubes, haeckalites, and schwarzites, and extending this inquiry to 2D materials like boron nitride and transition metal dichalcogenides. Since there is a multitude of possible structures of these materials, there are still some which have not been studied, especially with BN and TMDs. Here I propose a project where I will study the properties of holey graphene, boron nitride, and TMDs, and the coalescence of holey bilayers of these materials. I will use first principles calculations to investigate various properties of these structures, including the band structure, density of states, and magnetic and optoelectronic properties, utilizing the supercomputing facilities available to me, including Blue Gene.

Background & Significance

Basic properties of bilayers with holes have not been studied very thoroughly, especially in the case of non-carbon structures. There has been some study of bilayer graphene, but less of boron nitride and TMD bilayers, and while holey graphene has been studied, holey BN and TMDs have not received much attention in research, let alone holey bilayers. Therefore the goal of this project is to perform first principles calculations of electronic and magnetic of these materials, including the density of states and band structure.

A few significant and unique properties of graphene bilayers and perforated graphene have been shown theoretically and experimentally, the most interesting of which is a widely tunable band gap. By varying an external electric field, the band gap of bilayer graphene can be precisely changed to suit the needs of a given application, which could be used to optimize the performance of future electronic devices[3]. Holey graphene appears to have great potential for efficient energy storage as a super capacitor electrode[4]. It has been shown that bilayer graphene can be perforated using irradiation; some properties of periodically perforated graphene bilayers have also been calculated theoretically, giving promising semiconductor properties with wide-ranging possible applications[5]. Perhaps a holey graphene bilayer will also have interesting and unique properties with potential applications in electronics. Coalescent holey bilayers may possess some new and interesting properties different from holey graphene or bilayer graphene by itself.

Theoretical calculations and experiments in the past have demonstrated that it is possible for carbon structures to coalesce when irradiated with an electron beam. This has been demonstrated in carbon nanotubes and fullerenes, where irradiation was used to introduce negative curvature and cause the separate structures to coalesce (Fig. 1, 2)[6,7]. It should therefore

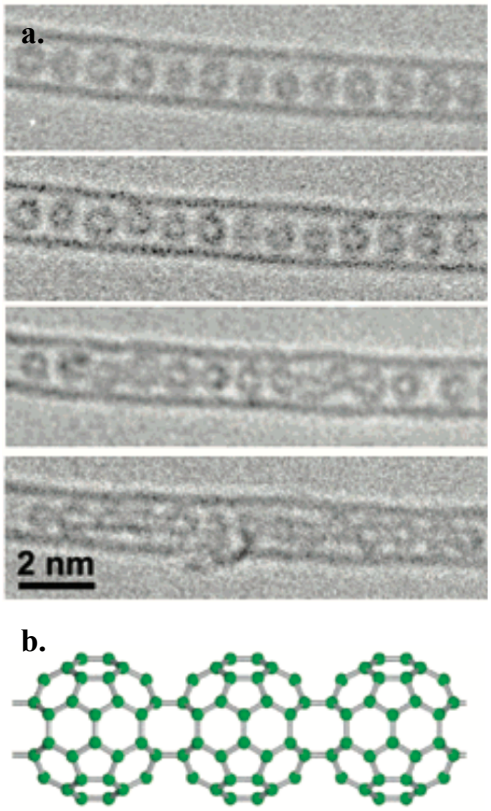

Fig. 1 The coalescence of fullerenes due to electron beam irradiation; negative gaussian curvature is introduced where the fullerenes coalesce. (a) experimental image of the coalescence of fullerenes. (b) a computer model showing the structure of the coalesced fullerenes. Figure courtesy of co-author Professor Humberto Terrones[6].

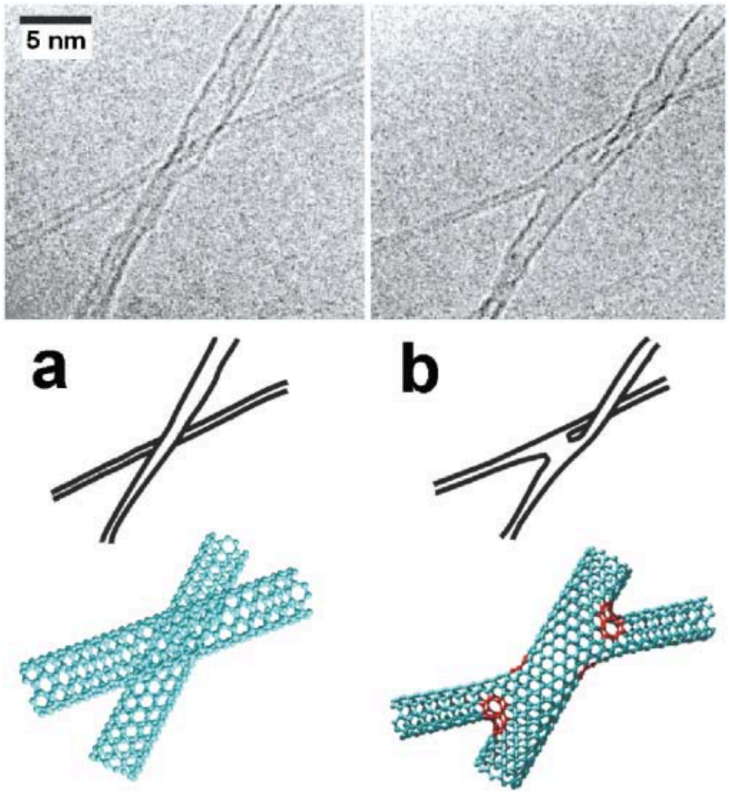

Fig. 2 Coalescing nanotubes under electron beam irradiation. (a) the crossed nanotubes prior to irradiation; first an experimental image, then a sketch and a computer model. (b) the coalesced nanotubes after irradiation; an experimental image, sketch, and a computer model showing in red the areas where negative gaussian curvature was introduced. Figure courtesy of co-author Professor Humberto Terrones[7].

be possible experimentally to use electron beam irradiation to coalesce perforated bilayered graphene by introducing negative curvature.

Boron nitride has been studied less than graphene, so less is known about the properties of bilayer BN and holey BN sheets. Bilayer BN has been used experimentally as a substrate for graphene electronics since its high band gap makes it an excellent insulator and prevents interaction of graphene monolayers and bilayers when separated by a BN sheet[8]. Holey BN has not been studied in detail and so holey bilayer BN may possess interesting properties not before known, which again could be taken advantage of in future electronic devices.

A perforated bilayered graphene/BN structure has been modeled and studied to a degree, though this structure is a bit different from the one I am focusing on. Electronic properties of the structure, like its band gap, were calculated, but there is a lack of further work on the topic thus far, so the structures I am proposing to research will have interesting properties[9].

Bilayer transition-metal dichalcogenides, like graphene, have been calculated to have a tunable band gap which depends on the intensity of an applied electric field, in addition to strain, doping, and defects; however, this has yet to be theoretically confirmed and shown

experimentally. This property has potential for use in applications in electronic devices[10]. Holey TMDs have not been studied in great detail and so little is known of their properties, so applying this holey bilayer geometry to TMDs could lead to some interesting properties. It could also provide the basis for further investigation and collaboration with experimentalists in the future.

Planned Approach

This project will take place over the course of ten weeks in the summer, during which I will work full time towards achieving the goals I have laid out. I will begin by modeling the unit cells of the structures, for example the holey graphene bilayer (Fig. 3), using VESTA software, obtaining the atomic coordinates for each structure along with the lattice vectors. From here, I will use Quantum Espresso 6.0 to perform first principles calculations on the graphene structure, first performing self consistent calculations to optimize the process, then calculating the band structure, magnetic properties, and other optoelectronic properties. This overall process will be repeated for the boron nitride structure and for a transition metal dichalcogenide; the first TMD I will use is molybdenum disulfide (MoS_2) because it is the simplest to calculate, and then I will repeat the calculations for other TMDs.

By the end of the summer, I will prepare a thorough report of my results, which will summarize what I have accomplished. In addition, I will participate in the undergraduate research symposium in the spring of 2018, where I will present my results along with any further results along this line of inquiry that I have obtained. Given the novelty of this investigation, I also expect to publish the results of my research.

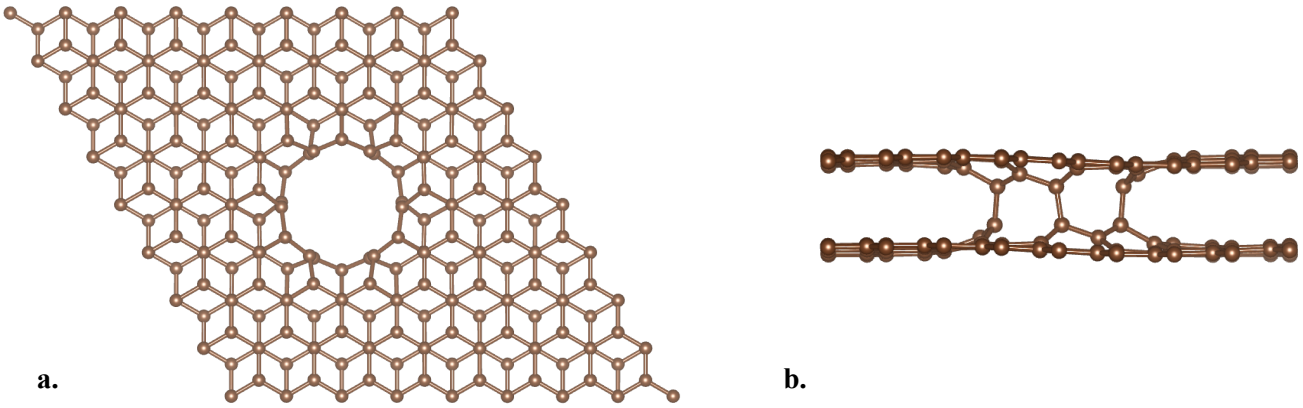

Fig. 3 The structure which will be the focus of my research. It is composed of two monolayers, each containing a hole which coalesces. The hole is composed of rings in the shape of octagons, a defect which introduces the curvature present. (a) the view looking down the hole; (b) a side view of the hole showing the octagonal structure that forms the hole

Personal Experience

My experiences at Rensselaer so far have prepared me for this research project well. As a sophomore physics and mathematics major, I will have completed courses like Quantum Physics I and II, which have given me a good general understanding of how particles and atoms interact.

Having completed Computer Science I, and keeping up with my computation skills, I am also prepared for the computational components needed for studying these systems. Additionally, I have been involved with Professor Humberto Terrones's group since fall of last year, and so I have been learning a great deal about these 2D materials, how first principles calculations are performed with them, and the general approach to looking at these systems. This has already taught me quite a lot about how computation-based theoretical research is conducted, and has made me even more excited about future prospects in physics research.

Summer research is an extraordinary aspect of my education that will be invaluable to me in the coming years as I further pursue a career in academia. At the moment I am not able to devote more than several hours per week to research as coursework is the priority, and I am involved in some clubs on campus that also require my time. Being able to work on this project full-time will be a wonderful opportunity to learn even more about what this kind of work entails, will help prepare me for graduate school in a way that no courses can, and may eventually lead to some publishable results. And of course, if this pursuit proves interesting, I will continue this research next semester and contribute more to the project.

References

[1] Wallace, P. R. The Band Theory of Graphite. 1947 *Phys. Rev.* **71** 622 – 634.

[2] Novoselov, K. S.; Geim, A. K.; Morozov, S. V.; Jiang, D.; Katsnelson, M. I.; Grigorieva, I. V.; Dubonos, S. V.; Firsov, A. A. Two-dimensional gas of massless Dirac fermions in graphene. 2005 *Nature* **438** 197 – 200

[3] Zhang, Y.; Tang, T.; Girit, C.; Hao, Z.; Martin, M. C.; Zetti, A.; Crommie, M. F.; Shen, Y.; Wang, F. Direct observation of a widely tunable bandgap in bilayer graphene. 2009 *Nature* **459** 820 – 823.

[4] Xu, Y.; Lin, Z.; Zhong, X.; Huang, X.; Weiss, N.; Huang, Y.; Duan, X. Holey graphene frameworks for highly efficient capacitive energy storage. 2014 *Nature Communications* **5** 4554.

[5] Kvashnin, D. G.; Vancsó, P.; Antipina, L. Y.; Márk, G. I.; Biró, L. P.; Sorokin, P. B.; Chernozatonskii, L. A. Bilayered semiconductor graphene nanostructures with periodically arranged hexagonal holes. 2015 *Nano Research* **8** 1250 – 1258.

[6] Hernández, E.; Meunier, V.; Smith, B. W.; Rurali, R.; Terrones, H.; Buongiorno Nardelli, M.; Terrones, M.; Luzzi, D. E.; Charlier, J. C. Fulleren Coalescence in Nanopeapods: A Path to Novel Tubular Carbon. 2003 *Nano Letter* **3** 1037 – 1042.

[7] Terrones, M.; Banhart, F.; Grobert, N.; Charlier, J.-C.; Terrones, H.; Ajayan, P. M. Molecular Junctions by Joining Single-Walled Carbon Nanotubes. 2002 *Phys. Rev. Lett.* **89** 075505.

[8] Golberg, D.; Bando, Y.; Huang, Y.; Terao, T.; Mitome, M.; Tang, C.; Zhi, C. Boron Nitride Nanotubes and Nanosheets. 2010 *ACS Nano* **4** 2979 – 2993.

[9] Chernozatonskii, L. A.; Demin, V. A.; Belluci, S. Bilayered graphene/h-BN with folded holes as new nano electronic materials: modeling of structures and electronic properties. 2016 *Scientific Reports* **6** 38029.

[10] Ramasubramaniam, A.; Naveh, D.; Tow, E. Tunable band gaps in bilayer transition-metal dichalcogenides. 2011 *Phys. Rev. B* **84** 205325.