Conductance Modulation in Bilayer Graphene Nanoribbons

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CONDUCTANCE MODULATION IN BILAYER GRAPHENE NANORIBBONS

A thesis submitted in partial fulfillment
of the requirements for the degree of
Master of Science in Engineering

By

KIRTI KANT PAULLA
B.E., GANDHI INSTITUTE OF TECHNOLOGY AND MANAGEMENT, 2006

2009
I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY SUPERVISION BY KIRTI KANT PAULLA ENTITLED Conductance Modulation in Bilayer Graphene Nanoribbons BE ACCEPTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF Master of Science in Engineering

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Abstract


Graphene nanoribbons are among the recently discovered carbon nanostructures, with unique characteristics for novel applications. One of the most important features of graphene nanoribbons, from both basic science and application points of view, is their electrical conductivity. In this research, we study the electrical conductance of single and double layer nanoribbons of specified widths and edge geometries. The calculations are carried out using ab initio quantum mechanical simulations for obtaining the optimized atomic configurations of the nanoribbons and their electronic structures. These results are then used to calculate the conductance characteristics via Green’s function approach to the Landauer’s formalism. We calculate the density of states and the zero-bias quantum conductance of single- and bi-layer systems, and investigate the modulation effects in bilayer conduction.

Our calculations show that for single-layer graphene nanoribbon with a width of ~10 Å, the one with armchair edge is semiconducting with a band gap of 0.22 eV whereas the one with zigzag edge is metallic. These are in excellent agreement with other works. For bilayer nanoribbons with armchair edge, two different stacking configurations (AA and AB) are considered. The AB-stacked one is semiconducting with a band gap of
0.02 eV whereas the AA-stacked one is metallic. Bilayer zigzag nanoribbons with AA stacking are found to be metallic. Our results show, in agreement with previous studies, that the band gap of a single-layer armchair graphene nanoribbon is reduced when another layer is stacked on top of it. The conductance characteristics of bilayer armchair and zigzag nanoribbons are shown to be different from those obtained by superimposing single-layer characteristics. In particular, the conductance characteristics strongly depend on stacking order (AA or AB). These interesting modulation effects are shown to arise from inter-layer interactions between electronic states. We discuss possible applications of these results in characterization of and device design based on graphene nanoribbons.
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Dedication

This dissertation is dedicated to my parents
1. Introduction

The fact that carbon forms many allotropes, compounds, and intricate networks, is essential to the existence of life on earth. There is no surprise, therefore, that carbon compounds and allotropes are the most studied and researched materials in the world. The capability of carbon atoms to form complicated networks\(^1\) is fundamental to organic chemistry. Even elemental carbon shows complicated bonding, forming a number of allotropic structures. Diamond and graphite are the two most ancient and well understood materials. It is due to the unusual bonding of carbon that diamond is considered to be one of the hardest naturally occurring materials known to humans. Recently discovered allotropes like fullerenes and nanotubes are the center of focus for many scientists researching in the fields of chemistry, physics, biology, and material science\(^2,3\). Thus far, I mentioned three dimensional (diamond, graphite), one dimensional (nanotubes) and zero-dimensional (fullerenes) symmetric allotropic structures of carbon. Until recently the two dimensional form was missing, resisting any attempt of experimental observation.

The missing two dimensional structure is now called graphene. Graphene is planar hexagonal arrangement of carbon atoms (Fig. 1). It is the name given to a flat monolayer of carbon atoms arranged tightly in honeycomb lattice, which is the building block of
graphitic materials (nanotubes and fullerenes contain pentagons). Graphene is the starting point of all calculations and structural studies on graphite, carbon nanotubes and fullerene. Importantly, in the mid 1930’s two scientists Landau and Peierls proposed that 2D crystals of carbon (graphene) could not exist and were thermodynamically unstable.

Fig. 1: Crystal structures of the different allotropes of carbon. (Left to right) Three-dimensional diamond and graphite (3D); two-dimensional graphene (2D); one dimensional nanotubes (1D); and zero-dimensional buckyballs (0D).

Graphene is a conceptually new class of materials that is only one atom thick, and, on this basis, offers new insight into low-dimensional physics. Single-layer graphene might be the thinnest material one has ever seen, being only one atomic layer thick.

The technique to make single layer graphene sheets is both interesting and surprising. A graphite flake is placed on a piece of adhesive tape, folding the tape over and pulling it apart, cleaving the flake in two. Folding and unfolding repeatedly, graphite
became thinner and thinner. Then the tape is stuck to a silicon wafer and rubbed. Some graphite flakes stick to the wafer, and these flakes are occasionally one atom thick\(^7\).

The main technique that changed the production ease was not the tape, but the way of spotting the single-layer graphene among the thicker flakes. The highest resolution of high-tech microscopes can spot the bump of a single atom, but using them to measure the thickness of each flake is impossibly slow. A one-atom-thick sheet is generally invisible, but a sheet that thin does change the color of the silicon oxide layer atop the wafer, much as sheen of oil on water generates a rainbow of colors.

Graphene is a semiconductor but it has the unusual feature that its band gap is exactly zero. Moreover, the velocity of the charge carriers in graphene does not decrease at the top of the valence band and the bottom of the conduction band, as is usual for most materials, but instead stays constant throughout the bands. The low scattering rates and the electronic structure of graphene give rise to good electronic transport that is easy to modify by doping or electrostatic fields. Its high conductivity could allow it to serve as interconnects. It can be gated so it could be used as the channel in novel transistors. Graphene is quite stable and inert so it is possible to prepare large areas that have low defect densities and low electronic scattering rates\(^8\).

Graphene has two atoms per unit cell. Although known as an integral part of 3D materials, graphene was presumed not to exist in free state. It was described as an 'academic' material and was believed to be unstable with respect to the formation of curved structures such as soot, fullerenes and nanotubes. Graphene and, to a good approximation, its bilayer derivative has simple electronic spectra: they are both zero-gap
semiconductors (they can also be referred to as zero-gap overlap semimetals). An important reason for the interest in graphene is a particular nature of its charge carriers. In condensed-matter physics, the Schrödinger equation is usually sufficient to describe electronic properties of materials. Graphene is an exception — its charge carriers mimic relativistic particles and are more easily and naturally described using the Dirac equation rather than the Schrödinger equation\textsuperscript{9,10}.

The nanoscale graphene platelets (NGPs) are predicted to have a range of peculiar electronic, optical, magnetic, and mechanical properties\textsuperscript{11,12}. In addition to single graphene sheets, double-layer or multiple-layer graphene sheets also exhibit unique and useful behaviors. Electrons in a single-layer NGP are believed to behave like massless chiral relativistic particles\textsuperscript{11-15}, as reflected by the anomalous quantization of the Hall conductance. NGP's peculiar properties can result in many device applications. One potential application of NGPs is in field effect transistors. In addition to much lower costs (compared to carbon nanotubes, CNTs), another major advantage of graphene-based nanocomposites is their capability of forming a thin film or coating for electromagnetic interference (EMI) shielding, and electrostatic charge dissipation (ESD)\textsuperscript{15-18}.

Due to the ultra-high thermal conductivity of NGPs (four times more thermally conductive, yet four times lower in density compared to copper), a nanocomposite thin film, paper, or coating can be used as a thermal management layer in a densely packed microelectronic device. NGP nanocomposites have a good combination of mechanical stiffness, strength, micro-cracking resistance, electrical and thermal conductivities. NGP composites can be an integral part of lightning strike protection strategies for aircraft, telecommunication towers, and wind turbine blades. NGPs can also be a component
material for lithium ion battery electrodes. Other uses of the material include sieves to filter light gases, and the manufacturing of micromechanical switches and electronic transistors. The most immediate application, however, is to aid Transmission Electron Microscopy (TEM). TEM allows one to study very complex molecules, but one has to put them on a substrate that is transparent. Graphene offers an incredible advantage. Not only is it the thinnest material possible, it is crystalline, so it has very well defined diffraction spots that one can easily account for. This is the most perfect substrate.

Scientists demonstrated the operation of graphene field-effect transistors at GHz frequencies and achieved the highest frequencies reported so far using this novel non-silicon electronic material. The operation speed of a transistor is determined by the size of the device and the speed at which electrons travel. The size dependence was one of the driving forces to pursue ever-shrinking Si transistors in semiconductor industries. A key advantage of graphene lies in its very high electron propagation, essential for achieving high-speed, high-performance transistors.

Nanoelectronics, like nanotechnology, is already positioned to be a major engine of change that drives economies well beyond the 21st Century. Nanoelectronics directly involve innovations in metrology, materials, manufacturing, or device technologies that directly impact semiconductor nanomanufacturing and electronic systems application areas.

Semiconductor nanomanufacturing sets the stage for tomorrow’s integrated circuits, the infrastructure upon which they depend, and the nanoelectronics products that they enable. Mixed-function electronic systems benefit from nanotechnology innovations in magnetic, optical, or electronic technologies. When merged with advanced
semiconductor electronics, it gives rise to broader utility of nanoelectronics in tomorrow’s economy. Nanoelectronics offer solutions to the demands for ever-increasing data rates. It enables a shift to optical communications within and between integrated chips. New low-cost ultra-high bandwidth optical communications, made possible by nanomanufacturing photonic crystals, will greatly improve the performance of computers and the internet. Other advancements include nanomaterials for solid-state lighting; precise deposition reactors for ultra-high density magnetic memory; and precisely controlled growth of nanomaterials for medical imaging systems, lamps, and displays. These innovations will be possible because of the benefits from mixed-function electronic systems. Three other nanoelectronics application areas are bioelectronics, fundamental materials discovery, and alternative energy generation/storage. Bioelectronics, an interdisciplinary research field that has recently emerged, will impact a range of industries. It seeks to exploit the growing technical ability to integrate biomolecules with electronics to develop a broad range of functional devices. Bioelectronics includes elements of chemistry, biology, physics, electronics, nanotechnology and materials science. Materials discovery is the process of creating wholly new materials, including electronic materials or nanomaterials, as a result of nanoscale metrology innovations being coupled with advanced electronic systems. Alternative energy, in particular renewable energy such as fuel cells, photovoltaics, and energy storage systems, all are poised to benefit from breakthroughs in nano-materials, devices and manufacturing. To be commercially successful, nanoelectronics, like other applications of nanotechnology, demands a broad range of innovations. New nanoscale devices and systems are built upon diverse nanotechnology innovations with improved
performance or new functionality. Cutting edge instrumentation and metrology are capable of resolution, precision, and throughputs that match industry’s exacting demands. New manufacturing and processing technologies allow for precisely controlled fabrication of nanometer-scale structures. New nanomaterials that capture uniquely new properties and functionalities as a result of their controlled composition and nanometer-scale structure are being developed⁶.

Fig. 2: Two different variations of graphene nanoribbons (GNR’s) depending on their edge geometries.

Graphene nanoribbons (GNR’s) are geometrically terminated graphene layers. They have infinite length and finite width. Due to recent developments in preparing single graphene layers on non-crystalline substrates, GNR’s having varying widths and can be cut from mechanically exfoliated graphene²¹,¹⁷ or by patterning epitaxially grown
Depending on their edge structures GNR’s can be either armchair or zigzag (Fig. 2). The time has come when the silicon industry is reaching its limitations. This is one of the primary reasons why nanoscale carbon materials like fullerenes and nanotubes have been the subject of intensive research in the past two decades\textsuperscript{11}. Fundamental scientific interest in the GNR’s is expected to be important for future nanoelectronics due to their versatile electronic properties.

In this research, we study the electrical conductance of single and double layer GNR’s, of both zigzag and armchair types, with fixed widths. These structures are relaxed using ab initio modeling techniques and their conductance properties are calculated. We discuss possible applications of the results in characterization of and device design based on GNR’s.
2. Method

Material properties can be modeled on various time- and length-scales, ranging from nanometers to meters. Multiscale modeling is the key to a deep understanding of materials, and bridging scales is a major challenge in current materials science. There is little doubt that most of low-energy physics, chemistry, and biology can be explained by the quantum mechanics of electron and ions. Computer simulations are among the principal tools for treating systems of practical importance. It has been a major breakthrough in materials science and engineering that the computers now offer help in reducing experimental efforts and interpreting experimental results, often leading to deeper understanding.

Theoretical modeling has become a very important research tool for modern material sciences. In a strong collaborative theoretical/experimental approach it will be possible to not only explain and support experimental observations, but also to predict and help with the development of new materials with exciting properties. The application of quantum mechanics has proven to explain a lot of phenomena seen practically like energy levels of atoms, the covalent bond, and many more. Theoretical modeling and simulation are most often used in collaboration with experimental research. The most common areas of applicability for these types of calculations are to support and explain
experimental observations. Another big area includes the possibility to predict how a choice of different experimental parameters will lead to materials with desired properties. We have already reached a stage where tremendously powerful computer modeling packages are now commercially available and the subject is now taught routinely in undergraduate degree programs.

Most molecular modeling studies involve three stages. In the first stage a model is selected to describe the intra- and inter- molecular interactions in the system. The two most common models that are used in molecular modeling are quantum mechanics and molecular mechanics. These models enable the energy of any arrangement of the atoms and molecules in the system to be calculated, and allow the modeler to determine how the energy of the system varies as the positions of the atoms and molecules change. The second stage of a molecular modeling study is the calculation itself, such as an energy minimization, a molecular dynamics or Monte Carlo simulation, or a conformational search23. Finally, the calculation must be analyzed, not only to calculate properties but also to check that it has been performed properly.

Theoretical material modeling has become one of the fastest growing parts of modern materials science. It includes a number of various computational methods, which in turn are based on different levels of applicability (ab initio, semi-empirical, classical force field, etc.). Density Functional Theory23 (DFT) has come to dominate as a calculation tool since this method is applicable for in principle all elements within the periodic table.
There are four kinds of fundamental interactions namely weak nuclear, strong nuclear, gravitational, and electromagnetic interactions. Among these the electromagnetic interactions are responsible for almost all of normal material structures and properties. The electromagnetic forces on both electrons and nuclei due to their electric charge are of the same order of magnitude, and so the changes that occur in their momentums as a result of these forces must also be similar. One might, therefore, assume that the actual momentums of the electrons and nuclei were of similar magnitude. In this case, since the nuclei are so much more massive than the electrons, they must accordingly have much smaller velocities. Thus it is possible that on the typical time-scale of the nuclear motion, the electrons will very rapidly relax to the instantaneous ground-state configuration. We can assume that the nuclei are stationary and solve for the electronic ground-state first, and then calculate the energy of the system in that configuration and solve for the nuclear motion. This separation of electronic and nuclear motion is known as the Born-Oppenheimer approximation\textsuperscript{23}. This simplification reduces the many-body problem to the solution of the dynamics of the electron in some frozen arrangement of nuclei.

Even after this simplification the solution to this problem remains formidable and requires high computing power. Further simplifications can be introduced to calculate the total energy more efficiently. These include density functional theory to model electron-electron interactions, psuedopotential theory to model electron-ion interactions, and iterative minimization to model ion-ion interactions\textsuperscript{23}.

To model any electronic structure we need to know the electron-electron interactions of that system. Due to Columbic interactions the electrons repel each other. This can be taken care of by treating the electrons individually, that is spatially separating
them and then has to be compensated by kinetic energy of deforming the electron wave in order to separate electrons. Exchange and correlation are two effects that are caused due to electron-electron interactions in a many-electron system. All the electrons in a many-electron system are anti-symmetric that is they follow Pauli’s exclusion principle. Thus the electrons having same spin are spatially separated. This reduces the total energy of the system. This effect is called exchange and the energy due to this effect is called the exchange energy. This energy is included in the total energy calculations referred to as Hartree-Fock approximation. The difference between the total energy and the energy of a system calculated by Hartree-Fock approximation is called correlation energy and is always negative.

Hohenberg and Kohn, in 1964, suggested that the problem really was that the many-electron wave-function was too complicated to deal with. Firstly, it cannot adequately be described without \( \sim 10^{23} \) parameters, and secondly it has the complication of possessing a phase as well as a magnitude. They chose instead to use the electron density as their fundamental variable. That is, they considered the ground state of the system to be defined by that electron density distribution which minimizes the total energy. Furthermore, they showed that all other ground state properties of the system (e.g. lattice constant, cohesive energy, etc) are functionals of the ground state electron density. That is, once the ground state electron density is known all other ground state properties follow.

In 1965, Kohn and Sham showed that the Hamiltonian equation derived from this variational approach took a very simple form. The so-called Kohn-Sham equation is
similar in form to the time-independent Schrödinger equation, except that the potential experienced by the electrons is formally expressed as a functional of the electron density. The Kohn-sham total energy functional for a set of doubly occupied electronic states \( \psi_i \) can be written as \(^{23}\)

\[
E[\{\psi_i\}] = \sum_i \left( -\frac{\hbar^2}{2m} \psi_i \nabla^2 \psi_i \; d^3r + \int v_{\text{ion}}(r)n(r)d^3r + \frac{e^2}{r} \int n(r)n(r') \frac{d^3r'd^3r}{|r-r'|} \right) + E_{\text{xc}}[n(r)] - E_{\text{ion}}[\{R_i\}]
\]

(1)

Where \( E_{\text{ion}} \) is the ionic Coulomb energy,

\( v_{\text{ion}} \) is the total electron-ion potential,

\( n(r) \) is the charge density or electron density, and

\( E_{\text{xc}} \) is the exchange and correlation functional.

Equation 1 is effectively a single-particle equation. Application of this theory to real-life situations involves heavy computational effort. Pseudopotential theory allows one to replace the strong electron-ion potential with a much weaker pseudopotential. The original solid is then replaced with valence electrons and pseudo-ion cores. In order to carry out a theoretical study of complex materials, it is important to model the interactions between the ions in these structures as accurately as possible, while keeping the calculations computationally feasible. One of the other important approximations is local density approximation. The local density approximation (LDA) states that, for regions of a material where the charge density is slowly varying, the exchange-
correlation energy can be considered the same as that for a locally uniform electron gas of the same charge density:

\[ E_{XC} = \int n(r)\varepsilon_{XC}(n)dr \]  

(2)

where \( \varepsilon_{XC} \) is the homogeneous electron gas exchange-correlation term.

In practice, however although these improvements seem to give better total energies the resultant structure is often worse, and at a greatly increased computational cost. In general, the LDA is worse for small molecules and improves with system size\(^2\)\(^3\).

As the LDA approximates the energy of the true density by the energy of a local constant density, it fails in situations where the density undergoes rapid changes such as in molecules. An improvement can be made by considering the gradient of the electron density within the so-called generalized gradient approximation (GGA). This can lead to a large improvement over LDA results with accuracy approaching that of correlated wave functions\(^2\)\(^3\).

Computational material modeling is the science of calculating materials structures numerically and simulating their behavior with the equations of quantum and classical physics. Computational modeling programs allow scientists to generate and present materials data including geometries (bond lengths, bond angles, and torsion angles), energies (heat of formation, activation energy, etc.), electronic properties (moments, charges, ionization potential, bandgaps, and electron affinity), spectroscopic properties (vibrational modes, chemical shifts) and bulk properties (volumes, surface areas, diffusion, viscosity, etc.)\(^2\)\(^4\).
All molecular modeling techniques can be classified under three major categories namely ab initio or “first principle” calculations, semi-empirical methods, and empirical or “molecular mechanics” methods.

With the onset of more powerful computers, the molecular dynamics technique has become an effective tool in the physics of condensed matter systems. In the molecular dynamics method, the forces acting on particles in a cell are found and the classical Newtonian equations of motion are solved numerically. The largest part of a molecular dynamics simulation is the evaluation of the forces that are required in order to find the relaxed ionic positions. In general each particle can interact with all the other particles in the simulation, although one method of increasing the computational speed is to limit the range of the potential.

There are several methods by which the forces on particles can be evaluated. One of the simplest and most computationally efficient is by the use of an empirical potential, where the nature of the interactions between particles is fitted to various properties that are found experimentally, such as lattice parameter and bulk modulus. In general, an empirical potential is constructed by summing contributions of pairwise interactions, 3-body interactions, and so on.

Although empirical potentials are of great use, they are limited by the fact that they can only describe a system to a certain point of accuracy. In general they are good at describing the interactions of the system to which their parameters were fitted but their transferability to other systems can be quite poor. There are many different interactions that are necessary to fit the potential to in order to describe even a small range of physical
properties. For example, the Tersoff silicon potential\textsuperscript{25} accurately describes properties such as lattice parameter, elastic constants and phonon dispersion curves but requires the complexity of 14 different fitted parameters. But such a complex empirical potential still gets some basic quantities such as the melting temperatures wrong because it was not designed to examine such properties\textsuperscript{24}. Thus transferability is limited. It may then be asked, why use empirical potentials that only reproduce the experimental results to which they fitted? It is because they will describe details of structures that may not be amenable to experimentation.

In order to perform molecular dynamics simulations using an empirical potential, one must know beforehand the type of structure (that is, the nature of the bonding in the material) in order to use the correct model to construct the potential. In many cases this is not possible. To model interactions in which no prior bonding information is known, an approach at a more fundamental level is required. One must turn to the formidable task of solving the Schrödinger equation for the electrons. In fact it is the Kohn-Sham equation that is solved where the many electron interactions are approximated by a local potential. Thus, calculations can be performed which would be computationally prohibitive in a strictly first principles quantum mechanical approach.

The first principles or ab initio methods employ quantum theory to directly calculate molecular properties and geometries. The equation from which materials properties can be derived is the Schrödinger equation,

\[ E \psi = H \psi \]  

(3)
where $E$ is energy of the system relative to one in which all atomic particles are separated by infinite distances, $\psi$ is the wave-function which includes the spatial and spin coordinates of the atomic particles, and $H$ is the Hamiltonian operator which includes both potential and kinetic energies.\(^26\)

The Schrödinger equation can be exactly solved only for very small systems such as hydrogen and helium. Approximations must be introduced in order to extend the utility of the method to polyatomic systems.

The first approximation attempts to differentiate nuclei and electrons. It assumes that nuclei are much heavier than electrons and move much more slowly so that molecular systems can be viewed as electrons moving in a field of fixed nuclei (the Born-Oppenheimer approximation) as discussed earlier. Solutions to the Schrödinger equation using this assumption lead to values of effective interaction energy which depend on relative nuclear coordinates. As the nuclei are moved to new coordinates and molecular energies are re-calculated, a quantitative description of interaction energy is derived. This description, which relates energy to geometry, is referred to as the potential energy surface for the system. The lowest point on this surface, with respect to energy, is the ground state energy (and its associated geometry) for the system.

The second approximation allows the wave function $\psi$ to be represented as the product of one-electron (or spin) orbitals. The functions that are used to describe these orbitals are referred to as basis functions. This formalism is referred to as the Linear Combination of Atomic Orbitals (LCAO) theory.\(^26\) Once the orbitals have been derived,
the orbital coefficients (which define the energy of the system) are calculated. Hartree-Fock theory is one of the methods that is used to accomplish this goal.

Hartree-Fock approximation assumes that the energy of a set of molecular orbitals can be derived from the basis set functions which are used to define each orbital and a set of adjustable coefficients, which are used to minimize the energy of the system. The energy calculation becomes an exercise in solving a set of \((N\times N)\) matrices to obtain optimal values for the orbital coefficients. Since this calculation requires a value for the coefficients in order to solve the equations, an iterative process is used in which an initial guess for the value of the coefficients is progressively refined until it provides consistent values. This method is referred to as the self-consistent-field (SCF) theory\(^{26}\).

Ab initio quantum methods compute a number of solutions to a large number of equations. While calculations on large systems are possible, the methods are generally limited to compounds containing a few hundred atoms due to the amount of computer time required for each calculation and the large amount of disk space needed to store intermediate data files. There are alternative approaches to computing structures and properties by simplifying portions of the calculation to circumvent these limitations. These methods are referred to collectively as semi-empirical quantum methods.

Semi-empirical methods utilize approaches that are similar to ab initio methods, but several approximations are introduced to simplify the calculations. Rather than performing a full analysis on all electrons within the molecule, some electron interactions are ignored. In these methods, the more complex portions of the ab initio calculation are
ignored or set to zero. Other semi-empirical approaches replace complex portions of the calculation with parameters which are derived from experimental data\textsuperscript{26}.

While semi-empirical methods require less computer resources than ab initio methods, they are still computationally intensive. In general, calculations are routinely performed on compounds that contain up to 10000 atoms or more. The chief drawback of the method is that its application is limited to systems for which appropriate parameters have been developed\textsuperscript{26}.

There are obviously great advantages in using ab initio methods where the specifications of the atomic numbers of the ions present are required. The drawback is the extremely intensive nature of the calculations. Before an evaluation of the forces on the ions can be performed, a massive minimization calculation is required. The size of this calculation can easily overwhelm any but the smallest simulations.

Although the empirical potential, modeling a system of complicated “springs”, is an invaluable tool in determining the microstructure of bulk systems, which are unfeasibly large for ab initio calculations, they give very little information about the electronic structure of a system. In ab initio calculations the electronic charge density is evaluated directly, and is in fact the fundamental quantity used in the calculations.

Of the three methods discussed namely ab initio, semi-empirical, and empirical, the ab initio molecular orbital methods are the most accurate and consistent because they provide the best mathematical approximation to the actual system. The term ab initio implies that the computations are based solely on the laws of quantum mechanics, the
masses and charges of electrons and atomic nuclei, and the values of fundamental physical constants. It is worth mentioning that recently developed hybrid methods combine high level quantum mechanical calculations on a small part of a system with a lower-level method on the rest of the system. Thus for large clusters or macromolecules, accurate calculations can be carried out on the area of interest without ignoring or making unnecessary assumptions about the remainder of the system.

There are many materials simulation software available in the market nowadays. The program that is used in this research to relax the structures, and to calculate the electronic configurations, was GAUSSIAN\textsuperscript{27}. This program is equipped with all the three types of modeling techniques namely ab initio, semi-empirical, and empirical (molecular mechanics). Some of the force fields are predefined for example AMBER, UFF etc. This program uses Hartee-Fock approximation with linear combination of atomic orbitals (HF-LACO) as one of the methods. Suppose we build the hydrogen molecular ion starting from the hydrogen atom and proton initially separated by a large distance. The electronic wave function will resemble a hydrogen $1s$ orbital unless the proton is close enough to have any effect on the wave function. So we might guess that molecular wave function should resemble an atomic $1s$ orbital, near its nucleus. Therefore the molecular orbital of H$^+$ can be represented by

$$\psi = c_A \phi_1 s_A + c_B \phi_2 s_B \quad (4)$$

Where $\phi_1$ and $\phi_2$ are atomic orbitals, $s_A$ and $s_B$ are spin components, and $c_A$ and $c_B$ have to be determined. This technique is called linear combination of molecular orbitals (LCAO).
In this research, for relaxing graphene nanoribbons and calculating their electronic structures, Hartree-Fock and BLYP methods were used, respectively. The latter is a hybrid method (not completely based on DFT). The basis set assumed for solving the quantum mechanical equations within the GAUSIAN program was 6-31G. Here we briefly explain these keywords:

BLYP hybrid density functional was originally developed to improve the description of the ground state energetics of small molecules. It has been demonstrated to be significantly more reliable than the local density approximation (LDA) and generalized gradient approximation (GGA) functionals for computing atomization enthalpies, geometries and vibrational frequencies\textsuperscript{28}. This method provides us with a more accurate tool as compared to the simple Hartree-Fock (HF) approximation which predicts the correct ground states of systems, while the energy gaps and magnetic moments are always overestimated due to the inadequate consideration of correlations. In the BLYP hybrid functional scheme, the nonlocal Hartree-Fock (HF) approach is mixed into the energy functional of the generalized gradient approximation (GGA)\textsuperscript{29}.

Historically, the quantum calculations for molecules were performed as Linear Combination of Atomic Orbitals (LCAO). This means that molecular orbitals are formed as a linear combination of atomic orbitals. A different convention was adopted by Pople and coworkers. The basis set structure is given for the whole molecule, rather than a particular atom. This notation emphasizes also a split valence (SV) nature of these sets. Symbols like $n$-$ijG$ or $n$-$ijkG$ can be encoded as: $n$ - number of primitive functions for the inner shells; $ij$ or $ijk$ - number of primitive functions for contractions in the valence shell. The $ij$ notation describes sets of valence double zeta quality and $ijk$ sets of valence triple
zeta quality. Generally, in basis sets derived by Pople's group, the \( s \) and \( p \) contractions belonging to the same “electron shell”, that is, they correspond to the same principal quantum number \( n \). They are assumed to be folded into a \( sp \)-shell. In this case, number of \( s \)-type and \( p \)-type primitive functions is the same, and they have identical exponents. However, the coefficients for \( s \)- and \( p \)-type contractions are different\(^{30}\).
3. Conductance

The dimensions of electronic devices are rapidly decreasing. There is a need for a new generation of modeling tools that can accurately calculate the electrical properties of devices where atomic scale details and quantum effects are important. Ohm’s law is normally used to calculate the conductance of various macroscopic systems. According to Ohm’s law, the conductance of a large macroscopic system is directly proportional to its cross sectional area and inversely proportional to its length, and can be calculated by incorporating a constant called conductivity which is a material property. What happens when the system is so small that one cannot define the material property “conductivity”? This question was unanswered until the late twentieth century because no one knew how to attach contacts to a small system such as a molecule. But now that we can do so the answers are fairly clear. This has given rise to new principles and theories.

Nowadays, one of the major themes in electronics is the construction, measurement, and understanding of the current-voltage response of an electronic circuit in which molecular systems act as conducting elements. Traditional metal-molecule-metal junctions comprise thin molecular films between macroscopic metal electrodes. In such junctions, the connection between the molecule and the electrodes greatly affects the current-voltage characteristics. Nanoscale molecular interconnects may help minimize
computer circuit dimensions and enhance performance. They can act as switches, gates, or transport elements, providing new molecular functions that need to be characterized and understood.

The simplest discussion of transport in a molecular junction is to assume that incoming electrons are scattered both at the interface and along the molecular wire itself\textsuperscript{31}. The conductance will then depend on the net probability of scattering. A point first noticed by Landauer\textsuperscript{32} is that such scattering does not have to be inelastic; even elastic scattering will prevent electrons making it through the junction. Once the simplest case of coherent single-molecule transport at fixed geometry is understood, major challenges still remain. Transport in single versus multiple molecule junctions, and many such systems are currently under investigation. The statistics of transport is also of interest, because of different geometric possibilities involved.

Landauer’s Formula is normally used in order to compute current in nanoscale devices. Electric current flow is often viewed as an electron (or charged carriers) response to an applied electric field. Landauer viewed current flow as a transmission process, or a consequence of the injection of carriers at contacts and probability of the carriers to reach the other end. This approach has proven to be extremely useful for transport properties of nanostructured materials and devices, including molecular systems. Landauer’s original result was obtained for a system of two one-dimensional leads connecting to a sample. The two leads are connected to two macroscopic electrodes or electron reservoirs. The sample is where scattering can take place and characterized by a transmission function $T(E,V)$. The conductance $C(E,V)$ of the system is given by
\[ C(E,V) = \frac{2q^2}{h} T(E,V) \]  \hspace{1cm} (5)

where \( q \) is the electron charge,

\[ h \] is the Planck constant, and

\[ T(E,V) \] is the transmission probability.

Landauer’s had the following assumptions\(^{33}\):

(a) transport occurs when a pair of leads connected to the device are set to different chemical potentials.

(b) the density mismatch causes the current.

(c) The difference in the chemical potentials causes the applied voltage across the device

(d) the Fermi energy is much larger than the thermal and electrical energies

(e) there are no inelastic processes to dissipate the electrical energy gained by the electrons\(^{33}\).

A closely related method is the nonequilibrim Green function method\(^{33}\). Due to new developments in the field of nanoscience and the molecular electronics, single molecules are being used as conducting elements attached to electrodes. Description of such situations is a challenge for the theorist as it requires a description of fast time-
dependent processes in strong external fields. The traditional quantum chemistry approaches that take into account electron correlations in stationary systems cannot deal with these situations. The nonequilibrium Green’s function method has had important applications within solid state, nuclear and plasma physics. However, due to its general nature it can equally deal with molecular systems\(^{34,35}\).

The method has as its main ingredient the Green function, which is a function of two space-time coordinates. From knowledge of this function one can calculate time-dependent expectation values such as currents and densities, electron addition and removal energies and the total energy of the system. In the absence of external fields the nonequilibrium Green function method reduces to the equilibrium Green function method which has had important applications in quantum chemistry. Green function is used in the transport calculation of graphene nanoribbons in our research.

Two quantum mechanical effects distinguish mesoscopic devices from bulk devices, reflecting the wave–particle duality of electron\(^ {32}\). One is the quantization of electronic charge which evidences itself in coulomb blockade and single-electron transistors\(^ {31}\). The other is the preservation of quantum phase coherence over a length with size comparable to one of the device dimensions and the resulting energy quantization of confined electrons, which leads to the observation of conductance quantization in transport\(^ {34}\). We consider molecular electronic devices formed by sandwiching a chemically synthesized molecule between two large (on the molecular scale) metallic electrodes\(^ {36}\) (Fig. 3). At the molecular scale, the simplicity associated with the effective-mass approximation breaks down and the electronic structure of the system has to be
taken explicitly into account. The quantum mechanical scattering problem involved is now the scattering of electrons under the potential of the atomic nuclei and the potential due to other electrons.

Fig. 3: Illustration of typical molecular devices.

The reduction to molecular scale also brings in another complication in transport study as compared to the microscopic systems: treatment of the interface to an external contact. In microscopic transport, the details of contact are often not important. The measuring electrodes, taken as infinite electron reservoirs, can either be simulated by reflectionless semi-infinite leads with simple confinement potential at the interface, or only come into the theoretical formulation as an appropriate boundary condition \(^{37,38}\). This is no longer true when the device is of molecular dimension. Since the electrodes can have atomic structures on the surface whose dimensions can be comparable to the molecule, the usually well-defined boundary between the active device region and the contact region is blurred. The interface to the external contact becomes an integral part of
the device and the measured electrical characteristics will depend on the details of the atomic arrangement of the contact. Moreover, the electronic and structural properties of the molecule could be modified by the bonding to the measuring contact, bringing in additional complications\(^{39}\). In summary, molecular electronic devices are different from their mesoscopic counterparts in two important aspects: (1) the effect of the electronic structure and (2) the effect of the interface to the external contact. Since the molecule can freely exchange energy and electrons with the electrodes, a rigorous treatment of molecular electronic device can only be achieved including these effects in the context of an open system\(^{40}\). As a result, a successful modeling of molecular electronic devices in general calls for combining the theory of quantum transport and the theory of electronic structure starting from first-principles\(^{37,38}\).

The program used to calculate the transport properties of graphene nanoribbons is called TRARABORD\(^{35}\). TARABORD uses the non-equilibrium surface Green's function in order to calculate the conductance of an open system that consists of a general finite system like the functional molecule described in Fig. 3. The starting point of the transport calculation is obtaining the necessary Hamiltonian and overlap matrices. The transport calculation is independent of the particular electronic structure calculation (ESC) procedure employed for obtaining the Hamiltonian and overlap matrices. The only requirement of the ESC is that the Hamiltonian and overlap matrices should be available in some spatially localized basis. Examples include linear combination of atomic orbitals (LCAO) ab initio and semi-empirical descriptions as described earlier. Within the localized basis, the infinite dimensional Green's functions\(^{35}\) \(G_{S,D}\) corresponding to the left and right (source and drain) contacts satisfy
\[(zS_{S,D} - H_{S,D})G_{S,D} = I\]  \hspace{0.5cm} (6)

Here, \(H_{S,D}\) and \(S_{S,D}\) are the infinite dimensional Hamiltonian and overlap matrices corresponding to the left (source) and right (drain) contacts, and \(z\) is the complex energy.

The Green’s function of the whole system can be calculated from its projection on the interface regions, together with “transfer” matrices of the contacts. Projecting Eq. (6) onto the spaces region defined by individual layers, we obtain a series of coupled equations for the layer Green's functions \(G_{S,D}^{n,0}\), where \(n\) is the layer index and 0 indicates the surface layer.

The following layer matrices are required for calculating the surface Green's functions of the left and right contacts, and matching them to the middle molecular junction\(^{41}\), the Hamiltonians of one layer of the left and right (source and drain) contacts, the Hamiltonians coupling one layer to its right neighboring layer for the left and right contacts, the Hamiltonian of the functional molecule sandwiched between the left and right contacts, \(H_M\) and the Hamiltonians coupling the middle system to the first layers of the left and right contacts, \(H_{S,M}\) and \(H_{D,M}\). The overlap matrices, indicated by \(S\), of the contact are also required. \(H\) and \(S\) matrices are obtained from ESC and are read by TARABORD as input data. Having obtained the necessary \(H\) and \(S\) matrices, we calculate the surface Green's functions of the left and right contacts. This includes the effects of semi-infinite contacts, by projecting their Green's function onto the spaces of their surface layers, and effectively closes the “open” system. A powerful algorithm\(^{41}\)
provides the transfer matrices $T_S$ and $T_D$. Using $T_S$ and $T_D$, we can calculate the propagation of an excitation from far within the left contact to its surface layer and from the surface layer of the right contact to far within the right contact. The transition across the molecular junction has to be calculated. This is done by matching the surface Green's functions of the left and right contacts to the Green’s function of the molecular junction.

By matching the surface Green's functions of the left and right contacts with the Green's function of the molecular junction, the total Green's function of the system projected onto the junction region, $G_{t:M}$ is given by

$$G_{t:M} = \left(zS_M - H_M - \Sigma_S - \Sigma_D\right)^{-1}$$

where $\Sigma_S$ and $\Sigma_D$ are self energies of source and drain contacts.

The local density of states (LDOS) at any position within the molecular junction is fairly easily calculated using the total Green's function $G_{t:M}$. This is done by adding the relevant diagonal elements of imaginary parts of $G_{t:M}/\pi$.

Using Eq. (5) the conductance is calculated using the transmission probability $T(E,V)$ which is given by

$$T(E,V) = \text{Tr}[\Gamma_D G_{t,m} \Gamma_S G^{+}_{t,m}]$$

with

$$\Gamma_{S,D} = i(\Sigma_{S,D} - \Sigma^+_{S,D})$$
The $I$-$V$ characteristics are obtained by

$$I(V) = \frac{2e \gamma}{h} \int_{-\infty}^{\infty} dE T(E,V)[f_S(E,V) - f_D(E,V)]$$

(9)

where $E$ is the carrier energy,

$V$ is the bias potential and

$f_{S,D}(E,V)$ are the Fermi–Dirac distributions of the contacts.
4. Results and discussion

4.1 Introduction to the system

Graphene, a single layer of graphite, has attracted considerable attention recently due to its intriguing physical properties and potential application in nanoelectronics. By patterning and cutting a graphene sheet into one-dimensional nanoribbons, both experimental and theoretical studies have shown that an electronic band gap can be opened up. Moreover, the band gap of the graphene nanoribbon (GNR) depends on its width and crystallographic orientation, rendering graphene-based band-structure engineering and nanoelectronic device possible. It is also reported that a finite graphene fragment with special edges can exhibit giant spin moments. Several theoretical studies have predicted that half-metallicity may be realized in GNR by applying an external in-plane electric field.

Recently, graphene sheets were successfully isolated and demonstrated to be stable under ambient conditions. Due to their unique two-dimensional (2D) honeycomb structures, their mobile electrons behave as massless Dirac fermions, making graphene an important system for fundamental physics. Moreover, graphene sheets have the potential to be lithographed to a lot of patterned graphene nanoribbons (GNRs) to make large-scale
integrated circuits. In addition, the electronic properties of GNRs have attracted increasing attention. Recent studies have shown that GNRs can be either metallic or semiconducting, depending on their shapes. This allows GNRs to be used as both connections and functional elements in nanodevices, similar to carbon nanotubes (CNTs). However, GNRs are substantially different from CNTs by having two open edges at both sides. These edges not only remove the periodic boundary condition along the circumference of CNTs, but also make GNRs more vulnerable to defects than CNTs. This is the primary reason that edges of GNRs are hydrogen terminated in our set of calculations. This avoids any edge effects that is evident\textsuperscript{2,3} from work done on bare GNRs.

When electronic properties of graphene nanoribbons are compared to those of carbon nanotubes, the nanoribbons are found to have qualitatively similar electron band structure which depends on chirality but with a significantly narrower band gap. Due to the inverse relationship between mobility and band gap, it is concluded that graphene nanoribbons operated as field-effect transistors and can achieve mobilities significantly higher than those of silicon and thus may be better suited for low power applications\textsuperscript{1}.

There are two basic geometries for graphene edges, namely, armchair and zigzag. The geometry of the two types of GNRs is shown in Fig. 4(a) and 4(b).
Fig 4: (a) Arrangement of armchair GNRs with ribbon with number \((N=5)\).

(b) Arrangement of zigzag GNRs with ribbon with number \((N=8)\)
GNRs (both armchair and zigzag) are classified based on the ribbon width number represented by “N” in Fig. 1(a) and 1(b), N being the number of armchair or zigzag carbon chains that extends along the infinite length. We use N to denote GNRs with different widths. Then the widths of ribbons with zigzag edges and armchair edges are

\[
W_z = \sqrt{3} N \frac{a_0}{2}, \quad W_a = N \frac{a_0}{2}
\]  

(10)

respectively, where \(a_0=2.49\ \text{Å}\) is the graphene lattice constant.
Fig. 5: (a) Armchair GNRs with a unit cell

(b) Zigzag GNRs with a unit cell
The program used for relaxing these structures is Gaussian\textsuperscript{27}. The index $N$ of the armchair and zigzag graphene nanoribbons in our calculation are 8 and 5 respectively as shown in Fig. 4 (a ) and (b). As GNRs are 2D crystals, they can be considered to be a periodic arrangement of two unequal sublattices. Fig. 5(a) and (b) shows such an arrangements with a unit cell for the purpose of calculation.

These structures are relaxed using 6-31G basis set. In this type of basis set, each inner shell is represented by a single basis function taken as a sum of four Gaussians and each valence orbital is split into inner and outer parts described by three and one Gaussian function, respectively. The method used is based on ab-initio techniques using density functional method. The name of the method is BLYP\textsuperscript{42}. BLYP is a hybrid method that is not solely based on DFT. A correlation-energy term is included, in which the correlation energy density is expressed in terms of the electron density and a Laplacian of the second-order Hartree-Fock density matrix involving the density and local kinetic-energy density. By insertion of gradient expansions for the local kinetic-energy density, density-functional formulas for the correlation energy and correlation potential are obtained. A gradient-corrected exchange-energy functional with the proper asymptotic limit is also included in BLYP. This functional, containing only one parameter fits the exact Hartree-Fock exchange energies of a wide variety of atomic systems with remarkable accuracy, surpassing the performance of previous functionals containing two parameters or more.

Using the method/basis BLYP/6-31G, calculation were performed to find the most stable structure configurations of armchair and zigzag ribbons. These relaxed structures were used to perform the conductance and Fermi energy calculations.
The armchair and zigzag nanoribbons were modeled so that they have seven unit cells. For calculation of conductance of an infinitely long ribbon, the system is divided into four zones as shown in Fig. 6:

1. Left side redundant
2. Left junction
3. Right junction
4. Right side redundant.

Fig. 6: A schematic diagram showing the separation of zones for the purpose of calculation

The left and right side redundant parts are buffer sections to simulate infinite ribbons form the junction parts. Left and right junctions are repeated infinitely to obtain
an infinitely long ribbon and to eradicate any edge effects. Similarly, the double layer grapheme nanoribbons were also considered following the exact same procedure.
4.2 Review of previous work and comparison with the present results

Nanoribbons have many interesting properties that are not seen in bulk or 3-D materials. This is because electrons in nanowires are laterally confined and thus occupy energy levels that are different from the traditional continuum of energy levels or bands found in bulk materials. Quantum confinement\textsuperscript{43} determines the electronic properties, i.e., the organization of electronic energy levels/bands. Some of the peculiar features of this quantum confinement, exhibited by certain nanoribbons, manifest themselves in discrete values of the electrical conductance. Such discrete values arise from a quantum mechanical restraint on the number of electrons that can travel through the wire at the nanometer scale. These discrete values are often referred to as the quantized conductance, whereby the current through a wire changes in a stepwise, rather than continuous, manner. This phenomenon has been observed in very narrow ribbons of graphene for the first time. The discovery was made by physicists, who claim that this first sighting is an important step towards using such graphene nanoribbons in transistors that are much smaller than those used in electronics devices today.

One way of creating energy gaps in a material is to make it into an extremely thin wire so that its electrons are effectively confined to move in only one dimension. This creates a series of electron energy levels separated by gaps. If the voltage along such a wire is increased, the conductance will increase in a stepwise manner because each energy level can accommodate a small fixed number of electrons. Although such quantized conductance has already been measured in tiny semiconductor nanowires and carbon nanotubes, it had yet to be seen in graphene nanoribbons. So we expect the quantum conductance vs energy values to be step graph.
Fig. 7: Density of states per unit volume and energy for a 3-D semiconductor (blue curve), a 10 nm by 10 nm quantum well (2-D) with infinite barriers (red curve) and a 10 nm quantum wire with infinite barriers (green curve) which is 1-D.

What is dimensionality mean here? Here dimensionality of a material means in how many dimensions do the carriers of the material act as free carriers. For example, in a nanowire the electrons or holes only act as free carriers in one direction. In a dot none of the carriers act as free carriers in any direction. As the dimensionality is reduced the density of states changes drastically. In 0-D the density of states of the material looks very much like that of an atom.

If we review work done on graphene nanoribbons, we find that two-thirds of ribbons with armchair edges, (armchair) ribbons are semiconducting. The bands of
zigzag GNRs are partially flat around Fermi energy\textsuperscript{45}. On the other hand, the bands of metallic armchair GNRs are linear around Fermi energy\textsuperscript{45,49}. All these calculations were performed by using ab-initio tight binding methods. Previous work shows that GNRs with hydrogen terminated armchair or zigzag shaped edges both have nonzero and direct band gaps. The ribbon widths and energy bandgaps of the GNRs are related to each other primarily in inverse proportion\textsuperscript{50}. Here we are considering a fixed width of N=8 for armchair and N=5 for zigzag nanoribbons. That translated to 9.98 (Å) for armchair and 10.78 (Å) for zig-zag nanoribbons. A point to be noted is that we use the Green’s function method for calculating the zero bias conductance and comparing our first set of results with previously published results on graphene nanoribbon obtained by other methods.

In this chapter we calculate the electronic transport in graphene ribbons with armchair and zigzag edges. Throughout this work, the dangling bonds at the edges are all assumed to be terminated by hydrogen atoms, and the dangling bonds make no contribution to the electronic state near the Fermi level. To calculate the electronic states for the ribbon, we employ a hybrid density functional approach, BLYP, in order to focus our attention on the conductance curves and density of states.

It should be noted that in all the conductance and density of states (DOS) curves that are presented in this chapter, the Fermi energy is shifted to zero.
4.3 Electronic transport properties of single layer GNRs

The quantum conductance values for single layer armchair and zigzag GNRs were calculated and are represented graphically in Fig. 8 (a) and (b). The comparison of quantum conductance of both these systems is represented in Fig. 8 (c). In these graphs the quantum conductance is plotted against energy in the units of electron volt (eV). The maximum units of conductance for both the systems occur at energies near the Fermi energy. The maximum conductance in case of armchair and zigzag GNRs is 8 and 12 quantum units respectively.
Fig. 8: (a) Quantum conductance graph of armchair graphene nanoribbon. (b) Quantum conductance graph of zigzag graphene nanoribbon. (c) Comparision of conductance curves for armchair and zigzag graphene nanoribbons

One can see the stepwise increment or decrement in the quantum conductance values of both the zig-zag and armchair nanoribbons as expected. One can observe that there is a remarkable difference in the shapes of the curves between armchair and zigzag GNR’s.
The graphs are so shifted that the Fermi energy coincides with the origin of the graph in both cases. One can clearly see an energy gap of 0.22 eV [Fig. 9 (a)] in the case of armchair GNR. This is in excellent agreement with previous results published \(^{50}\) using similar ab-initio techniques, but using a different basis set. We found that zig-zag graphene nanoribbon has no band gap [Fig. 9 (b)] and it is metallic in nature. The density of state graphs confirms this result with a peak at the Fermi energy [Fig. 10 (b)] meaning that many states are available for conduction at that energy. The zigzag GNRs has a maximum five units of conductance at Fermi energy [Fig. 9 (b)]. This is not in accordance to a previous study\(^{50}\) that state that zigzag edges also have band gaps which decrease as the widths of the systems increase. They predicted that a zigzag edged GNR with width equal to 10.78 (Å) would have an energy gap equal to 0.3 eV. But this claim was later disproved by researchers who used first principle based tight binding method and experiments \(^{49}\). Their calculation proved that hydrogen-passivated zigzag GNR of specified width is metallic with zero band gap. We support our results with the density of state graphs that clearly shows a number of electronic bands available for occupation at Fermi energy.
Fig. 9: Graphs with more resolution to see the energy gaps (a) Armchair (b) Zig-zag
Fig. 10: Density of states vs energy curves for (a) Armchair (b) zigzag GNR
A closer look near the Fermi energy with higher resolution suggests that there are 5 to 7 conductance units available near Fermi energy of zig-zag GNR. This clearly states that zigzag GNR is metallic in nature, while the zero conductance at Fermi energy of armchair GNR tells us it is semiconducting. The density of state curves shows us that there are no electronic bands available for occupation near Fermi energy for armchair GNR. This was not the case for zigzag GNRs that have several states available for conduction near Fermi energy.
4.4 Double layer GNR’s

Similar methods were employed to construct double layered Graphene nanoribbons. The width of armchair is same as \( N=8 \) and for zigzag it is \( N=5 \). Two different structures were considered\(^\text{11}\), one by shifting one layer over the other in the direction of the infinite edge, so that there are atoms at the center of the hexagons in the top layer. This formation of double layer GNR is referred to as AB stacking, as is the normal arrangement of graphene planes in graphite. The other structure is obtained by placing one layer right above the other so that each atom is placed right beneath the other. This type of arrangements is called AA stacking. These formations are shown in Figs. 11, 12 and 13. The distance between the two layers is 3.335Å\(^\text{11}\) in both the zigzag and armchair edge structures. The major difference in AB stacking of armchair and zigzag GNRs is that the second layer is shifted towards the finite edge of the ribbon in case of zigzag and second layer is moved along the infinite edge in case of armchair GNRs, as is shown by first principle tight binding calculations\(^\text{11}\). Each layer in the armchair structures was relaxed by using the method and basis functions explained earlier. Energy difference between AB- and AA-stacked structures of armchair GNR was found to be in the order of 0.49 eV for the width that was considered. This energy difference will depend on the width of the ribbons. The AB structure (one layer moved over the other) was more stable than the AA structure. We calculated the transport properties for both of these structures. We also calculated the transport properties of zigzag AA structure.
Fig. 11: (a) side view of Armchair, one atom over the other (AA) bilayer structure.

(b) top view of Armchair, one atom over the other (AA) bilayer structure.
Fig. 12: (a) side view of Armchair, one layer shifted over the other (AB) bilayer structure. (b) top view of Armchair, one layer shifted over the other (AB) bilayer structure.
Fig. 13: (a) side view of Zigzag, one atom over the other (AA) bilayer structure.

(b) top view of Zigzag, one atom over the other (AA) bilayer structure
4.5 Comparing single and double layer structures

We expected that due to quantization of conductance, if the two layers do not interact with each other, then we should just observe the conductance values to be twice of that we got in the single layer GNR case. This theory is disproved as we see that the maximum conductance is certainly not twice, but at certain energies the conductance values drops to half of the values of single layer GNR. There is also a considerable reduction of energy gap. For the armchair AB structure it was found to be 0.01 eV, and the armchair AA structure had zero band gap. The armchair AA structure shows a maximum conductance of 2 units at Fermi energy [Fig. 15 (b)]. The density of state curves provide further evidence of metallicity of bilayer AA-stacked structure [Fig. 16 (a) and (b)]. That means that the AB structure is semiconducting but the AA structure is semi-metallic with a zero band gap.

The band gap we observed for single layer armchair GNR was 0.22 eV, and for double layer AB stacking it has closed to 0.01 eV [Fig. 14 (b)]. This closing of gap was also predicted by some recent publications\textsuperscript{43,52,53} according to which, in case of armchair GNRs with AB stacking the band gap decreases as the number of layer increases and an armchair GNR will behave like bulk graphene if five or more layers are stacked together\textsuperscript{51}. Such systems with five or more layers are predicted to have zero bad gap and behave like bulk graphene.
**Fig. 14:** Quantum conductance vs energy graphs for bilayer armchair AB-stacked structure. (a) full range (b) near Fermi energy showing the narrow gap.
Fig. 15: Quantum conductance vs energy graphs for bilayer armchair AA structure (a) full range (b) near Fermi energy showing zero gap
Fig. 16: Density of state vs Energy curves for armchair double layer structures with high resolution at Fermi energy (a) AB stacking (b) AA stacking
Fig. 17: Comparing the conductance graphs of (a) Armchair bilayer AB-stacked to single layer Armchair (b) Armchair bilayer AA-stacked to single layer
In the same way as we assumed for the bilayer armchair, in the absence of interlayer interactions we expected the double layer zigzag GNR to have double the conductance values of single layer. But this is not confirmed by the calculated values. The conductance of double layer zigzag GNR is remarkably different that of the single layer one. The maximum conduction for single layer zigzag structure was 12 quantum units and for zigzag bilayer AA stacking structure it is 18 units. This states that the quantum conductance of two layer of zigzag GNR placed one over the other don’t just add up. Same is the case at many carrier energy values. This shift in the maximum conductance is caused by interaction effects between the two layers.

Fig. 18: Comparing the conductance graphs of bilayer AB and AA stacking.
Fig. 19: Quantum conductance vs energy graphs for bilayer zigzag AA structure

(b) full range (b) near Fermi energy showing zero band gap
Fig. 20: Comparing the conductance graphs of bilayer straight zigzag structures with single layer zigzag structures.
4.6 Overall review of electronic transport in armchair and zigzag GNRs

Recent publications\textsuperscript{53} have suggest that the bandgap observed in, e.g., double layer armchair AB-stacked structure, can be controlled by an electric field or by using a different substrate like SiC\textsuperscript{51}. Electrons in single layer GNR appear to behave as if they have no mass\textsuperscript{51} and move like particles of light - photons. In tunable bilayer graphene, the electrons suddenly act as if they have masses that vary with the bandgap\textsuperscript{55}. In bilayer graphene, one can independently control the two most important parameters in a semiconductor: One can change the electronic structure to vary the bandgap continuously, and independently control electron doping by varying the Fermi level.

Since graphene was first isolated from graphite, in 2004\textsuperscript{55}, it has been a hot topic of research, in part because solid state theory predicts unusual electronic properties, including high electron mobility more than 10 times that of silicon\textsuperscript{51}. Another critical property of graphene that can be altered is its Fermi energy\textsuperscript{53}, that is, the maximum energy of occupied electron states, which controls the electron density in the material.

In the past it was not possible to see in experiment these interesting properties of GNRs, because of charge impurities and defects in experimental devices. This has given computational researchers a chance to show different aspects of graphene engineering and has been followed by successful practical demonstration in experiments to illustrate these properties.
Our work shows that, in the case of GNR with a width of ~10 Å, the maximum bandgap that could be produced was 220 meV in single layer armchair structure. In comparison, other semiconductors like germanium and silicon have about 740 and 1,200 meV bandgaps, respectively. Because the zero to 220 meV bandgap range allows graphene to be tuned continuously from a metal to a semiconductor, one may speculate turning a single sheet of bilayer graphene into a dynamic integrated electronic device with millions of gates deposited on the top and bottom.

Here we use molecular orbital coefficients, together with basis set information, to create electronic state images. These images portray molecular orbitals in the form of isodensity surfaces. A degeneracy threshold isovalue of 0.002 is used in these images in order to make the diagram appear more clearly. Degeneracy threshold is a point where two levels will be degenerate if their energies agree to less than the threshold value.

Important electronic properties can be attributed to the highest occupied and lowest unoccupied molecular orbitals (HOMO and LUMO). In Fig. 21, we present LUMO distributions for the structures considered in this research. A site where the lowest occupied orbital is localized, is a good electrophilic site. For example, instead of thinking about the total electron density in a system, we should think about the localization of LUMO orbital because electrons jump into these sites/orbitals from HOMO and cause conduction. The distribution of LUMO orbitals with different symmetries (red and green) along the GNR’s in Fig. 21 provides an indication of the conduction characteristics. Better interpretation can be obtained by considering the density of states and distributions
for the whole periodic structures, and by tacking the effects of other orbitals/bands (beyond LUMO) into account, as discussed earlier.
Fig. 21: Molecular orbital arrangement for lowest unoccupied molecular orbitals (LUMO) of (a) single layer armchair (b) single layer zigzag (c) bilayer armchair AB stacking (d) bilayer armchair AA stacking (e) bilayer zigzag AA stacking
5. Conclusion

We have discussed the electronic transport in graphene nanoribbons of specified width. We show that different graphene nanoribbons have different conductance values due to different types of edges geometries. They can be metallic or semiconducting in the single layer configuration. The double layer ribbons show deviations from the expected superimposed curves, owing to interlayer interactions. They can behave like a semiconductor or show metallic properties depending on factors like stacking arrangements and edge geometries.

Despite its intriguing properties, one of the biggest hurdles for graphene to be useful as an electronic material is the lack of an energy gap in its electronic spectra for more than five layer stacking. The band gap of a material being one of the most important properties as it determines both the electrical and optical properties\textsuperscript{51}. This, for example, prevents the use of multilayer graphene in making transistors. Although several proposals have been made to open a gap in graphene's electronic spectra\textsuperscript{53}, they all require complex engineering of the graphene layer. Here, we show that single layer armchair structure has bandgap of 0.22eV which can be engineered to make nanoelectronic devices. This gap decreases as the sample thickness increases and eventually approaches zero\textsuperscript{53}. We believe that our results highlight a promising direction for bandgap engineering of graphene.
Graphene nanoribbons have an electronic structure that can be controlled by an electrical field, an effect that can be exploited to make tunable electronic and photonic devices\textsuperscript{54}. While such properties were predicted for a double layer of graphene, this is a demonstration showing armchair bilayer graphene exhibit a bandgap. Because tuning the bandgap of bilayer graphene can turn it from a metal into a semiconductor, bilayer graphene could potentially hold differently tuned electronic devices that can be reconfigured at will. The ability to simply put a material between two electrodes, apply an electric field and change the bandgap is a huge advancement and a major breakthrough in the field of materials engineering, because it means that in a device configuration we can change the bandgap just by sending an electrical signal to the material. For the first time you can use an electric field to close the bandgap and open the bandgap\textsuperscript{53,56}. This is a unique property of bilayer graphene. This is not just a technological advance; it also opens the door to some really new and potentially interesting materials.

Our results on the bandgap engineering of graphene nanoribbons upon layer stacking are beneficial for characterization of nanoribbons based on their electric conduction, and for device design based on nanoribbons.
References


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Presentation and publication

This work will be presented at the Materials Research Society (MRS) Fall 09 Meeting in Boston.