Quantum Transport in Graphene Nanotransistors

By

Anuj Girdhar

Dissertation

Submitted in partial fulfillment of the requirements
for the degree of Doctor of Philosophy in Physics
in the Graduate College of the
University of Illinois at Urbana-Champaign, 2015

Urbana, Illinois

Doctoral Committee:

Professor Nadya Mason, Chair
Professor Jean-Pierre Leburton, Director of Research
Professor Klaus Schulten
Professor Rashid Bashir
Abstract

Over the past decade, interest in using graphene in condensed-matter physics and materials science applications has exploded, owing to its unique electrical properties. Narrow strips of graphene, called graphene nanoribbons, also display exotic behavior. A nanoribbon’s edge geometry determines its electronic transport properties, and the rich behavior of conductance of nanoribbons in response to external potentials makes them ideal for use within transistors.

In this thesis, we work towards creating an accurate model of graphene nanoribbon transistors, and we assess two possible applications which exploit their amazing potential. We begin by outlining the basic theoretical and computational framework for the model developed in this work. We then demonstrate the capability of graphene nanoribbon transistors, with nanopores, to electronically detect, characterize, and manipulate translocating DNA strands. Specifically, we explore the tunability of such devices, by examining the role of lattice geometry, such as a quantum point contact constriction, on their performance. We perform a demonstration of the ability to detect the passage of double and single-stranded DNA, through molecular dynamics simulations. The transistors presented are capable of sensing the helical shape of double-stranded DNA molecules, the unraveling of a DNA helix into a planar-zipper form, and the passage of individual nucleotides of a single strand of DNA through the nanopore. We outline a preliminary analysis on the proper design of a multi-layer transistor stack to control both the electronic properties of the conducting membrane, as well as the motion of the DNA. Lastly, we present another type of nanoribbon device, an all-carbon spintronic transistor for use in cascaded logic circuits. A thorough analysis of the transport properties of zigzag nanoribbon transistors in magnetic fields, in addition to the design and construction of logic gate circuits containing these spintronic transistors, is presented.
“Five-card stud, nothing wild.
... and the sky’s the limit.”

Captain Jean-Luc Picard
Acknowledgements

This work was supported, in part, by the National Institutes of Health grants NIH 9P41GM104601 and NIH 5 R01 GM098243-02, National Science Foundation grant PHY0822613, Oxford Nanopore Technologies, and the Beckman Institute for Advanced Science and Technology Graduate Fellowship. We gratefully acknowledge supercomputer time provided by XSEDE grant MCA93S028.

This thesis would not have been possible without the help of a great number of individuals.

First, for providing me with the means to survive, I want to thank Oxford Nanopore Technologies, the National Science Foundation, the National Institutes of Health, the Beckman Institute for Advanced Science and Technology, and the Physics Department at the University of Illinois at Urbana-Champaign.

My advisor, Dr. Jean-Pierre Leburton, has guided me throughout the past 5 years, providing immense help, advice, (constructive) criticism, and positivity throughout my graduate education. Without his constant assurance and confidence in my work and my abilities, I would have given up long ago, and I am thankful for his patience during my times of doubt and difficulty. I can safely say he is the best advisor I could have asked for.

I want to thank Drs. Nadya Mason, Rashid Bashir, and Klaus Schulten for serving on my committee. Their guidance has been instrumental in completing my goals this past year.

All of the work presented in this thesis is the fruit of numerous collaborations. Dr. Chaitanya Sathe has been a wonderful colleague, sharing with me my proudest academic achievements as well as my most humbling moments. Without his expertise, enthusiasm, and cool composure, I could not have reached this point. Dr. Klaus Schulten’s efforts have been integral to my research, and I am honored to have worked alongside such a distinguished scientist. Dr. Hu Qiu, though we have only collaborated for a short time, has already proven to be an exemplary researcher and has surpassed my highest expectations. I would also like to thank Jiwook Shim, Shouvik Banerjee, and Joseph Friedman for many useful discussions.

I would also like to thank the members of my group, whose shared experiences and conversations gave color to an often dreary cubicle. My classmates, with whom I spent many sleepless nights completing impossibly large homework assignments, provided companionship and encouragement during the most intimidating portion of my graduate education. I could not have survived the loneliness of Urbana without the companionship of my classmate, Dr. Ethan Brown, who I now consider to be one of my dearest friends. On the same note, the numerous friends I have made during my time in Urbana, within and outside of the department, have provided some of the best times I have experienced.

I wish to thank Richard D. James, Jodey Kendrick, Aleks Perala, Dave Monolith, Bogdan Raczynski, Reid Dunn, Luke Vibert, and the rest of the Rephlex Krew, for giving me the greatest pleasure on planet Earth and motivating me to constantly improve myself.

Lastly, I want to thank those dearest to me. I want to thank Andrea Jennings, my partner, for giving me strength during the most difficult times, for providing love and friendship without hesitation, and for putting up with the stresses and difficulty of graduate school. I want to thank my sister, Dr. Manika Girdhar, for being the only one who understands my humor and for showing me what true strength really is. I want to thank my mother and father, Drs. Kiran and BK Girdhar, who have shown endless love and support, and have provided me with the means to reach my fullest potential. Without their guidance throughout my life, I would have never been able to begin in the first place.

There are too many people to mention here, but I lastly want to thank each and every person I have had the privilege of meeting and spending time with. Without you all, I would be nowhere.
Contents

List of Figures .......................................................... vii
List of Tables ............................................................ xiv

1 Introduction ........................................................... 1
  1.1 DNA Detection with Graphene Nanopore Transistors ............... 2
  1.2 All-Carbon Spin Logic Device ..................................... 3
  1.3 Outline ............................................................ 4

2 Methods ................................................................. 6
  2.1 Lattice Structure ................................................ 6
    2.1.1 Carbon ...................................................... 6
    2.1.2 Hexagonal Lattice ........................................ 6
  2.2 Tight-Binding Model ............................................. 8
    2.2.1 Secular Equation .......................................... 8
    2.2.2 Periodic Lattice .......................................... 8
    2.2.3 Second Quantization ..................................... 10
  2.3 Electron Transport in Mesoscopic Systems ......................... 12
    2.3.1 Landauer-Büttiker Formalism ............................. 12
    2.3.2 Non-Equilibrium Green’s Functions ..................... 13
  2.4 Multi-Scale Device Model ..................................... 15
    2.4.1 Electrostatic Potential on Conducting Membrane .......... 16
    2.4.2 External Magnetic Fields ................................ 17

3 Electronic Properties of Graphene and Graphene Nanoribbons ...... 18
  3.1 Dirac Fermions in Single Layer Graphene ......................... 19
  3.2 Nanoribbons .................................................... 22
    3.2.1 Armchair Nanoribbons .................................... 22
    3.2.2 Zigzag Nanoribbons ....................................... 23
  3.3 Nanopores and Irregular Edges ................................ 25

4 Solid-State Nanopore Transistors for DNA Detection, Characterization, and Manipulation ........................................ 26
  4.1 DNA Detection and Characterization with Single Layer Graphene Nanoribbons ....................................... 26
    4.1.1 Transmission Probability of Patterned GNRs .............. 27
    4.1.2 Variation of Electronic Conductance with Fermi Energy .. 30
    4.1.3 Conductance Variations due to External Charges .......... 32
    4.1.4 Observation of dsDNA Helicity and Translocation Through Nanopore ........................................... 35
    4.1.5 Characterization of Helix to Zipper Transformation Under Forced Extension of dsDNA ................................. 38
    4.1.6 Detection of the Passage of Single Nucleotides from Translocating Stretched ssDNA ................................. 47
  4.2 Expanding Transistor Functionality with Additional Gate Electrodes ........................................ 53
List of Figures

2.1 (L) Hexagonal lattice, composed of $A$ and $B$ carbon atomic sites. Each $A$ site has three nearest neighbors, displaced by vectors $\delta_l$. Each sublattice is generated by the lattice vectors $a$. (R) First Brillouin zone of hexagonal lattice, showing selected high symmetry points. Adapted from [1] ............................ 7

2.2 Two terminal mesoscopic device. Conductor region, $C$, is connected via the potential $V$ to left and right leads, held at chemical potentials $\mu_L$ and $\mu_R$, respectively. .......................... 12

3.1 Electronic band structure of graphene, as calculated by eqn. 3.3. The Fermi energy lies at the meeting of the conduction and valence bands, at the six Dirac points, one of which is shown in the inset. Taken from [1] ............................... 19

3.2 (L) Armchair nanoribbon with $N$ transverse sites. The wavefunction is zero on both sublattices at $x = 0$ and $x = W$. (R) Zigzag nanoribbon with $N$ transverse sites. The wavefunction is zero at $A$ sites at $x = 0$ and at $B$ sites at $x = W$. .............................. 21

3.3 Band structures of a (top) zigzag nanoribbon, with $K$ and $K'$ points labelled, (middle) semiconducting armchair nanoribbon, and (bottom) metallic armchair nanoribbon. Adapted from [2] ........................... 22

4.1 Schematic diagram of a prototypical solid-state, multilayer device containing a GNR layer (black) with a nanopore, sandwiched between two oxides (transparent) atop a heavily doped Si back-gate, $V_G$ (green). The DNA is translocated through the pore, and the current is measured with the source and drain leads, $V_S$ and $V_D$ (gold). Taken from ref [3]. (See figure C.5 in the Appendix for a cross-sectional schematic diagram) .......................... 27

4.2 Transmission functions for various edge geometries and pore configurations: a) 5 nm (5-GNR) and b) 15 nm (15-GNR) wide GNR-edged devices, c) 8 nm (8-QPC) and d) 23 nm (23-QPC) wide QPC-edged devices. Pristine (solid), a 2 nm pore at point P (long dash), a 2 nm pore at point Q (short dash), and a 4 nm pore at point P (dot dash). Taken from ref [3] ................................. 28

4.3 Conductance versus Fermi energy (as a function of carrier concentration) for the four edge geometries with four pore configurations for each geometry. a) 5-GNR, b) 15-GNR, c) 8-QPC and d) 23-QPC. Pristine (solid), 2 nm pore at point P (long dash), 2 nm pore at point Q (short dash), and 4 nm pore at point P (dot dash). Taken from ref [3] .............................. 31

4.4 Change in the conductance due to adding an external charge within the 2 nm pore. ‘S’ means the charge is placed one half radius south of the center of the pore, and ‘W’ means the charge is placed one half radius west of the center of the pore. a) 5-GNR, b) 15-GNR, c) 8-QPC and d) 23-QPC. Taken from ref [3] .............................. 34
4.5 a) Schematic of an AT DNA strand translocating through a pore. b) Potential maps in the graphene plane due to the DNA molecule at eight successive snapshots throughout one full rotation of the DNA strand. Taken from ref [3].

4.6 Conductance as a function of DNA position (snapshot) for multiple Fermi energies, .04 eV (solid), .08 eV (long dash), .12 eV (short dash), and .16 eV (dot dash), as the DNA strand rigidly translocates through a 2.4 nm nanopore pore located at the device center (point P). a) 5-GNR, b) 15-GNR, c) 8-QPC and d) 23-QPC. Taken from ref [3].

4.7 Five representative snapshots (A-E) from a single SMD trajectory of poly(A-T)$_{15}$ DNA during a B-DNA (A) to zip-DNA (E) transition. The atoms colored in red were pulled in the $z$-direction at a rate of 1 Å ns$^{-1}$; the blue colored atoms were harmonically restrained to the initial positions. Also shown is the evolution of two sets of base pairs, P-P' and Q-Q', which are a half pitch (namely 5 bp) apart. The black arrows, joining P to P' and Q to Q', initially pointing in opposite directions corresponding to a pure helical conformation (B-DNA) align themselves in the same direction once the zipper conformation (zip-DNA) is reached. The numbers below each snapshot represent the corresponding molecular extension. Taken from ref [4].

4.8 Force-extension curves for poly(A-T)$_{15}$ DNA. Shown are the force-extension curves that resulted from five independent SMD simulations, Sim 1-5, performed at a pulling speed of 1 Å ns$^{-1}$. The force-extension curve begins with a region corresponding to the elastic extension of B-DNA followed by a B-DNA to zip-DNA transition plateau. In the region beyond the plateau the zip-DNA undergoes elastic extension, which is characterized by a sharp linear increase in force. The inset shows the zip-DNA conformation at the end of the transition plateau. Figure C.9 of the Appendix shows the force-extension curves for the poly(G-C)$_{15}$ strand. Taken from ref [4].

4.9 Evolution of the angle between base pairs P-P’ and Q-Q’ (see Figure 4.7) for five independent SMD simulations, Sim 1-5, performed on poly(A-T)$_{15}$ DNA; the angle changes from -180° to 0° as the DNA segment between P-P’ and Q-Q’ transitions from helical to zipper form. Figure C.10 of the Appendix shows the corresponding curve for the poly(G-C)$_{15}$ strand. Taken from ref [4].

4.10 Transverse electronic conductance as a function of poly(A-T)$_{15}$ DNA position (snapshot) for (a) graphene nanoribbon with armchair edge, and (b) graphene nanoribbon with QPC edge. Base pairs P-P’ were initially aligned with the nanopore, and subsequently translocated at a rate of 0.5 Å, along -$z$ direction, per snapshot until base pairs Q-Q’ reached the pore. The transverse electronic conductance changes from an oscillating type response, corresponding to B-DNA (A), to a constant conductance when the DNA adopts a zipper-like conformation, i.e., zip-DNA (E). Sinusoidal variation in the transverse electronic conductance diminishes as the DNA passes through the intermediate stages B, C, and D. A QPC edge geometry shows larger variations in transverse electronic conductance when compared to the armchair edge geometry. Taken from ref [4].
4.11 Variation in the transverse electronic conductance as a function of DNA extension for a QPC edge graphene nanopore. Shown in (a) and (b) are conductance variation, for the stages A, B, C, D, and E (see Figure 4.7) arising in the B-DNA to zip-DNA transition corresponding to KCl molar concentrations of 1 M and 0.1 M, respectively. The error bars are obtained from sampling over five independent force-extension simulations performed on poly(A-T)$_{15}$ as well as on poly(G-C)$_{15}$ strands. Taken from ref [4].

4.12 Schematic of the g-QPC system used to calculate transverse electronic conductance. Shown in the figure is an ssDNA, which arose from a MD simulation of forced extension, being translocated through the nanopore under a translocation bias. Transverse electronic conductance was computed for the five base pairs shown in the inset of the figure. Taken from ref [5].

4.13 Conductance as a function of DNA position (snapshot) arising in a g-QPC due to translocation of 5 base pairs of a ssDNA molecule in a linear ladder-like conformation (see inset Figure 4.12). The dips in the conductance correspond to the translocation of a single base pair through the nanopore. Three different 1.2 nm diameter nanopore geometries are investigated: the nanopore center is (a) aligned to the geometric center of the graphene membrane, (b) offset by 1 nm from the geometric center, and (c) offset by 2 nm from the geometric center. (d) A schematic of the g-QPC nanopore with ssDNA inside. For each of the geometries the base pairs were translocated in two different configurations: ssDNA-x, where the base pairs are aligned in the direction of transverse electronic current (x direction) and ssDNA-y where the base pairs are aligned in direction perpendicular to the transverse electronic currents (y direction). Taken from ref [5].

4.14 Influence of pore size and shape on the electronic conductance variation due to translocation of a 5 base pair long ssDNA segment in a linear ladder-like conformation. (a) circular pore with diameter = 1.2 nm, (b) circular pore with diameter = 2 nm, and (c) elliptical pore with major and minor axis diameters equal to 1.2 nm and 0.8 nm respectively. Taken from ref [5].

4.15 Schematic diagram of a 4 layer device containing a two graphene layers (black) to control the translational motion of DNA through the nanopore. The top graphene layer ($V_{C1}$) controls the translational speed of the DNA, while the second ($V_{C2}$) controls the lateral confinement of the DNA within the nanopore. The third graphene layer ($V_{DS}$) measures the sheet current. Finally, a heavily-doped back gate (green) lies underneath the sheet current layer to control the carrier concentration. Oxide barriers (transparent) between different graphene layers provide electrical isolation. Taken from ref [3]. (See figure C.7 in the Appendix for a cross-sectional schematic diagram).

4.16 (a) Diagram of a graphene transistor with a single-layer graphene (SLG) nanoribbon sandwiched between two oxide layers. (b) (above) Top view of the QPC GNR with nanopore. (below) Cross-sectional schematic diagram of the simulated multilayer device, displaying all parameters chosen for the simulation. These figures are not to scale. Taken from ref [6].
4.17 (a) (above) Color plots of the local electric potential in the graphene layer at three gate voltages (-4 V, 0 V, 4 V). (below) Potential profile through the center of the nanopore within the graphene plane at three gate voltages. (b) (above) Local electron (left) and hole (right) concentration in the QPC at the same gate voltages. (below) Total carrier concentration profile along the current propagation direction, averaged along the width (y axis) of the nanoribbon. Taken from ref [6].

4.18 (a) Vertical cross section of the absolute electric potential of the system through the nanopore center at $V_G = -4$ V. (b) Spatial distribution of electrolytic ions in solution at various gate voltages. Taken from ref [6].

4.19 a) (above) GNR conductance versus gate bias for different DNA positions along the nanopore axis using the expanded three-orbital basis. (below) GNR conductance versus gate bias using the traditional single-orbital tight-binding model of graphene. b) The electron transmission versus energy around the Fermi energy for the expanded three-orbital basis (solid black), the expanded basis without hydrogen passivation (dashed green), and the single orbital basis without hydrogen passivation (dashed red). Taken from ref [6].

4.20 (Above) Electrostatic potential and (Below) electric field, in $xy$ plane and line across nanopore diameter, of a 0.5 V gated cylindrical nanopore, in a 0.3 M solution.

4.21 (Above) Electrostatic potential and (Below) electric field, in $xy$ plane and line across nanopore diameter, of a 0.5 V gated cylindrical nanopore, in a 1.0 M solution.

4.22 a) Center of mass (CM) displacement from center of nanopore, at five gate voltages and 0.3 M ion concentration. The thick line is the moving average over 100 data points. b) Moving standard deviation over 100 data points of CM displacement at 0.3 M. c) and d) are the moving CM displacement and SD at 1.0M.

4.23 CM displacement of DNA from center of nanopore in (left) 0.3 M solution and (right) 1.0 M solution.

4.24 (Above) CM displacement of DNA from center of nanopore, during pulsing of 0.5 V gate. Moving average is thick line. Shaded regions correspond to on voltage, while unshaded regions are off. (Below) SD of CM displacement during pulsing of 0.5 V gate.

5.1 All-carbon spin logic OR/XOR basis gate, controlled by two CNTs ($I_{CTRL}$) parallel to the unzipped CNT-GNR ($I_{GNR}$) grown on an insulating material. As all voltages are held constant, the currents $I_{CTRL}$ and $I_{GNR}$ are the same in magnitude. The currents are then defined by $-1, 0,$ or $+1$, where $\pm$ signifies the current direction.

5.2 (a) On-site magnetization profile of a zigzag GNR. The color of each circle represents the spin species, while the radius corresponds to the magnitude of the magnetization. (b) The on-site magnetization of each site in a unit cell as a function of distance from the edge. (c) The global magnetic orientation of the AFM (left) state with oppositely oriented edge magnetizations and the FM (right) state with parallel edge magnetizations.
5.3 (a and b) Band diagrams for the (a) AFM and (b) FM states of a zigzag GNR. In the AFM state, both up and down spins have identical band structures, while in the FM state, each spin species has a unique band structure. (c and d) Magnetic instability energy for zigzag GNRs measuring (c) 20 nm with a CNT to GNR separation of 10 nm and (d) 35 nm with a CNT to GNR separation of 1 nm. The critical switching current which separates the AFM (blue) phase from the FM (red) phase is denoted with a black dashed line. (e) The transmission function around the band gap for a zigzag 12-GNR at \( U = 2.7 \) eV for the (blue) AFM state and (red) FM state. (f) A typical switching event, where the GNR conductance increases by \( G_0 \) when the CNT current passes the critical switching current \( I_C \).

5.4 Half adder with all-carbon spin logic. CNTs are partially unzipped to create GNRs with negative magnetoresistance that perform the half adder logic function. CNT input currents A and B are connected to the output of a GNR elsewhere in the circuit, and flow in parallel alongside XOR1 to compute \( A \oplus B \), which outputs the sum \( S \). Current \( A \) crosses over insulated CNTs without making an electrical connection, flowing opposite \( B \) to compute \( A + B \) with OR1. The outputs of XOR1 and OR1 flow in the same direction alongside XOR2 to compute \( (A \oplus B) \oplus (A + B) \). The current through XOR2 is output as carry \( C \). The gate is held at a constant voltage to maximize the GNR magnetoresistance.

5.5 All-carbon spin logic parity gate, used in error detection and correction, computes \( P = (A \oplus B) \oplus (C \oplus D) = A \oplus B \oplus C \oplus D \). Thus, when there is an odd number of ‘1’ inputs, the output is ‘1’; the output is ‘0’ if there are an even number of ‘1’ inputs.

C.1 Conductance variations of placing an eighth of an electron test charge in the south and west positions of a 2 nm nanopore located at point P (inset) in a) 5-GNR, b) 15-GNR, c) 8-QPC, and d) 23-QPC. Taken from ref [3].

C.2 Conductance variations of placing a full electron test charge in the south and west positions of a 2 nm nanopore located at point Q (inset) in a) 5-GNR, b) 15-GNR, c) 8-QPC, and d) 23-QPC. Taken from ref [3].

C.3 Conductance variations of placing an eighth of an electron test charge in the south and west positions of a 2 nm nanopore located at point Q (inset) in a) 5-GNR, b) 15-GNR, c) 8-QPC, and d) 23-QPC. Taken from ref [3].

C.4 Illustration depicting the precise lattice configuration used to simulate the a) 5-GNR and b) 8-QPC nanoribbons with a 2.4 nm diameter nanopore. Taken from ref [3].

C.5 Cross-sectional schematic diagram through the central axis of the nanopore of the multilayer device illustrated in figure 4.1 showing source (\( V_S \)) and drain (\( V_D \)) contacts as well as the back gate (\( V_G \)). Taken from ref [3].

C.6 Cross-sectional schematic diagram through the central axis of the nanopore of the multilayer device illustrated in figure 4.15 showing source (\( V_S \)), drain (\( V_D \)), and control (\( V_{C1} \) and \( V_{C2} \)) contacts, as well as a back gate (\( V_G \)). Taken from ref [3].

C.7 Cross-sectional schematic diagram through the central axis of the nanopore of the multilayer device illustrated in figure 4.15 showing source (\( V_S \)), drain (\( V_D \)), and control (\( V_{C1} \) and \( V_{C2} \)) contacts, as well as a back gate (\( V_G \)). Taken from ref [3].

C.8 Molecular extension of poly(A-T)\textsubscript{15} DNA over the course of a 60-ns SMD simulation performed at a constant pulling speed of 1 Å/ns. Taken from ref [4].
C.9 Force-extension curves for poly(G-C)$_{15}$ DNA. Shown are the force-extension curves that resulted from five independent SMD simulations, Sim 1-5, performed at a pulling speed of 1 Å/ns. The force-extension curve begins with a region corresponding to the elastic extension of B-DNA followed by a B-DNA to zip-DNA transition plateau. In the region beyond the plateau the zip-DNA undergoes elastic extension, which is characterized by a sharp linear increase in force. The inset shows the zip-DNA conformation at the end of the transition plateau. Taken from ref [4].

C.10 Evolution of the angle between base pairs P-P' and Q-Q' (see figure C.9) for five independent SMD simulations, Sim 1-5, performed on poly(G-C)$_{15}$ DNA; the angle changes from -180° to 0° as the DNA segment between P-P' and Q-Q' transitions from helical to zipper form. Taken from ref [4].

C.11 Snapshots of the electrostatic potential profile of B-DNA in the graphene membrane at 1 M KCl concentration. The electrostatic potential profiles (a-i) correspond to translocation of the DNA segment, comprising of base-pairs between P-P' and Q-Q', through the nanopore. The B-DNA, due to the helical DNA conformation, rotates by 180° in the plane of the graphene membrane. Along with the DNA rotates the electrical field inside the graphene nanopore, which induces oscillations in the transverse electronic conductance. Taken from ref [4].

C.12 Snapshots of the electrostatic potential profile of zip-DNA in the graphene membrane at 1 M KCl concentration. The electrostatic potential profiles (a-i) correspond to translocation of the DNA segment, comprising of base-pairs between P-P' and Q-Q', through the nanopore. The zip-DNA does not rotate in the plane of the graphene membrane leading to a constant transverse electronic conductance. Taken from ref [4].

C.13 Graphene lattices with pore diameter = 2.4 nm, employed in the calculation of transverse electronic conductance: (a) 5 nm-wide armchair edge nanoribbon (b) 8 nm-wide QPC edge nanoribbon. Taken from ref [4].

C.14 Snapshots of the electrostatic potential profile of B-DNA in the graphene membrane at 0.1 M KCl concentration. The electrostatic potential profiles (a-i) correspond to translocation of the DNA segment, comprising of base-pairs between P-P' and Q-Q', through the nanopore. Due to reduced screening the electrostatic potential profile in case of 0.1 M KCl has a slower spatial decay than in case of 1 M KCl (see figure C.11). Taken from ref [4].

C.15 Radial distribution of electrostatic potential at the nanopore edge under KCl molar concentrations of 1 M and 0.1 M. The potentials correspond to a DNA conformation, where the base pair P-P' is inside the nanopore. At low molarity (0.1 M) the potential in the vicinity of the pore is much larger (in magnitude) than in case of high molarity (1 M KCl) due to reduced screening. Taken from ref [4].

C.16 Half adder truth table. The one-bit half adder computes binary addition on two inputs, A and B, to compute their sum S and an overflow bit C that is carried to the next digital bit. For example, the binary computation of 1 + 0 is a sum S of ‘1’ and a carry C of ‘0’. Similarly, 1 + 1 results in a sum S of ‘0’ and a carry C of ‘1’ used for adding the next bit.
C.17 All-carbon spin logic half adder symbolic implementation. Shown here with conventional symbols, the all-carbon spin logic one-bit half adder uses inputs $A$ and $B$ are input to XOR1 to compute $S = A \oplus B$, and to OR1 to compute $A + B$. XOR2 performs the XOR function on $A \oplus B$ and $A + B$ to calculate $C = (A \oplus B) \oplus (A + B)$, which is equivalent to $C = A \cdot B$. 

\begin{align*}
C &= A \cdot B.
\end{align*}
List of Tables

A.1 Relative permittivities (dielectric constants) of dielectric materials ............ 79
A.2 Commonly used symbols and constants ................................................. 80
A.3 Third Nearest Neighbor Basis Overlap Matrix Elements ............................. 81
A.4 Expanded Nearest Neighbor Basis Overlap Matrix Elements (Atomic) ............. 82
A.5 Third Nearest Neighbor Basis Overlap Matrix Elements (Hybridized) ............. 83
1

Introduction

Graphene’s popularity has grown rapidly since its initial isolation in 2004 [7]. Its rise has been marked by a plethora of innovations and discoveries, revealing the great potential of this exotic material [8–15]. Graphene is a member of a new class of two-dimensional crystals, whose atomic thinness provides a natural way to study the properties of two-dimensional electron gasses. Graphene’s hexagonal lattice yields an extremely unique band structure. As a result, the charge carriers behave like massless Dirac particles, providing a tangible environment to probe relativistic physics [16, 17]. If boundary conditions are introduced by way of geometrical modifications, such as by nanopores or defects, the allowed electronic states are restricted, and the resulting electronic structure becomes very complex [2]. In the case of narrow strips of graphene, called graphene nanoribbons (GNRs), the exact edge shape dictates the behavior of the conductance, particularly in response to an external perturbation [18]. As a result, the geometry of GNRs plays an extremely important role in their ability to sense changes in surface potential of the GNR.

In this work, we examine the electronic properties of GNRs, as well as how they can be exploited to create novel electronic devices. We first explore the ability of GNRs, acting as sensing membranes in transistors, to detect, characterize, and control the motion of DNA strands. Second, we describe a new type of spintronic logic gate, made with GNRs and carbon nanotubes (CNTs), forming an all-carbon spintronic device.
1.1 DNA Detection with Graphene Nanopore Transistors

In recent years, there has been a surge in interest in finding a low-cost, rapid genome sequencing method [19–21]. Amongst such techniques, the use of solid-state nanopore (SSN) membranes is a promising new technology that can lead to tremendous advancement in the field of personalized medicine [22]. In a SSN device, a nanometer-sized membrane, with a nanopore, separates an ionic solution into two chambers. When a DNA molecule is electrophoretically driven across the membrane through the nanopore, it can be probed electronically, allowing the passing nucleotides to be detected. The detection methods include measuring ionic blockade currents [23], recording the electrostatic potential induced by the DNA using a semiconductor capacitor [24], and using transverse currents to probe translocating DNA in a plane perpendicular to the translocation direction [25].

For these approaches, biomolecular sensors with graphene membranes appear well suited for DNA sequencing. Graphene, whose thickness of $\sim 3.35 \, \text{Å}$ is comparable to the DNA base separation, can resolve translocating DNA at a very high resolution, revealing detailed information about its nucleotides [1, 26, 27]. Recent experiments have demonstrated the successful detection of both double-stranded DNA (dsDNA) [28–30] and single-stranded DNA (ssDNA) [31] using graphene-based nanopores. Unlike many solid-state membranes, graphene is electrically active and can readily conduct electronic currents. Moreover, it can be cut into graphene nanoribbons, whose electronic properties are determined by edge shape [2, 18, 32, 33]. The size of the graphene bandgap and the density of electronic states at a particular energy can be tailored by changing the width, edge shape, lattice chirality, and presence of any nanopores. In addition, the position and shape of a nanopore can similarly affect the electronic states, influencing the magnitude of the graphene electrical conductance as well as its behavior under electrostatic disturbances [3].

Theoretical and first-principles-based calculations suggest micro-Ampere edge currents pass through GNR membranes as well as the possibility of distinguishing base pairs of DNA with graphene nanopores [26, 27]. Experiments have demonstrated that micro-ampere sheet currents can arise in GNRs with nanopores [34]. Such structures have the ability to detect DNA molecules
by observing variation in the sheet current when the biomolecules pass through the pore [35].

In this context, a multi-layer graphene nanopore transistor with a gate-controlled, electrically active GNR membrane shaped as a quantum point contact (QPC) can be employed to detect the rotational and positional orientation of dsDNA. The QPC edge shape offers advantages over pristine edges as it introduces stringent boundary conditions on the electronic wavefunctions with selective sensitivity on the electrostatic environment. This property results in a large enhancement of the conductance sensitivity whenever the carrier density is modulated by a transistor gate, thereby improving the capability of discerning a nucleotide signal from the background noise. The proposed device architecture also allows for the presence of additional electronic layers within the membrane to alter the electrostatic profile of the nanopore, such as for the control of DNA motion, as has been shown in a previous study with doped silicon capacitor layers [36, 37].

1.2 All-Carbon Spin Logic Device

Theoretical predictions [38–40] and experimental results [41] have independently shown that a GNR transistor can exhibit exceptional negative magnetoresistance (MR) under the application of a perpendicular magnetic field, displaying conductance amplification by a factor of over 10,000 at cryogenic temperatures [41]. A decrease in electron cyclotron radius at high fields, which reduces the influence of edge scattering, is a possible explanation for a GNR’s magnetoresistive behavior. However, this phenomenon requires high field strengths (∼10 T for a 15 nm GNR [41]) to be observed. Another mechanism, which can also account for the large MR, albeit at lower field strengths, is a semiconducting-to-metallic phase transition appearing in zigzag GNRs under application of a magnetic field [38, 42], arising from the repulsive, on-site Hubbard interaction between electrons of opposing spin. The phase transition, facilitated by the reduction and eventual inversion of the magnetic instability energy via the Zeeman interaction [43], closes the energy band gap and switches the magnetic ground state from an antiferromagnetic (AFM) semiconductor to a ferromagnetic (FM) conductor, significantly enhancing the GNR conductance and giving rise to a spin-polarized current at particular gate biases.

CNT wires placed parallel to the GNR can provide the magnetic fields required to switch the
transistor on and off, and the recent discovery of carbon nanotube (CNT) unzipping mechanisms [44–48], and therefore partially unzipped CNTs [46, 49], enables the creation of an all-carbon GNR transistor consisting of a partially unzipped CNT between two CNT wires (figure 5.1). The GNR region of such a device is covalently-bonded bonded to CNT source and drain leads, eliminating the need for additional contacts or an intermediary device, while exploiting the fast switching speeds [50] and tremendous current density [51, 52] (∼10^9 A cm^{-2} for single-walled CNTs) of low-dimensional carbon materials. Because the spin of the electron plays a fundamental role in the semiconductor to metal phase transition, an all-carbon device of this nature can be classified as a type of spintronic logic, in which the electron spin degree of freedom is manipulated along with electron charge to efficiently perform logical functions in addition to creating entirely new logic families [53–60]. Spintronic logic circuits have been suggested as replacements for silicon complementary logic as transistor scaling approaches its inherent limits [61], because even though CNT [62] and GNR [63] logic circuits have already been fabricated for conventional complementary metal-oxide-semiconductor (CMOS) logic, large leakage currents in graphene transistors have inhibited their use in the CMOS logic family [50].

Until now, spintronic circuit development has been hampered by the difficulty in creating cascading logic gates. Cascading, in which the output of one device directly drives another, has been observed as a fundamental requirement and major obstacle of any logic family since the first proposal for a stored-program, electronic computer [64], and few spintronic logic families can support cascaded circuits, with notable exceptions [57, 58].

1.3 Outline

Chapter 2 outlines the theoretical framework of the results presented in this work. First, the graphene lattice composition and structure are defined in section 2.1, followed by a detailed derivation of the tight-binding model used to describe the electronic structure of crystal lattices, in section 2.2. Subsequently, in section 2.3, we outline the theory of electron transport in mesoscopic systems, such as graphene nanoribbons. Finally, in section 2.4, we present a theoretical framework to take into account the effects of a large, multilayer stack, in aqueous solution, on the electronic properties
of a sensing membrane layer.

In Chapter 3, the theoretical methodology developed in Chapter 2 is used to determine the electronic properties of various carbon allotropes. The emergence of Dirac particles in graphene, as well as a detailed discussion of its consequences, is discussed in section 3.1. The electronic properties of armchair and zigzag GNRs are later discussed in sections 3.2.1 and 3.2.2. Last, a discussion on the boundary conditions introduced by nanopores and a QPC edge geometry takes place in section 3.3.

We analyze the viability of using graphene nanoribbon SSN transistors for DNA detection, characterization, and manipulation in Chapter 4. First, in sections 4.1.1 and 4.1.2, we discuss the electrical properties of single-layer graphene nanoribbons with nanopores in both pristine and QPC edge configurations. The conductance response of these GNRs, to both point charges as well as translocating, helical dsDNA within the nanopore, is thoroughly explained in sections 4.1.3 and 4.1.4. In addition, in section 4.1.5, we assess the degree to which a GNR with a nanopore can observe and measure a conformational phase transition of dsDNA within the pore. The ability of GNRs to detect the motion of single nucleotides in ssDNA, as well as the influence on pore position and shape on the conductance response, is outlined in section 4.1.6. The inclusion of single-layer graphene, as a sensing layer, in a multilayer transistor, with additional gated electrode layers, is described in section 4.2.1. Finally, the ability of gate electrodes to adjust the electrical properties of the GNR sensing layer, as well as to control the stochastic motion of DNA strands, is discussed in sections 4.2.2, 4.2.3, and 4.2.4, respectively.

Chapter 5 discusses an all-carbon spintronic switch made from only CNTs and GNRs, which exploits the spontaneous magnetization found in zigzag nanoribbons. In section 5.1.1, an analysis of the various magnetic states of zigzag GNRs is performed, and a thorough discussion on the resulting magnetic phase diagram in such systems takes place in section 5.1.2. We outline specific design considerations when constructing transistors using all carbon materials in section 5.1.3, and various basic logic elements, which can be built from these spin switches, are presented in section 5.2.
2

Methods

2.1 Lattice Structure

2.1.1 Carbon

Graphene is a hexagonal lattice composed of carbon atoms, each with four valence electrons, occupying the $2s^2$ and $2p^2$ atomic orbitals, and two core $1s^2$ electrons, which do not contribute to the electronic properties of graphene. Three of the four valence electron orbitals hybridize into three planar, directed $sp^2$ orbitals, at 120° one another (see figure 2.1). These orbitals are referred to as $\sigma$ orbitals, and form the lattice $\sigma$ bonds in the $xy$ plane. The remaining electron occupies a $2p_z$ orbital, forming delocalized $\pi$ bonds between each lattice site. These bonds are distributed across the entire lattice, and are responsible for the exotic electronic transport properties of graphene.

2.1.2 Hexagonal Lattice

The graphene lattice is hexagonal, with two atoms per unit cell, labeled $A$ and $B$ respectively (see figure 2.1). The interatomic bond distance $a$, measures 1.42 Å, and the hexagonal lattice is generated by the following lattice vectors,

$$a_1 = a\left(\frac{\sqrt{3}}{2}, \frac{3}{2}\right) \quad a_2 = a\left(-\frac{\sqrt{3}}{2}, \frac{3}{2}\right)$$

(2.1)
The three nearest neighbor vectors to an A atom are, in real space,

$$\delta_1 = \frac{a}{2} \begin{pmatrix} \sqrt{3} \\ 1 \end{pmatrix} \quad \delta_2 = \frac{a}{2} \begin{pmatrix} -\sqrt{3} \\ 1 \end{pmatrix} \quad \delta_3 = a \begin{pmatrix} 0 \\ -1 \end{pmatrix}$$

(2.2)

as seen in figure 2.1. The reciprocal lattice vectors are given by,

$$b_1 = \frac{2\pi}{\sqrt{3}a} \begin{pmatrix} 1, \frac{1}{\sqrt{3}} \end{pmatrix} \quad b_2 = \frac{2\pi}{\sqrt{3}a} \begin{pmatrix} -1, \frac{1}{\sqrt{3}} \end{pmatrix}$$

(2.3)

which define the Brillouin Zone (BZ), as shown in figure 2.1. The BZ is hexagonal, and only two of its corners are inequivalent, which are at the positions in reciprocal space,

$$K = \frac{4\pi}{3\sqrt{3}a} (1, 0) \quad K' = \frac{4\pi}{3\sqrt{3}a} (-1, 0)$$

(2.4)

These points are also known as Dirac points, as will be made clear in chapter 3. The other corners of the hexagonal BZ can be reached by a translation by a linear combination of reciprocal lattice vectors, eqn. 2.3, from the \(K\) and \(K'\) points.
2.2 Tight-Binding Model

2.2.1 Secular Equation

The Hamiltonian of lattice is written as

$$\hat{H} = -\frac{\hbar^2}{2m} \nabla^2 + \sum_R V(r - R)$$  \hspace{1cm} (2.5)

where the summation is over all atomic sites $R$, and $V$ is the atomic potential energy centered at each lattice site. A trial wavefunction can be constructed using the linear combination of atomic orbitals (LCAO) method,

$$\psi_j(r) = \sum_i c_{ij} \varphi(r - R_i)$$  \hspace{1cm} (2.6)

Here, $\varphi$ is a single atomic orbital centered at a lattice point $R$, and $c_{ij}$ are the amplitudes of each component in the total wavefunction $\psi_j$. In order to find the values of $c_{ij}$, the energy $E_j$ must be minimized.

$$\frac{\partial E_j}{\partial c^*_{ij}} = \frac{\partial}{\partial c^*_{ij}} \langle \psi_j | \hat{H} | \psi_j \rangle = 0$$  \hspace{1cm} (2.7)

Eqn. 2.7 yields the secular equation, which can be solved for the values of the coefficients $c_{ij}$ and corresponding energies $E_j$.

$$Hc = ES$$  \hspace{1cm} (2.8)

$$H_{mn} \equiv \int \varphi^*(r - R_m) \hat{H} \varphi(r - R_n) d\mathbf{r} \equiv \langle \varphi_m | \hat{H} | \varphi_n \rangle,$$

$$S_{mn} \equiv \int \varphi^*(r - R_m) \varphi(r - R_n) d\mathbf{r} \equiv \langle \varphi_m | \varphi_n \rangle$$  \hspace{1cm} (2.9)

$H_{mn}$ and $S_{mn}$ are the matrix elements of elements of $H$ and $S$, respectively.

2.2.2 Periodic Lattice

If the lattice is periodic, we can replace the basis functions $\varphi$ with Bloch functions based on the $\alpha$th atom in the unit cell.

$$\varphi_{\alpha k}(r) = \frac{1}{\sqrt{N}} \sum_{R_\alpha} e^{i k \cdot R_\alpha} \varphi(r - R_\alpha)$$  \hspace{1cm} (2.10)
We assume that there are \(N\) unit cells in the lattice, the position of atom \(\alpha\) is \(R_\alpha\), and \(k\) is one of \(N\) wavevectors located in the first BZ. Thus, the total wavefunction \(\psi_k\) can be written as a linear combination of Bloch functions for each atom \(\alpha\) in the unit cell.

\[
\psi_k(r) = \sum_\alpha c_{\alpha k} \varphi_{\alpha k}(r) \tag{2.11}
\]

In graphene, when considering a single \(p_z\) orbital on each lattice site, there are two orbitals in each unit cell, and \(\alpha\) refers to the A and B sublattices.

In the Bloch function basis, \(H\) is diagonal in the wavevector \(k\), and the matrix elements of \(H\) between atomic orbitals \(\alpha\) and \(\beta\) are written,

\[
H_{\alpha\beta}(k) \equiv \langle \varphi_{\alpha k} | \hat{H} | \varphi_{\beta k} \rangle \tag{2.12}
\]

\[
= \frac{1}{N} \sum_{R_\alpha, R'_\beta} e^{i k \cdot (R'_\beta - R_\alpha)} \langle \varphi(r - R_\alpha) | \hat{H} | \varphi(r - R'_\beta) \rangle \tag{2.13}
\]

Because the interactions between a unit cell and each other unit cell is independent of the unit cell considered, the summation is composed of \(N\) identical terms, which add to,

\[
H_{\alpha\beta}(k) = \sum_R e^{i k \cdot (R + \rho_\beta - \rho_\alpha)} H_{\alpha\beta}(R), \tag{2.14}
\]

\[
H_{\alpha\beta}(R) \equiv \langle \varphi(r - \rho_\alpha) | \hat{H} | \varphi(r - R - \rho_\beta) \rangle \tag{2.15}
\]

\(H(k)\) is simply the sum of the elements of submatrices \(H(R)\) between atoms at positions \(\rho_\alpha\) from the origin and \(\rho_\beta\) from the cell position \(R\), weighted by a factor \(e^{ikr}\). The elements of \(S\) can be similarly written

\[
S_{\alpha\beta}(k) \equiv \langle \varphi_{\alpha k} | \varphi_{\beta k} \rangle = \sum_R e^{i k \cdot (R + \rho_\beta - \rho_\alpha)} S_{\alpha\beta}(R) \tag{2.16}
\]

Thus, the secular equation can now be written in terms of the wavevector \(k\)

\[
H(k)c(k) = E(k)S(k)c(k) \tag{2.17}
\]

Once eqn. 2.17 is solved, the electronic properties of graphene nanoribbons can be calculated.
In general, any number of atomic orbitals, chosen to the desired accuracy, can be used to construct the tight-binding basis. The dimensions of the secular equation are larger, but the general problem description is the same. A complete description of the basis functions used can be found in section A.2 of the Appendix.

2.2.3 Second Quantization

In second quantized notation, with one $p_z$ orbital per site, the Hamiltonian can be written in terms of electron creation ($\hat{c}^\dagger$) and annihilation ($\hat{c}$) operators,

$$\hat{H} = \sum [\epsilon_i + V_i] \hat{n}_i - \sum t_{ij} \hat{c}_i^\dagger \hat{c}_j + h.c.$$  \hspace{1cm} (2.18)

where $\hat{n}_\sigma \equiv \hat{c}_i^\dagger \hat{c}_i$ is the number density, $\epsilon_i$ and $V_i$ are the orbital and potential energies of site $i$.

The transfer matrix element $t_{ij}$ between sites $i$ and $j$ is taken to be positive. The overlap matrix $S$ can be written similarly, but as only the on-site elements are significant, $S$ is usually taken as the identity matrix. It will herein be omitted altogether and will be included if greater accuracy is desired, although it can be shown that it is generally not needed [65].

Interactions up to the third nearest neighbor are often included to improve the model, as is the case in the study of the magnetic properties of zigzag nanoribbons. These do not change the dimension of the secular equation, and thus can be added without sacrificing too much computer power. In the case of armchair nanoribbons, especially when considering hydrogen-passivated edges [66], it is essential to include additional $d$ orbitals in the tight-binding basis. The creation operators are then replaced with a sum $\hat{c} \rightarrow \sum_\mu \hat{c}_\mu$ over the basis states $\mu$, and the transfer and overlap matrices become rank 4 tensors, $t_{ij}^{\mu\nu}$, where the Hamiltonian dimension increases as $N_\mu^2$, the number of basis states per atom. Clearly, the secular equation becomes quite expensive to solve as additional basis orbitals are included.

When considering higher order interactions, such as in the case of zigzag edged graphene nanoribbons and nanoflakes [43, 67], electron-electron interactions can be included by adding the
Hubbard interaction to the Hamiltonian,

\[ \hat{V}_{e-e} = U \sum_i \hat{n}_{i\uparrow}\hat{n}_{i\downarrow} \]  \hspace{1cm} (2.19)

where \( U \) is the on-site Coulomb repulsion energy.

**Mean Field Method**

If the lattice is very large, or if the unit cell is very large in periodic lattices, directly solving the secular equation is very difficult. As a result, iterative mean field models are used in order to approximate the true solution without spending excessive resources. The occupation \( \hat{n}_{i\sigma} \) of an electron with spin \( \sigma \) on site \( i \) can be written in terms of its expectation,

\[ \hat{n}_{i\sigma} = (\hat{n}_{i\sigma} - \langle \hat{n}_{i\sigma} \rangle) + \langle \hat{n}_{i\sigma} \rangle \equiv \delta \hat{n}_{i\sigma} + \langle \hat{n}_{i\sigma} \rangle \]  \hspace{1cm} (2.20)

If the expectation is not too far from the true value, the interaction Hamiltonian can be written,

\[ \hat{V}_{e-e} = U \sum_i \hat{n}_{i\uparrow} \langle \hat{n}_{i\downarrow} \rangle + \hat{n}_{i\downarrow} \langle \hat{n}_{i\uparrow} \rangle - \langle \hat{n}_{i\uparrow} \rangle \langle \hat{n}_{i\downarrow} \rangle \]  \hspace{1cm} (2.21)

The expectation of the occupation \( \langle \hat{n} \rangle \) can be calculated by summing the wavefunction components \( c_{ij} \) over all energies \( E_j \), weighted by the Fermi-Dirac distribution function,

\[ \langle \hat{n}_{i\sigma} \rangle = \sum_j f_{FD}(E_j)|c_{ij}|^2 \]  \hspace{1cm} (2.22)

\[ \langle \hat{n}_{\alpha\sigma} \rangle = \sum_k f_{FD}(E_k)|c_{\alpha}(k)|^2 \]  \hspace{1cm} (2.23)

A detailed explanation on how to solve for the electron occupation numerically is in section B.1 of the Appendix.
2.3 Electron Transport in Mesoscopic Systems

2.3.1 Landauer-Büttiker Formalism

The Landauer-Büttiker formalism is a simple approach to model ballistic transport in mesoscopic systems, particularly where one or more dimensions is much smaller than the rest, resulting in significant quantization of the electronic states, such as in graphene nanoribbons. In one-dimensional conductors, it yields the Landauer conductance formula, which describes the quantization of conductance in equally-sized steps.

Consider a simple mesoscopic device, shown in figure 2.2, consisting of a conductor region connected to two large reservoirs of conduction electrons, called leads. Any mesoscopic device can be modeled in this fashion with a variable number of leads. In all of the following studies, we only consider the case of a conductor connected to one source and one drain lead.

![Figure 2.2: Two terminal mesoscopic device.](image)

Conductor region, $C$, is connected via the potential $V$ to left and right leads, held at chemical potentials $\mu_L$ and $\mu_R$, respectively.

The current originating from the lead $\alpha$ flowing into (+) the conductor can be written

$$I_\alpha^+ = \frac{2e}{L} \sum_{n, k>0} v(k) T_n(E_k) f(E_k - \mu_\alpha) \quad (2.24)$$

Here, $L$ is the length of the entire one-dimensional system, $k$ is the value of the wavevector of each conduction electron, $v$ is the velocity, $T_n$ is the transmission probability of mode $n$ across the conductor, and $f$ is the Fermi-Dirac distribution function. It is assumed that lead $\alpha$ is held at chemical potential $\mu_\alpha$. In addition, the summation is over all conduction modes $n$ and over all positive wavevectors (assuming lead $\alpha$ is to the left of the conductor).

The conductor is assumed to be very long, making the separation between $k$ states negligible, allowing the sum to be transformed into an integral, and the velocity to be written as a derivative of the energy

$$\sum_k \rightarrow \frac{L}{2\pi} \int dk; \quad v(k) = \frac{1}{\hbar} \frac{dE}{dk} \quad (2.25)$$
Thus, the current out of lead $\alpha$ becomes

$$I_\alpha^+ = \frac{2e}{\hbar} \sum_n T_n(E) f(E - \mu_\alpha) dE \quad (2.26)$$

The total current is the difference between the currents leaving leads 1 and 2

$$I = I_1^+ - I_2^+ = \frac{2e}{\hbar} \int \bar{T}(E)[f(E - \mu_1) - f(E - \mu_2)] dE, \quad (2.27a)$$

where $\bar{T}(E) \equiv \sum_n T_n(E) \quad (2.27b)$

If the source-drain bias is small compared to the thermal energy, i.e. $\mu_1 - \mu_2 \ll k_B T$, the difference in Fermi functions can be approximated by a derivative of the Fermi function, which is only significant within a small energy window around the Fermi energy, $E_F \pm 10k_B T$. The current becomes linear with source-drain bias, yielding a simple conductance formula

$$G \equiv \frac{I}{\mu_1 - \mu_2} = \frac{2e^2}{h} \int_{E_F - 10k_B T}^{E_F + 10k_B T} T(E) \left(-\frac{\partial f}{\partial E}\right) dE \quad (2.28)$$

At very low temperatures, the derivative of the Fermi function becomes a Dirac delta function, and the integral selects only the transmission at the Fermi energy, which is very close to the chemical potential $\mu$ at either lead.

$$\left.-\frac{\partial f}{\partial E}\right) \approx -\delta(E)$$

$$G = \frac{2e^2}{h} T(E_F) \quad (2.29)$$

This is the well-known Landauer conductance formula in one-dimensional systems. Unless otherwise specified, in all subsequent conductance calculations, the temperature is not close to zero, and the conductance must be calculated from eqn. 2.28.

### 2.3.2 Non-Equilibrium Green’s Functions

The upshot of eqn. 2.28 is that in order to find the conductance in a mesoscopic device, the transmission function (eqn. 2.27b) must be determined within a small energy range around the
Fermi energy. The transmission function can be determined using non-equilibrium Green’s functions (NEGF) formalism.

The retarded (+) and advanced (−) Green’s functions of transfer and overlap matrices $H$ and $S$ are written

$$G^\pm(E) \equiv \lim_{\eta \to 0} [ES - H \pm i\eta]^{-1}$$

where $E$ is the energy and $\eta$ is an infinitesimally small real number. The overlap matrix $S$ will be taken as the identity matrix and omitted henceforth. The matrix element of $G$ between sites $m$ and $n$ is

$$G^\pm_{mn}(E) \equiv \langle \varphi_m | \hat{G}^\pm(E) | \varphi_n \rangle \quad (2.31)$$

If we represent the device in the same manner as figure 2.2, we can rewrite eqn. 2.30 by explicitly defining each section of the device.

$$\begin{bmatrix} G_L & G_{LC} & 0 \\ G_{CL} & G_C & G_{RC} \\ 0 & G_{CR} & G_R \end{bmatrix}^\pm = \begin{bmatrix} E - H_L \pm i\eta & V_{LC} & 0 \\ -V_{CL} & E - H_C \pm i\eta & V_{RC} \\ 0 & -V_{CR} & E - H_R \pm i\eta \end{bmatrix}^{-1} \quad (2.32)$$

$$\Rightarrow G_C^\pm \equiv [E - H_C + i\eta - \sum_\alpha \Sigma_\alpha]^{-1} \quad (2.33)$$

Here, $\Sigma_\alpha \equiv V_{C\alpha}g_LV_{\alpha C}$ is the self energy of lead $\alpha$. Eqn. 2.33 shows that if the Green’s function of the isolated (disconnected) lead $\alpha$, $g_\alpha$, is known, the total Green’s function of the conductor region $G_C$ can be found without needing to directly calculate the Green’s function of the entire device. Rather, only the Hamiltonian of the conductor region needs to be specified, reducing the complexity of the problem significantly. The lead Green’s function $g$ can be calculated using the renormalization-decimation algorithm, described in section B.2 of the Appendix.

Using the s-matrix formalism [68], it can be shown that the transmission function can be found from the Green’s function and the lead self-energies.

$$\bar{T}_{12}(E) = -Tr[(\Sigma_1 - \Sigma_1^\dagger)G_C^+(\Sigma_2 - \Sigma_2^\dagger)G_C]. \quad (2.34)$$
As described earlier, the conductance across the conductor at a particular bias $V_{DS}$ can be expressed as

$$G = \frac{2e}{V_{DS}h} \int_{-\infty}^{\infty} \tilde{T}(E)[f_1(E) - f_2(E)]dE$$

(2.35)

where $f_\alpha(E) = f(E - \mu_\alpha)$ is the probability an electron occupies a state at energy $E$ in the lead $\alpha$, $\mu_1 - \mu_2 = V_{DS}$ is the bias across the conductor. Along with the transmission function, the local density of states (LDOS) at atomic position $m$ can be determined from the Green’s function as well.

$$\rho(R_m, E) = -\frac{1}{\pi} \text{Im}[G_{mm}^+(E)]$$

(2.36)

The local electron (hole) concentrations in the conduction (valence) bands can then be found

$$n_e(R) = 2 \int_{E_c}^{\infty} \rho(R, E)f(E)dE$$

(2.37)

$$n_h(R) = 2 \int_{-\infty}^{E_v} \rho(R, E)(1 - f(E))dE$$

(2.38)

Here, $E_c$ and $E_v$ refer to the conduction and valence band edges, respectively. If the external potential $V_R$ at site $R$ is small, it can be treated as a perturbation, and the replacement $f(E) \rightarrow f(E + V_R)$ can be made, where $\rho$ is calculated from the unperturbed Hamiltonian.

### 2.4 Multi-Scale Device Model

The theory described in sections 2.2 and 2.3 outline how to calculate the electronic and transport properties of a mesoscopic conductor. Once the transfer and overlap matrices are specified, all properties of the conductor are determined. However, solving the secular equation for systems containing more than a few thousand atoms becomes computationally expensive very quickly. Fortunately, such large systems can be accurately modeled by calculating the potential induced on the conductor by the rest of the system, as long as there is no significant electrochemical interaction between the conductor and the environment.
2.4.1 Electrostatic Potential on Conducting Membrane

The influence of floating dielectric layers and gate electrodes, in addition to external charges, including dielectric surface charge, DNA molecules, and electrolytic ions, is completely encapsulated within the electrostatic potential term $V_i$ in the Hamiltonian, eqn. 2.18. The electrostatic potential $\phi$ can be obtained by solving Poisson’s equation in three dimensions.

\[
\nabla \cdot [\epsilon(r) \nabla \phi(r)] = -e[K^+(r) - Cl^-(r)] - \rho_{fixed}(r). \tag{2.39}
\]

Here, $\epsilon(r)$ is the position-dependent permittivity (dielectric constant), whose values are denoted in table A.1 in Appendix A. The right-hand-side charge term includes ions in solution ($K^+, Cl^-$) and fixed charges $\rho_{fixed}$ such as dielectric surface charge or molecular charges present in the solution. We assume the electrolyte distributions obey Boltzmann statistics [24]

\[
K^+(r) = c_0 \exp\left[-\frac{e\phi(r)}{k_BT}\right], Cl^-(r) = c_0 \exp\left[\frac{e\phi(r)}{k_BT}\right] \tag{2.40}
\]

Here, $K^+$ and $Cl^-$ are the local ion concentrations, and $c_0$ is the nominal molar concentration of $KCl$.

The system is discretized within a Cartesian box onto a nonuniform, rectilinear grid. Neumann boundary conditions are imposed on the sides of the box,

\[
\frac{\partial \phi}{\partial x}\bigg|_{x=\pm L_x/2} = \frac{\partial \phi}{\partial y}\bigg|_{y=\pm L_y/2} = 0 \tag{2.41}
\]

while the top and bottom of the box are subjected to Dirichlet boundary conditions,

\[
\phi(z = \pm L_z/2) = \phi_{\pm} \tag{2.42}
\]

Any gate electrode points are also subjected to Dirichlet conditions.

Once eq. 2.39 is solved, the resulting potential in conducting layer can be included in eqn. 2.18, and the transport properties are determined. Eqn. 2.39 can be solved self-consistently using a number of methods. For this work, we choose to use a Newton-Multigrid [69–71] method, which
discretizes the system on a series of grids with varying coarseness. Starting from the finest grid, Jacobi relaxation is performed to obtain an initial guess for the solution $\phi$. Then, the solution is interpolated and relaxed on subsequently coarser grids to smooth out high-frequency errors. Finally, the error to the solution is relaxed and interpolated on finer grids until the original, fine-grid solution is corrected. Once the solution $\phi$ has been obtained, it is re-inserted back into the Poisson equation, and this process is repeated until the desired convergence has been reached. A full description of the exact procedure followed is quite extensive, and as such has been omitted from this work. The reader is directed to look at refs. [69–71] for a detailed explanation on the implementation of this method.

2.4.2 External Magnetic Fields

In chapter 5, we describe a magnetic-field driven phase transition in zigzag nanoribbons. To do so, we include the effects of external magnetic fields by making two modifications to the Hamiltonian.

First, we model the field by introducing an external vector potential $A(r)$, created by electric charges in motion, by adding a phase factor to the transfer matrix elements in the Hamiltonian.

$$t_{ij} \rightarrow t_{ij} e^{i \int_{r_i}^{r_j} A(r) \cdot d\mathbf{l}}$$  \hspace{1cm} (2.43)

The integral in the exponent is along a straight line between the positions of lattice sites $i$ and $j$. When calculating the band structure of periodic nanoribbons, it is important to choose a gauge which is translationally invariant in the direction of electron propagation. This is to ensure that the renormalization-decimation algorithm, described in section B.2, can be properly implemented.

Second, because each electron is a fermion with spin $\frac{1}{2}$, a term describing the magnetic Zeeman interaction is also added to the Hamiltonian.

$$V_{Zeeman} = -g_S \mu_B \sum_i B_z^i (\hat{n}_{i\uparrow} - \hat{n}_{i\downarrow})$$  \hspace{1cm} (2.44)

Here, $g_S \approx 2$ is the electron Landé g-factor, $\mu_B = \frac{e \hbar}{2m_e}$ is the Bohr magneton.
In the absence of magnetic fields, the tight-binding Hamiltonian of graphene can be written

\[ H = \sum_i (\epsilon_i + V_i) \hat{c}_i^\dagger \hat{c}_i - \sum_{ij} t_{ij} \hat{a}_i^\dagger \hat{b}_j + h.c. \]  

(3.1)

where \( \epsilon_i \) and \( V_i \) are the on-site orbital and potential energies of site \( i \), the latter sum is over all pairs of neighbors \( i \) and \( j \), \( \hat{a} \) and \( \hat{b} \) are annihilation operators for electrons on sublattice \( A \) and \( B \), and \( t_{ij} \) is the transfer matrix element between neighboring sites \( i \) and \( j \). Eqn. 3.1 can be used to calculate the electronic properties of any allotrope of carbon in arbitrary lattice configurations. Nanoribbons, nanoflakes, nanotubes, and graphene with nanopores are all represented with this simple Hamiltonian.

For defected, finite, non-periodic allotropes of carbon, or lattices with external potentials, the real space equations must be used. However, for periodic lattices, such as monolayer graphene or pristine nanoribbons, the secular equation can be solved in \( k \) space, and it reveals very useful information about the behavior of graphene materials.
3.1 Dirac Fermions in Single Layer Graphene

Let us first assume the external potential $V$ is zero and each lattice site is identical and contains a single $p_z$ orbital. Then, the graphene lattice is periodic with a unit cell of two atoms, labelled $A$ and $B$. As a result, the electronic structure can be calculated, according to eqns. 2.10 to 2.17, using Bloch functions based on each atom of the unit cell.

The $k$th component of the transfer and overlap matrices are

$$
H(k) = \begin{bmatrix} \epsilon & -tf(k) \\ -tf^*(k) & \epsilon \end{bmatrix}; \quad S(k) = \begin{bmatrix} 1 & sf(k) \\ sf^*(k) & 1 \end{bmatrix}; \quad \text{with } f(k) \equiv \sum_{l=1}^{3} e^{ik\delta_l} \tag{3.2}
$$

where $\epsilon$ is the energy of a carbon $p_z$ orbital, $t$ is the magnitude of the transfer integral between two adjacent lattice sites, $s$ is the overlap between adjacent sites, and $\delta_l$ are the displacements of the three nearest neighbors defined in eqn. 2.2.

Solving the secular equation yields the energy spectrum of the $\pi$ bands,

$$
E(k) = \frac{\epsilon \pm tf(k)}{1 \mp sf(k)} \tag{3.3}
$$

There are $N$ states below $\epsilon$, and since there are two atoms per unit cell, they are all filled at zero temperature, yielding a Fermi energy $E_F = \epsilon$. The most notable feature of the energy spectrum is the meeting of the valence and conduction bands at the six $K$ points in the BZ, yielding a zero gap semiconductor (see figure 3.1).

If we define $q$ as the distance from a particular $K$ point in reciprocal space, $f(k)$ can be expanded

![Figure 3.1: Electronic band structure of graphene, as calculated by eqn. 3.3. The Fermi energy lies at the meeting of the conduction and valence bands, at the six Dirac points, one of which is shown in the inset. Taken from [1]](image-url)
around $K$ (see figure 2.1) in terms of $q$,

$$f(K + q) = \sum_{\delta} e^{i(K + q)\delta} \approx \sum_{\delta} e^{iK\delta}(1 + iq\delta)$$

$$= i \sum_{\delta} e^{iK\delta} q\delta \left( \sum_{\delta} e^{iK\delta} = 0 \right)$$

$$= \frac{3a}{2}(-q_x + iq_y)$$

Similarly, we can expand $f(k)$ around the $K'$ point.

$$f(K' + q) \approx \frac{3a}{2}(q_x + iq_y)$$

Defining the Fermi velocity $v_F \equiv \frac{3at}{2\hbar}$, we can then write the secular equation 2.17, for the component vector $\Psi_q$, in terms of $q$, assuming the overlap matrix $S$ is the identity,

$$H_q\Psi_q = \hbar v_F \begin{bmatrix}
0 & q_x - iq_y & 0 & 0 \\
q_x + iq_y & 0 & 0 & 0 \\
0 & 0 & 0 & -q_x - iq_y \\
0 & 0 & -q_x + iq_y & 0
\end{bmatrix}
\begin{bmatrix}
\psi_{Aq} \\
\psi_{Bq} \\
\psi'_{Aq} \\
\psi'_{Bq}
\end{bmatrix} = E_q \begin{bmatrix}
\psi_{Aq} \\
\psi_{Bq} \\
\psi'_{Aq} \\
\psi'_{Bq}
\end{bmatrix}$$

with eigenfunctions and eigenenergies, corresponding to each Dirac point,

$$\Psi_{K\pm,q} = \begin{bmatrix}
e^{-i\theta_q/2} \\
\pm e^{i\theta_q/2} \\
0 \\
0
\end{bmatrix}, \quad \Psi_{K',\pm,q} = \begin{bmatrix}
0 \\
0 \\
e^{i\theta_q/2} \\
\mp e^{-i\theta_q/2}
\end{bmatrix}, \quad E_q = \pm \hbar v_F q$$

defining the wavevector angle $\theta_q \equiv \tan^{-1}(q_y/q_x)$. Each state $\Psi_q$ is now a four component Dirac spinor, due to the additional degree of freedom from the $K$ and $K'$ points.
Figure 3.2: (L) Armchair nanoribbon with $N$ transverse sites. The wavefunction is zero on both sublattices at $x = 0$ and $x = W$. (R) Zigzag nanoribbon with $N$ transverse sites. The wavefunction is zero at $A$ sites at $x = 0$ and at $B$ sites at $x = W$.

In real space, we can write the total wavefunction, with accepted sign convention,

$$\psi_q(r) = \frac{1}{\sqrt{N}} \sum_{R_A} \left( \psi_{AQ} e^{iKR_A} - \psi'_{AQ} e^{iK'R_A} \right) \varphi(r - R_A) + \frac{1}{\sqrt{N}} \sum_{R_B} \left( \psi_{BQ} e^{iKR_B} - \psi'_{BQ} e^{iK'R_B} \right) \varphi(r - R_B)$$

and the $K$ and $K'$ components of the wavefunction separately obey the Dirac equation

$$i\hbar v_F \sigma \cdot \nabla \psi^K_q(r) = E_q \psi^K_q(r)$$

$$- i\hbar v_F \sigma^* \cdot \nabla \psi^{K'}_q(r) = E_q \psi^{K'}_q(r)$$

The main consequence of eqn. 3.9 is the appearance of massless, Dirac particles near the Fermi level. These particles exhibit exotic behavior, such as Klein tunneling [17], and a have nonzero conductivity at the Fermi energy.
3.2 Nanoribbons

Graphene nanoribbons are narrow strips of graphene, with edge geometries determined by their lattice orientation (see figure 3.2). They can either be cut from graphene [72–74], or created from unrolled carbon nanotubes [48], among other methods. These edges impart complex boundary conditions to the wavefunction $\psi(\mathbf{r})$, resulting in very unique electronic properties [2]. We explore the two basic types of nanoribbon edges, namely, armchair and zigzag, and their impact on the electronic spectra of nanoribbons.

Following the reasoning of Ando et al. [75], it can be shown that the components $\psi$ of the wavefunction obey the Dirac equation 3.9. As a result, taking into account the translational invariance in the $\hat{y}$ direction, we can write an ansatz for components of the wavefunction,

$$\psi^{(l)}_{\alpha q}(r) = e^{iq_y y} \phi^{(l)}_{\alpha q x}(x) \quad (3.10)$$

Here, $q_y$ is the component of the wavevector in the longitudinal direction, and $\phi$ is to be determined by the boundary conditions imposed by the nanoribbon edge.

3.2.1 Armchair Nanoribbons

Eqn. 3.6 can be expressed in terms of the wavefunction components $\psi$ with the ansatz introduced above. The resulting set of equations, defining $\tilde{E} \equiv E/hv_F$ and substituting $q_x \rightarrow -i\partial_x$, reads,

\begin{align}
(-i\partial_x + iq_y)\phi_A &= \tilde{E}_q \phi_B \quad (3.11a) \\
(-i\partial_x - iq_y)\phi_B &= \tilde{E}_q \phi_A \quad (3.11b) \\
(i\partial_x + iq_y)\phi'_A &= \tilde{E}_q \phi'_B \quad (3.11c) \\
(i\partial_x - iq_y)\phi'_B &= \tilde{E}_q \phi'_A \quad (3.11d)
\end{align}

Figure 3.3: Band structures of a (top) zigzag nanoribbon, with $K$ and $K'$ points labelled, (middle) semiconducting armchair nanoribbon, and (bottom) metallic armchair nanoribbon. Adapted from [2].
As seen in figure 3.2, for armchair nanoribbons, the total wavefunction $\psi_q(r)$ must satisfy the following boundary conditions,

$$\psi_q(R_A)|_{x=0} = \psi_q(R_A)|_{x=W} = \psi_q(R_B)|_{x=0} = \psi_q(R_B)|_{x=W} = 0$$  (3.12)

where we have defined $W \equiv (N + 1)\sqrt{3a}/2$ which, for the transverse component $\phi$, translates into,

$$\phi_\alpha(x = 0) = \phi'_\alpha(x = 0)$$
$$\phi_\alpha(x = W) = \phi'_\alpha(x = W)e^{i\Delta KW}$$  (3.13)

Here, $\Delta K = \frac{4\pi}{3\sqrt{3a}}$ is the distance between $K$ points in the BZ. We can then solve for the transverse component $\phi$,

$$\phi_B(x) = e^{iq_n x} \quad \phi'_B(x) = e^{-iq_n x}$$  (3.14)

and $\phi_A^{(t)}$ can be found from eqn. 3.11a.

The allowed values of transverse wavevector $q_x$ are now quantized,

$$q_n = \frac{\pi n}{W} + \frac{2\pi}{3\sqrt{3a}}$$  (3.15)

where $n$ is an integer and $\tilde{E}_q = \pm \sqrt{q_n^2 + q_y^2}$ is the energy spectrum.

Example band structures for different nanoribbons are shown in figure 3.3. If the number of transverse sites $N$ is one less than a multiple of three, i.e. $N = 3m - 1$ where $m$ is an integer, there is an integer $n$ such that $q_n = 0$. As a result, the nanoribbon stays conducting as $q_y \to 0$, as shown in figure 3.3c. In reality, as higher order interactions are considered [66], all armchair nanoribbons are semiconducting, as in figure 3.3b, and we include these in our simulations.

### 3.2.2 Zigzag Nanoribbons

To study zigzag nanoribbons, we first have to make the transformation $q_x \to -q_y$ and $q_y \to q_x$ to match the lattice described in figure 3.2. Then, the secular equation yields, for the transverse
components $\phi$,

\[
(\partial_x - q_y)\phi_A = \tilde{E}_q\phi_B \quad \text{(3.16a)}
\]

\[
(-\partial_x - q_y)\phi_B = \tilde{E}_q\phi_A \quad \text{(3.16b)}
\]

\[
(\partial_x + q_y)\phi'_A = \tilde{E}_q\phi'_B \quad \text{(3.16c)}
\]

\[
(-\partial_x + q_y)\phi'_B = \tilde{E}_q\phi'_A \quad \text{(3.16d)}
\]

The boundary conditions the total wavefunction $\psi_q(r)$ must satisfy are,

\[
\psi_q(R_A)|_{x=0} = \psi_q(R_B)|_{x=W} = 0 \quad \text{(3.17)}
\]

where $W \equiv (N + \frac{2}{3})\frac{3a}{2}$ and for the transverse components, this yields,

\[
\phi_A(x = 0) = \phi'_A(x = 0) = \phi_B(x = W) = \phi'_B(x = W) = 0 \quad \text{(3.18)}
\]

This yields the general solution for $\phi$,

\[
\phi^{(t)}_\alpha(x) = C^{(t)}_1 e^{zx} + C^{(t)}_2 e^{-zx}, \quad z \equiv \sqrt{q_y^2 - \tilde{E}_q^2} \quad \text{(3.19)}
\]

The allowed wavevectors can be either real or imaginary, depending on the value of $q_y$. If $q_y > \frac{1}{W}$, $z$ takes real values and satisfies the following transcendental equation, with corresponding energies,

\[
\frac{q_y - z}{q_y + z} = e^{-2Wz} \quad \tilde{E}_q = \pm \sqrt{q_y^2 - z^2} \quad \text{(3.20)}
\]

These are surface states localized at the nanoribbon edge, and are dispersionless, contributing to the flat band at the Fermi level (see figure 3.3a). If $q_y < \frac{1}{W}$, $z$ is purely imaginary, i.e. $z = iq_n$, and $q_n$ satisfies the following relation,

\[
q_y = \frac{q_n}{\tan(q_nW)}; \quad \tilde{E}_q = \pm \sqrt{q_n^2 + q_y^2} \quad \text{(3.21)}
\]
In this case, the wavefunction components around $K$ can be written,

$$\phi_A(x) = \sin(q_n x) \quad (3.22a)$$

$$\phi_B(x) = \pm \frac{i}{E_q} \left[ -q_n \cos(q_n x) + q_y \sin(q_n x) \right] \quad (3.22b)$$

These states are called confined states, and are responsible for the Dirac-like bands of zigzag nanoribbons.

### 3.3 Nanopores and Irregular Edges

In section 3.2, we saw that the dispersion of electronic states in nanoribbons is strongly dependent on the boundary conditions of the wavefunction at the ribbon edge. This suggests that further modifications to the ribbon geometry will introduce complex boundary conditions that will affect the electronic states responsible for transport.

In reality, nanoribbons have rough, irregular edges [18, 74, 76] and can contain defects such as nanopores [30, 77, 78]. The additional boundary conditions required by edge roughness, as well as any nanopores, are too complex to derive analytically, as was done previously. However, the very unique and unexpected behavior revealed by the zigzag and armchair boundary conditions is indicative of the large role the geometry plays on the electronic properties of the nanoribbon, alluding towards exotic behavior in more complex systems.

In particular, in chapter 4, we choose to study nanoribbons with a variety of nanopore and quantum point contact (QPC) edge geometries, such as those showed in figure C.4 of the Appendix. The main purpose of the nanoribbons considered is to sequence DNA strands which are threaded through nanopores. As a result, it is very important to characterize and understand the implications of different nanopore geometries. In addition, the effect of a QPC edge is explored, due to the fact that it can represent the complex edge conditions imposed by spontaneous roughness, in addition to forcing any conduction electrons to interact with a nanopore present in the QPC constriction.
Solid-State Nanopore Transistors for DNA Detection, Characterization, and Manipulation

In this chapter, we explore the ability of graphene nanoribbon transistors to detect the presence and motion of DNA strands passing through nanopores. We also discuss their ability to detect the conformation of DNA strands and reveal detailed information about the structure of these biomolecules. Finally, we discuss how additional gate layers can be used to modify both the electronic properties of the nanoribbon as well as the motion of the DNA molecule itself.

4.1 DNA Detection and Characterization with Single Layer Graphene Nanoribbons

We first investigate the electronic properties and conductance sensitivity of graphene nanoribbons with four edge geometries, namely a 5 nm wide and a 15 nm wide pure armchair-edge GNR (figure 4.2a inset) as well as an 8 nm wide and a 23 nm wide QPC edge (Figure 4.2c inset) GNR. These geometries will herein be referred to as 5-GNR, 15-GNR, 8-QPC, and 23-QPC. The QPC geometries have pinch widths of 5 nm and 15 nm (\(\frac{2}{3}\) total width), the same as the widths of the armchair-edged
GNRs. For each edge geometry, we consider four pore configurations: pristine (no pore), a 2 nm pore in the center (point P in Figure 4.2), a 2 nm pore centered at 75% of the total (pinch) width for the GNR (QPC) (point Q in Figure 4.2), and a 4 nm pore at the center (point P in Figure 4.2). The exact lattices of the 5-GNR and 8-QPC, with a 2 nm pore at point P, are shown in figure C.4 in the Appendix.

4.1.1 Transmission Probability of Patterned GNRs

In figure 4.2, we demonstrate the transmission spectra of suspended graphene nanoribbons in vacuum. The transmission for the pristine (no pore) 5-GNR edge exhibits the classic staircase shape resulting from the armchair-edge boundary conditions (figure 4.2a)[1]. The presence of a nanopore introduces a scatterer in the GNR, which manifests itself by imposing additional boundary conditions at the pore edge, restricting the transmission in two ways: first, the number of allowed electronic states is reduced, due to the requirement of the wavefunction to satisfy more stringent boundary conditions; second, the electronic states that do satisfy these boundary conditions gen-
Figure 4.2: Transmission functions for various edge geometries and pore configurations: a) 5 nm (5-GNR) and b) 15 nm (15-GNR) wide GNR-edged devices, c) 8 nm (8-QPC) and d) 23 nm (23-QPC) wide QPC-edged devices. Pristine (solid), a 2 nm pore at point P (long dash), a 2 nm pore at point Q (short dash), and a 4 nm pore at point P (dot dash). Taken from ref [3].
erally have smaller probability currents due to scattering off of the nanopore. The resulting transmission probability varies greatly within narrow carrier energy ranges, and exhibits resonances at particular carrier energies, revealing the strong dependence of transmission probability on carrier energy. Increasing the pore diameter enhances the scattering nature of the nanopore, thereby reducing the transmission probability, as can be seen in figure 4.2a, where the 5-GNR with a 4 nm pore has an almost negligible transmission probability for most carrier energies in the represented range. By changing the nanopore position, the particular wavelengths of the electronic states that satisfy the boundary conditions vary, which further affects the transmission probability. For instance, the transmission of the GNR with the pore at Q is higher at lower energies compared to the GNR with the pore at P, since the allowed electronic states at these lower energies have larger wavelengths.

Similar trends can be seen for the transmission probability determined for the 15-GNR (figure 4.2b). Because of the larger width, there are significantly more electronic states within a particular carrier energy range, increasing the transmission probability for all pore configurations. This results in more closely-spaced transmission steps in the pristine GNR. As with the pristine 5-GNR, pore boundary conditions destroy the stair-case behavior of the transmission seen for pristine 15-GNR, as well as reduce the magnitude of the transmission probability. In contrast, because of the larger width, the density of allowed electronic states in the 15-GNR is larger at high energies compared to the respective density in the 5-GNR. As a result, both pore configurations P and Q in the 15-GNR have a similar number of allowed electronic states within a specific energy range, minimizing the difference in transmission between the two configurations at higher carrier energies.

Figure 4.2c shows the transmission probability for the 8-QPC which exhibits strong variations as compared to that in the 5 or 15-GNR, because the non-uniform QPC edge introduces more stringent boundary conditions on the electronic states, especially when the QPC contains a nanopore. The transmission probability curves for the pristine 8-QPC and for the 8-QPC with a pore exhibit many resonance peaks throughout the Fermi energy range. It can be seen that the 4 nm pore (green curve) exhibits negligible transmission probability over the whole Fermi energy range, except around the band gap, which is reflected in two resonance peaks in both the conduction and valence bands. Increasing the width, in going from the 8 to 23-QPC, increases the density of states within
a particular energy range, smoothing out the transmission at higher carrier energies as in the case of the 15-GNR (Figure 4.2d). The influence of the position and size of the nanopore on the transmission function follows the same trend as with the 15-GNR at high carrier energies as mentioned above.

4.1.2 Variation of Electronic Conductance with Fermi Energy

The electronic conductance as a function of the Fermi energy of charge carriers is shown in figure 4.3. The conductance at a particular Fermi energy can be thought of as the average of the transmission probability around that carrier energy weighted by the derivative of the Fermi-Dirac distribution as described in eqn. 2.28. Here we choose a Fermi energy range from 0 to 0.3 eV, which corresponds to carrier concentrations varying from \( \sim 10^{11} \text{ cm}^{-2} \) to \( 3 - 5 \times 10^{12} \text{ cm}^{-2} \) at a temperature of 300 K, easily achievable in a conventional g-FET. In figure 4.3a we observe that the conductance of the 5-GNR as a function of carrier energy is strongly dependent on nanopore size and position. As expected, the pristine 5-GNR has the largest conductance and increases relatively monotonically over a wide range of carrier energies. Compared to the pristine 5-GNR, the conductance of the 2 nm pore at P is much smaller over the range of Fermi energies up to 0.3 eV, while the conductance with the pore at Q is at least one order of magnitude larger, exhibiting a plateau beyond 0.15 eV. The 4 nm pore in the 5-GNR displays the lowest conductance values compared to all other 5-GNRs (pristine, 2 nm hole at P, 2 nm hole at Q) because of its suppressed transmission probability as discussed earlier (figure 4.2).

Figure 4.3b shows the conductance of the 15-GNR geometries. All four systems (15-GNR: pristine, 2 nm hole at P, 2 nm hole at Q, 4 nm hole at P) show a relatively monotonic increase in conductance with Fermi energy. The conductances achieve values about three times larger than those seen for the 5-GNR, exhibiting the expected scaling with GNR width. The positional effects are mitigated as the 2 nm Q and P curves are almost identical. However, the pore size effects are retained, illustrated by a decrease in the conductance with increased (4 nm) pore size.

Figure 4.3c shows the conductance properties of the 8-QPC. The conductance changes at varying rates throughout the investigated range of Fermi energies. It is remarkable to see how the introduction of a 2 nm pore at either P or Q actually enhances the magnitude of the conductance
Figure 4.3: Conductance versus Fermi energy (as a function of carrier concentration) for the four edge geometries with four pore configurations for each geometry. a) 5-GNR, b) 15-GNR, c) 8-QPC and d) 23-QPC. Pristine (solid), 2 nm pore at point P (long dash), 2 nm pore at point Q (short dash), and 4 nm pore at point P (dot dash). Taken from ref [3].
dramatically compared to that of the pristine 8-QPC, contradicting the intuitive notion that the pore acts as a scattering barrier. This behavior can be attributed to the rich interaction of the electronic states with the edge and pore boundaries as described in section 3.3. Even more remarkable is the appearance of a negative differential transconductance (NDTC) region in the conductance in the case of the 8-QPC with a 4 nm pore, a feature unobserved in the GNR systems. Apparently, tailoring the pore properties within a QPC geometry can result in large changes in the conductance behavior.

Figure 4.3d shows the conductance properties of the four 15-QPC systems investigated. Comparison with the 8-QPC results shows that the increased width renders the conductance less sensitive to pore geometry; in particular, NDTC regions are not recognized in the 15-QPC with a 4 nm pore. However, conductance values at Fermi energies above 0.15 eV differ greatly for different pore sizes. Paradoxically, one notices that the conductance at low Fermi energies of the 15-QPC with a 4 nm pore is larger than in the case of the 15-QPC with a 2 nm pore at P. This behavior is due to enhanced transmission probability at low Fermi energies, caused by the particular shape of the edge near the 4 nm nanopore.

Most of the conductances curves in figure 4.3 exhibit different regions of high and low “sensitivity,” which we define as the slope of the conductance with Fermi energy. As a result, small changes in the Fermi energy can result in large variations in conductance similar to the transconductance in a field-effect transistor (FET)[79]. Because the local carrier potential energy will be influenced by a nearby charge, which in our case translates into changes in Fermi energy, deviations in such a charge’s position can significantly modify the device conductance. This behavior can be exploited to build an ultra-sensitive charge sensing device.

4.1.3 Conductance Variations due to External Charges

The influence of the solvent is treated as a mean-field approximation based on Boltzmann-statistics in the electrolyte to determine the on-site potentials on graphene, as described in section 2.4.1. We neglect electrochemical interactions between graphene and solution, since in practice the graphene will be capped by an insulator, preventing, for the most part, direct interaction between graphene and the solvent.
The effect of a test charge, placed within a pore, on electronic transport in graphene is illustrated in figure 4.4. Shown are the conductance changes upon placing a single electron charge $e$ at two positions within a 2 nm pore at P; one position is at $\frac{1}{2}$ radius to the west of the pore center (W or west) and the other at $\frac{1}{2}$ radius south of the pore center (S or south). Figures 4.4a and 4.4b display the conductance response for the 5-GNR and 15-GNR respectively, while figures 4.4c and 4.4d display conductance responses for the 8-QPC and 23-QPC, respectively.

The difference in conductance upon charge placement varies between 0 and 0.8 $\mu$S for all geometries, which is well within the sensing range of most current probes. Conductance changes for the 5-GNR (figure 4.4a) are negligible over most of the energy range for both angular charge (W & S) positions, due to the suppressed transmission probability at low carrier energies (blue curve of figure 4.2a). For the 15-GNR, 8-QPC, and 23-QPC cases (figures 4.4b, 4.4c, and 4.4d) the angular position of the charge within the pore has a significant effect on the conductance, causing not only large differences in conductance over the investigated energy range but also a different sensitivity of the conductance to the Fermi energy. In these cases, the maximum difference in conductance occurs for a test charge in the west (south) position at smaller (larger) Fermi energies.

The conductance can be either enhanced or reduced by the test charge, depending on the value of the Fermi energy. In the case of the 15-GNR (figure 4.4b), for example, when the Fermi energy lies between 0 and .18 eV, the conductance change for the electron test charge in the west position is positive, while the change is negative for Fermi energies above this range. Similar behavior is seen for the 8-QPC and 23-QPC, but over different Fermi energy ranges (figures 4.4c and 4.4d).

One also notes that in figure 4.4, for all cases, the differences in conductance are anti-symmetric with respect to the Fermi energy. This is a direct consequence of the symmetry between electrons and holes in graphene. Because of this symmetry, electrons and holes tend to react to the same potential with opposite sign, such that the conductance changes are an odd function of Fermi energy. For instance, in figure 4.4b, there is a peak in the conductance change for the 15-GNR around 0.1 eV for all four charge configurations; a similarly shaped peak, but with opposite sign, is located at -0.1 eV. Similarly, one finds for the 23-QPC, as shown in figure 4.4d, peaks at 0.15 eV and opposite peaks at -0.15 eV. The reader can notice, however, the different parity between the differential conductance curves at low energy in figures 4.4c and 4.4d, which are negative for the
Figure 4.4: Change in the conductance due to adding an external charge within the 2 nm pore. ‘S’ means the charge is placed one half radius south of the center of the pore, and ‘W’ means the charge is placed one half radius west of the center of the pore. a) 5-GNR, b) 15-GNR, c) 8-QPC and d) 23-QPC. Taken from ref [3].
8-QPC (figure 4.4c) and positive for the 23-QPC (figure 4.4d).

Similar conductance curves for a reduced electron charge are included in C.1 and display the same behavior as the full electron test charge but scaled by a constant factor, as expected.

4.1.4 Observation of dsDNA Helicity and Translocation Through Nanopore

In order to demonstrate a potential application of a charge-sensing device exploiting the sensitivity of geometrically-tuned GNRs, we simulated the translocation of a strand of DNA through a 2.4 nm pore located at the center (point P above) of the four edge geometries. We translocate a 24 base-pair B-type double-stranded DNA segment consisting of only AT nucleotide base-pairs. The DNA is initially placed such that the bottom of the strand is 3.5 Å above the graphene membrane, and the axis of the DNA passes through the center of the nanopore (figure 4.5a). The DNA is then rigidly translocated through the nanopore at a rate of 0.25 Å per time step (snapshot) until the DNA has passed through the pore completely. After the last (400th) snapshot, the top of the DNA strand is 13.5 Å below the graphene membrane. The charge distribution from the DNA at each time step (snapshot) is mapped into the Poisson solver, and the electric potential on the graphene membrane is calculated for each snapshot as the DNA rigidly translocates through the pore, as described in section 2.4.1.

Due to strong screening from ions and water near the graphene membrane, the on-site electric potential of the nanopore is dominated by charges contained within a slice coplanar with the graphene membrane, directly inside the nanopore. Hence, during the translocation of the biomolecule through the nanopore, the graphene membrane will sense a succession of DNA slices, which appear as an in-place rotation of the double helix in the absence of translocation. Since it is only the charges in the plane of the pore that matter (due to the strong screening effects), the electric potentials around the pore due to the DNA being pulled through are virtually identical to the potential arising if the DNA slice coplanar with the membrane was rotated without translocation. Figure 4.5b shows the on-site potentials for eight successive positions of the DNA (A-B-C-D-E-D'-C'-B’) in the graphene plane, representing one half cycle of this pseudo-rotational
The lattices considered, due to the choice of nanopore center, may not be reflection symmetric about the x-axis and y-axis. For example, the 15-GNR with a 2.4 nm pore exhibits y-axis reflection symmetry, but not x-axis reflection symmetry, as in the shape of the letter “Y” (the x and y-axes are defined in the inset of figure 4.2a.) In contrast, the 5-GNR, 8-QPC, and 23-QPC geometries with a 2.4 nm pore exhibit both y-axis and x-axis reflection symmetry, as in the shape of the letter “X.” These symmetries have an effect on the electronic conductance in GNRs when the DNA strand is introduced. When calculating the conductance from the transmission probability, it is important to note that the transmission probability itself does not represent a particular direction of current flow. In other words, a reflection about either the x- or y-axis of the lattice and its on-site electric potential map leaves the transmission probability, and hence the conductance, unchanged.

When the DNA strand is translocated, the electric potential maps of successive snapshots look like $A \rightarrow B \rightarrow C \rightarrow D$ in figure 4.2b corresponding to the translocation of one half pitch of the DNA helix, and for the second half of the cycle the successive snapshots look like $E \rightarrow D' \rightarrow C' \rightarrow B'$. The $D'$, $C'$, and $B'$ potential maps are effectively the mirror images (y-axis reflected) of $D$, $C$, and
B, respectively. As a result, assuming the DNA potential is reflection symmetric about its own axis ("DNA axis"), the conductance curves corresponding to geometries with only y-axis reflection symmetry should display a half-cycle "mirror" effect, repeating only after a full A→E→A rotation, i.e. the conductance should be identical for snapshots D and D′, C and C′, etc. On the other hand, because the electric potential maps B and D (and therefore B′ and D′) are identical after an x-axis reflection, the conductance should mirror after a quarter-cycle translation of the DNA and should repeat itself after a half-cycle (A→B→C→D) in the 5-GNR, 8-QPC, and 23-QPC.

Figures 4.6a-d show the conductance as a function of the snapshot number (time) for Fermi energies 0.04 eV, 0.08 eV, 0.12 eV, and 0.16 eV above the Dirac point for each of the four geometries with a 2.4 nm pore at point P. The lines marked A-B-C-D-E-D′-C′-B′ correspond to the eight potential maps in figure 4.5b, representing the translation of one full helix of the DNA. As can be seen in figure 4.6b, the 15-GNR displays the half-cycle mirroring behavior described above, only repeating after each full helix translocates through the pore. On the other hand, the 5-GNR, 8-QPC, and 23-QPC conductances shown in figures 4.6a, 4.6c, and 4.2d respectively, display the quarter-cycle mirror effect; lines A-C represent one quarter of the helix, C-E represent the second quarter, etc. The DNA molecule in figure 4.5a, contains 24 AT base pairs, which give rise to 2.5 full turns of the double-helix. As a result, full translocation of the DNA molecule should result in 2.5 periods in the conductance curves of the 15-GNR, and 5 periods in the case of 5-GNR, 8-QPC and 23-QPC which is indeed the case as shown in Figure 4.6. In these latter conductance curves, the peaks of each cycle correspond to potential map A, when the DNA axis is parallel to the y-axis, while the troughs correspond to potential map C, when the DNA axis is parallel to the x-axis. The DNA molecule is not perfectly symmetric, as the bases in a base-pair are different nucleotides; additionally, there may be a small discretization asymmetry in the potential map of the DNA. The cumulative effect is a slight difference in the conductance after a y-axis reflection, which can be recognized in figures 4.6a, 4.6c, and 4.6d.

The large conductance variations accompanying DNA translocation through the pore demonstrate the high sensitivity of the device to external charges and their conformation. With a source-drain bias of 5 mV, the conductance (current) displays maximum variations of .8 to 8 µS (4 to 40 nA) depending on the particular geometry (figure 4.6), well detectable with present technology.
These large variations reinforce the idea that angular position and Fermi level, in concert with each other, can strongly change the magnitude of the electrical sensitivity of the devices. Additionally, for some geometries, such as the 8-QPC (figure 4.6c), a small change in Fermi energy (0.12 eV to 0.16 eV) results in a threefold change in the magnitude of the conductance (13 \( \mu \)S to 40 \( \mu \)S) and a threefold increase in the magnitude of conductance variations (0.9 \( \mu \)S to 2.8 \( \mu \)S). Interestingly, because of the presence of NDTC regions within the investigated Fermi energy range, an increase of Fermi energy may actually decrease the conductance, as in case of the 5-GNR (figure 4.6a).

Studies on electrochemical activity at the edge of graphene nanopore have been reported recently [78], which can lead to an electrochemical sheet current in graphene of the order of 0.5 nA for a pore diameter of 2.4 nm. Although this is a large electrochemical current, the sensitivity reported here to DNA translocation is much larger than the electrochemical current measured, especially at larger Fermi energies.

In our simulation, a new nucleotide is within the plane of the nanopore after \( \sim \)13 time steps. However, no such periodic modulation is visible in the conductance curves of figure 4.6. The reason for this is the strong screening due to the phosphate backbone on the DNA strand. As a result, the conductance variation reflects the positional changes of the backbone charges as opposed to the movement of the nucleotide charges themselves. In order to sequence DNA, one must be able to detect these nucleotides, either by translocating a single strand of DNA to prevent screening of the nucleotides by the backbone, or by making the DNA and its backbone undergo nucleotide-specific conformational changes.

### 4.1.5 Characterization of Helix to Zipper Transformation Under Forced Extension of dsDNA

The previous results describe the conductance response of graphene nanoribbons to the rigid translocation of a helical DNA strand in order to demonstrate the high sensitivity and tunability of the nanoribbon conductance. In addition to detecting the motion of translocating molecules, such devices can be also used to detect conformational changes of dsDNA, which can complement ionic current measurements and potentially extend the molecular sensing capability of graphene-based
Figure 4.6: Conductance as a function of DNA position (snapshot) for multiple Fermi energies, .04 eV (solid), .08 eV (long dash), .12 eV (short dash), and .16 eV (dot dash), as the DNA strand rigidly translocates through a 2.4 nm nanopore pore located at the device center (point P). a) 5-GNR, b) 15-GNR, c) 8-QPC and d) 23-QPC. Taken from ref [3].
devices. To this end, we perform stochastic molecular dynamics simulations of DNA being stretched within a nanopore, and we show that the conductance variations due to the translocating molecule show significant changes at progressive stages of the stretching process.

The mechanical response of DNA to external forces can be studied \textit{in silico} using SMD simulations \cite{80, 81}. Earlier simulation studies investigated force-induced stretching of dsDNA by applying a pulling force to the 5’ and 3’ termini on one end of the dsDNA and by constraining the corresponding termini at the opposite end, causing the strands to stretch parallel to each other and to undergo the B-DNA to zip-DNA transformation \cite{39, 82, 83}. Simulation studies performed under different pulling conditions, like pulling the 3’ or 5’ termini of both strands in opposite directions or torsionally constraining the dsDNA while pulling, can produce more complex structural changes including local DNA melting \cite{84–86}. Pulling only one of the termini (3’ or 5’) and constraining the corresponding termini on the opposite end can lead to strand separation. In fact, various types of SMD simulations have been employed to study the effects of methylation and hydroxymethylation on DNA strand separation \cite{87, 88}.

In the present study, dsDNA was stretched by pulling both strands on one end of the dsDNA (atoms colored red in figure 4.7) at a constant velocity of 1 Å ns\(^{-1}\) along the \(z\)-direction, while harmonically restraining the other end (atoms colored blue in figure 4.7). The pulled atoms were attached to one end of a virtual spring; the other end of the spring, a dummy atom, was moved at a constant pulling speed \(v\) (1 Å ns\(^{-1}\)) along the \(z\)-direction. The pulled atoms experience a force \(f = -k[z(t) - z(t_0) - v(t - t_0)]\), where \(z(t_0)\) is the initial position of the dummy atom attached to the spring. The spring constant \(k\) was chosen to be equal to \(3k_B T_0/\text{Å}^2\), which corresponds to a thermal RMSD deviation of \(\sqrt{k_B T_0/k} \approx 0.6\ \text{Å}\), which is typical for SMD simulations \cite{80, 81, 89, 90}. Figure 4.7 shows a sequence of snapshots, during forced stretching, of one independent SMD simulation for poly(A-T)\(_{15}\) DNA. The DNA is seen to undergo a series of conformational changes starting from helical form (marked A in figure 4.7) and gradually unwinding itself into planar zipper form (marked E in figure 4.7). During the A to E transition the hydrogen bonds between complementary base pairs break; the base pairs are seen to interdigitate and finally all stack on top of each other in a zipper like fashion. Also highlighted in figure 4.7 are two sets of base pairs, P-P’ and Q-Q’, which are spaced half a pitch apart (5 bp apart) from each other. The
Figure 4.7: Five representative snapshots (A-E) from a single SMD trajectory of poly(A-T)$_{15}$ DNA during a B-DNA (A) to zip-DNA (E) transition. The atoms colored in red were pulled in the z-direction at a rate of 1 Å ns$^{-1}$; the blue colored atoms were harmonically restrained to the initial positions. Also shown is the evolution of two sets of base pairs, P-P’ and Q-Q’, which are a half pitch (namely 5 bp) apart. The black arrows, joining P to P’ and Q to Q’, initially pointing in opposite directions corresponding to a pure helical conformation (B-DNA) align themselves in the same direction once the zipper conformation (zip-DNA) is reached. The numbers below each snapshot represent the corresponding molecular extension. Taken from ref [4].

The length of the entire DNA changed from 52 Å to 103 Å over the course of the simulation. A 60-ns MD trajectory showing the untwisting and gradual elongation of the DNA from B-form to zip-form can be viewed in figure C.8 of the Appendix.

Figure 4.8 shows force-extension curves for five independent SMD simulations performed on the poly(A-T)$_{15}$ DNA strand stretched with a constant pulling speed of 1 Å ns$^{-1}$. At the initial stage, the B-DNA undergoes an elastic transformation, where the force increases gradually from 0 to 100 pN accompanied by a molecular extension of 10 Å. Beyond this extension the force-extension curve is characterized by a plateau region, where the DNA transforms cooperatively from B-DNA to zip-DNA. The transition is characterized by coexistence of helical, stretched and zipper DNA domains. During the initial stages of the transition, a zip-DNA nucleation site appears near the
Figure 4.8: Force-extension curves for poly(A-T)$_{15}$ DNA. Shown are the force-extension curves that resulted from five independent SMD simulations, Sim 1-5, performed at a pulling speed of 1 Å ns$^{-1}$. The force-extension curve begins with a region corresponding to the elastic extension of B-DNA followed by a B-DNA to zip-DNA transition plateau. In the region beyond the plateau the zip-DNA undergoes elastic extension, which is characterized by a sharp linear increase in force. The inset shows the zip-DNA conformation at the end of the transition plateau. Figure C.9 of the Appendix shows the force-extension curves for the poly(G-C)$_{15}$ strand. Taken from ref [4].

pulling end of the DNA whereas the restrained end retains its helicity. Gradually, the DNA extends and unwinds, with parts of the DNA (middle portion) acquiring a stretched conformation (S-DNA), where the complementary base-pairs partially unwind but are still bound through hydrogen bonds. Eventually the S-DNA and B-DNA domains transform into zip-DNA domains and at an extension of 38 Å the entire DNA transforms into zip-DNA (see inset in figure 4.8). The zip-DNA extends elastically beyond 38 Å and is marked by a steep increase in the force experienced by the DNA. The computed peak force (1 nN) experienced by the DNA is much higher than the experimental ones ($\approx 150$ pN) [91–93]. The discrepancy is attributed to the pulling speeds employed in simulations.
(1 Å ns⁻¹) which, due to limited computational resources, is much larger than the typical pulling speeds in experiments (1 Å µs⁻¹).

The evolution of the angle between base pairs P-P’ and Q-Q’ (see figure 4.7) for the poly(A-T)₁₅ case is shown in figure 4.9. The two base pairs are a half-pitch apart and the angle is initially -180°, when the DNA assumes a helical form. After the transition to zip-DNA the base pairs are vertically stacked on top of each other, reducing the angle between the base pairs to 0°. The change in the angle (from -180° to 0°) occurs over a short range of extension, ranging from 10 Å to 25 Å. However, there is a significant variation in the observed dynamics across the five independent simulations. This variation can be attributed to fast pulling employed in the simulation, which does not allow dsDNA’s slower degrees of freedom to relax completely during the simulation time covered (60 ns).
Figure 4.10: Transverse electronic conductance as a function of poly(A-T)$_{15}$ DNA position (snapshot) for (a) graphene nanoribbon with armchair edge, and (b) graphene nanoribbon with QPC edge. Base pairs P-P' were initially aligned with the nanopore, and subsequently translocated at a rate of 0.5 Å, along -z direction, per snapshot until base pairs Q-Q' reached the pore. The transverse electronic conductance changes from an oscillating type response, corresponding to B-DNA (A), to a constant conductance when the DNA adopts a zipper-like conformation, i.e., zip-DNA (E). Sinusoidal variation in the transverse electronic conductance diminishes as the DNA passes through the intermediate stages B, C, and D. A QPC edge geometry shows larger variations in transverse electronic conductance when compared to the armchair edge geometry. Taken from ref [4].

Charge distributions corresponding to DNA conformations at five intermediate steps of the B-DNA to zip-DNA transition, A through E in Figure 4.7, were extracted from the all-atom MD trajectory. The DNA charge distribution, for each of the intermediate stages, was then placed inside a graphene nanopore with a diameter equal to 2.4 nm, such that the base pair P-P' resides inside the graphene nanopore; in addition, the DNA axis was also aligned with the nanopore axis. These charge distributions were then “translocated” along the -z direction in steps of 0.5 Å, until the base pairs Q-Q' reached the pore. At each step the electrostatic potential induced by the DNA on the graphene nanopore was calculated using the Poisson-Boltzmann approach, described in section 2.4.1. The electrostatic potential maps, in the plane of the graphene membrane, altered step-by-step due to DNA translocation, are provided for both B-DNA and zip-DNA cases in Appendix figures C.11 and C.12.

The electrostatic potentials obtained from eqn. 2.39 were then included in the Hamiltonian of the graphene membrane, eqn. 2.18. Shown in figure 4.10 is the transverse conductance as a function of DNA position inside the nanopore. The DNA inside the graphene nanopore was assumed to be
in one of the different intermediate stages (A-E) during the B-DNA to zip-DNA transformation obtained from a SMD simulation performed on poly(A-T)$_{15}$. The calculations described were carried out for two graphene nanopore geometries: an armchair edge geometry with width of 5 nm, and a quantum point contact (QPC) edge with width of 8 nm. The QPC edge has an irregular edge shape, leading to more stringent boundary conditions for electron transport when compared to the flat armchair edge geometry, as described in section 3.3. (The exact lattice of the armchair and QPC edge are provided in Appendix figure C.13).

As one can see in figure 4.10, the conductance varies sinusoidally as the DNA in stage A is translocated through the nanopore, is constant for DNA in stage E, and adopts an intermediate variation for DNA in stages B, C, and D. As explained in section 4.1.4, translocation of the DNA segment, comprising of nucleotides between P-P' and Q-Q', in the helical form results in an apparent rotation of the surrounding electric field inside the nanopore (see Appendix figure C.11). As a result, the transverse electronic conductance in the graphene membrane varies with this rotation. In case of zip-DNA being translocated through the pore, the field is rotationally invariant, and as a result, the transverse conductance remains constant (see Appendix figure C.12). In the case of progressive extension of the DNA that occurs during a B-DNA to zip-DNA transition, the sinusoidal variation of the transverse conductance diminishes as the translocating DNA passes through the A, B, C, D, and E stages shown in figure 4.7. Translocation of the DNA segment, comprised of base pairs between P-P and Q-Q', is equivalent to a rotation in the plane of the graphene nanopore, by an amount equal to the angle between the base pairs P-P' and Q-Q' (see figure 4.9). Thus, the conductance variation is a measure of the helicity of the DNA and can be used to detect the DNA conformation. The total variation in conductance for the B-DNA is about 1.5 $\mu$S for the armchair edge and about 10 $\mu$S for the QPC edge. The conductance variation is enhanced for the QPC edge case due to the constriction, which affects the electron transport near the nanopore. In addition, the boundaries also influence the shape of the response which no longer looks perfectly sinusoidal in case of a QPC edge pore.

The conductance variation as a function of DNA extension is shown in figure 4.11 for poly(A-T)$_{15}$ and poly(G-C)$_{15}$ strands computed at two different KCl molar concentrations, namely, 1 M (figure 4.11a) and 0.1 M (figure 4.11b). The error bars were obtained from sampling over five inde-
Figure 4.11: Variation in the transverse electronic conductance as a function of DNA extension for a QPC edge graphene nanopore. Shown in (a) and (b) are conductance variation, for the stages A, B, C, D, and E (see Figure 4.7) arising in the B-DNA to zip-DNA transition corresponding to KCl molar concentrations of 1 M and 0.1 M, respectively. The error bars are obtained from sampling over five independent force-extension simulations performed on poly(A-T)$_{15}$ as well as on poly(G-C)$_{15}$ strands. Taken from ref [4].

As discussed previously, the conductance variation is a measure of the helicity, and there is a large heterogeneity in the helical angle, between P-P' and Q-Q' (see figure 4.9), which can be observed in regions where DNA transitions from B-DNA to zip-DNA. In the present study, limited though by small sampling, conductance variations are indistinguishable for poly(A-T)$_{15}$ and poly(G-C)$_{15}$ cases. The general trend in conductance does not change when the molarity is changed from 1 M to 0.1 M. However, the magnitude of conductance variations is suppressed for the low molarity case, e.g., conductance variation for B-DNA (A in Figure 4.11) reduces from 10 $\mu$S to 2 $\mu$S for a change in molar concentration from 1 M to 0.1 M. In the low molarity case, due to reduced screening, the average potential induced on the graphene membrane is much larger in
magnitude compared to the high molarity case (see figures C.14 and C.15), which is equivalent to a gating effect and changes the bias point of the QPC significantly. Although reduced screening at low molar concentrations, increases the magnitude of the potential induced at the pore mouth, the variation in conductance itself is not enhanced.

4.1.6 Detection of the Passage of Single Nucleotides from Translocating Stretched ssDNA

The previous simulations described the conductance variations due to translocating dsDNA molecules through nanopores in graphene nanoribbon conductors. Sensing and characterizing the conformational structure of dsDNA is important, considering most experiments on graphene nanopore devices are used to sense dsDNA molecules. However, in order to sequence DNA molecules, detailed information about the nucleotides must be extracted, and to do so, single-stranded DNA (ssDNA) molecules must be used. The QPC and pristine-edged graphene nanoribbon conductors described are also capable of sensing the passage of single nucleotides through the nanopore.

We use SMD to stretch a 16 base pair ssDNA, comprising of 4 repetitions of the DNA segment A-T-G-C, from a canonical helical conformation to a linear, ladder-like form. The ssDNA molecule was solvated in a 0.3 M KCl electrolyte solution, and the terminal phosphate atom on the 5’ end of the ssDNA was pulled with a constant velocity of 10 Å/ns. The terminal phosphate atom on the 3’ end of the DNA was harmonically constrained to its initial position, until the nucleotides in the central region of the ssDNA acquired a linear conformation. The molecular length of the ssDNA changed from 55 Å to 128 Å over the course of the simulation, and the base pairs collectively tilted towards the 5’ end of the DNA [94].

The stretched ssDNA, which adopts a linear configuration due to forced extension, was placed inside a nanopore within a 8-QPC and translocated at a rate of 1 Å per snapshot along a direction perpendicular to the graphene plane to mimic electrophoretic translocation of the DNA through the graphene nanopore (see figure 4.12). As mentioned earlier, we showed that the rotation of the electrical potential of the DNA charge distribution, arising from DNA helicity, within the graphene plane causes a modulation in the electronic conductance through the graphene membrane. In the
present study, we choose a ladder-like conformation for ssDNA to ensure that the conductance modulations are solely due to the linear translocation of the DNA as opposed to any effective rotation of the electrostatic potential in the graphene plane.

First, we investigate the ssDNA translocation through a circular nanopore with a 1.2 nm diameter at three different locations in the g-QPC at a Fermi energy $E_F = 0.25$ eV. Figure 4.13 shows the transverse electronic conductance of the g-QPC as a function of ssDNA snapshot. We consider two orientations of the DNA molecule, one where the base pairs are aligned in the direction of transverse electronic current, herein referred to as ssDNA-x (see figure 4.13d), and the second where the base pairs are aligned in the direction perpendicular to the transverse electronic currents, herein referred to as ssDNA-y (see figure 4.13d).
Figure 4.13 displays the conductance traces for the center of the nanopore aligned to the geometric center of the g-QPC. For both DNA orientations, the conductance displays a series of peaks and valleys corresponding to the passage across the graphene membrane of individual nucleotides attached to the negatively charged phosphate backbone. The variation in electrical potential on the nanopore edge due to the motion of charges on the DNA molecule during the translocation process induces a variation of the local carrier concentration along the edge of the graphene nanopore, altering its conductance [3].

The particular snapshot when a nucleotide’s center of mass passes the graphene membrane is denoted with a vertical black dashed line in figure 4.13. As can be readily seen, these snapshot locations correlate with the valleys in the conductance curve, identifying a conductance valley with the passage of a single nucleotide. The magnitude of the conductance at a particular snapshot is determined by the spatial orientation of the nucleotide within the nanopore, which can fluctuate significantly. However, the percentage change in conductance between nucleotides can be in excess of 15%, indicating the possibility to distinguish the charges of a passing nucleotide from the rest of the system.

In particular, the magnitude of the conductance variations for ssDNA-y is ~0.03 $\mu$S to ~0.05 $\mu$S, or 10 to 17% of the overall signal. These variations are approximately three times larger than those
for ssDNA-x for two reasons. First, there is a larger electronic density of states in g-QPCa above and below the nanopore (along the y-direction) compared to the density of states on either side (x-direction). Secondly, the nucleotides of ssDNA-y are closer to the larger electron density compared to ssDNA-x. As a result, changes in electrical potential have a more significant effect on the conductance.

As described previously, when the pore geometry is altered, such as when changing its position, shape, or size, the boundary conditions restricting the allowed electronic states in the QPC are likewise changed, so various conduction channels around the Fermi energy may open or close. Depending on the transmission probability of each of these channels, an overall larger or smaller current can arise.

In order to determine the effect of the pore position on the conductance sensitivity, we chose to study g-QPCs with a 1.2 nm diameter pore in two alternate positions, shown in figure 4.13b and c, where the nanopore center is offset from the QPC geometric center by 1 nm and 2 nm, respectively, along the y-direction defined in figure 4.13. Because the trajectory of ssDNA remains unchanged for each pore position, the conductance of the QPC with a pore at position ‘b’ (figure 4.12b) has conductance minima at the same nucleotide positions as that with the pore at ‘a’ (figure 4.13a). However, for ssDNA-y, the width of these variations is noticeably smaller. Similarly, for ssDNA-y, the width of the minima is further reduced for a QPC with a pore at position ‘c’ (figure 4.13c). This is because there is a smaller interaction between the charges on the DNA backbone and the GNR electronic conduction states as the pore is placed closer to the edge. The negative backbone charges tend to attract positive holes in the g-QPC, enhancing the hole conduction and masking the nucleotide signal. As the nanopore is placed closer to the edge, however, the influence of the backbone becomes negligible, especially when the backbone is outside of the g-QPC, as in the case of pore ‘c’ (figure 4.13c). As a result, the nucleotide charges are solely responsible for the conductance variation, enhancing the detection of the nucleotide passage event.

In the case of the ssDNA-x, as the pore is placed closer to the edge, the nucleotide signal becomes indiscernible. The nucleotide and the conducting holes of the GNR are too far to interact strongly, when the nanopore is far from the QPC center, and cannot to be detected. On the other hand, in the ssDNA-y orientation, the nucleotides are adjacent to the conduction charges, and the
conductance dips can be clearly seen.

The most striking effect of the changing boundary conditions when varying the pore position is their influence on the conductance magnitude. When the pore is moved from the nanopore center ‘a’ to position ‘b’, the conductance is amplified by almost two orders of magnitude, while at position ‘c’, the conductance is reduced by a factor of \(\sim 10\). Such drastic changes in the conductance magnitude with alternate pore positions suggest that the conductance magnitude is a strong function of lattice geometry. However, finer control of the conductance magnitude can be achieved by adjusting electronic carrier concentration in the g-QPC via a gate electrode [6]. It is clear that positioning the pore closer to the boundary negates the influence of the phosphate backbone on the conductance, and hence increases the ability for the current to detect only the nucleotide.

In figure 4.14 we display the conductance variation due to ssDNA-\(y\), for a 2 nm circular pore (figure 4.14b), and a 0.8 nm by 1.2 nm elliptical pore at the g-QPC center (figure 4.14c), in addition to the 1.2 nm circular pore (figure 4.14a) discussed earlier. The primary result of increasing the circular pore diameter to 2 nm is the suppression of the interaction between the ssDNA molecule and the electronic conduction states (figure 4.14b). Since the ssDNA is in the center of the pore, the electrolytic screening, with a Debye length of 0.5 nm, causes the electric potential to become significantly smaller at the pore edge. Variations can still be seen at the same locations as the 1.2 nm pore, but they are significantly smaller, varying in magnitude by \(\sim 1\%\).

One of the main issues encountered when electrically sensing a DNA molecule, translocating through a nanopore, is the stochastic fluctuations of the DNA molecule itself, disrupting the conductance variations due to the passage of a nucleotide. Employing an elliptical pore can restrict the lateral fluctuations of translocating base pair. For this purpose we analyze the conductance due to ssDNA-\(y\) translocating in an elliptical pore with a major and minor axis diameter equal to 1.2 nm and 0.8 nm respectively (figure 4.14c). As can be seen, the conductance variations become much more uniform and well defined when the ssDNA-\(y\) is translocating through the elliptical pore. The pore edge is screened less by the electrolyte, because the phosphate backbone of the DNA is closer to the pore atoms. As a result, the conductance signal reflects the passage of the phosphate atoms more than the nucleotides themselves. The conductance variations are still significant, having a magnitude 3% of the overall conductance.
Figure 4.14: Influence of pore size and shape on the electronic conductance variation due to translocation of a 5 base pair long ssDNA segment in a linear ladder-like conformation. (a) circular pore with diameter = 1.2 nm, (b) circular pore with diameter = 2 nm, and (c) elliptical pore with major and minor axis diameters equal to 1.2 nm and 0.8 nm respectively. Taken from ref [5].
4.2 Expanding Transistor Functionality with Additional Gate Electrodes

Until now, we have been describing the interaction between DNA molecules and graphene nanoribbons with nanopores. In addition to tuning the nanoribbons’ sensitivities to external charges by changing their geometrical parameters, such as width, edge shape, and pore geometry, we use the Fermi energy, $E_F$, as an adjustable parameter to tune the sensitivity of the nanoribbons to external charges. The Fermi energy, the inflection point of the Fermi-Dirac distribution function, roughly defines the average energy of the current carriers in graphene. It is not truly an adjustable parameter in the sense of a controllable knob in the laboratory, rather, it is a property of the conductor, determined by all of the interactions defined in the Hamiltonian. Thus, the Fermi energy can be altered, either by placing an external charge distribution near the conductor, as previously described, or by applying an external potential to the nanoribbon via a gate electrode. In addition, gated electrode layers can be used to stabilize the stochastic fluctuations of a DNA molecule inside the pore. An example of a transistor with multiple gate control layers is shown in 4.15. We now describe the effects of adding properly insulated gate electrode layers to the nanoribbon transistor, and how they can be used to adjust the Fermi energy and, hence, the electronic properties of the graphene nanoribbon.

4.2.1 Nanopore Transistor

A schematic diagram of multilayer device simulated in this study is shown in figure 4.16. The device consists of a single-layer, 59 carbon site (7.13 nm) wide armchair graphene nanoribbon, with hydrogen passivation of any dangling bond, in a QPC geometry, between two SiO$_2$ layers to insulate the GNR from both the solution and the back-gated electrode. The layer thickness of the top (bottom) oxide layer is 10 nm (65 nm). Underneath the bottom oxide is a 2 nm thick gate electrode, which will be used to vary the carrier concentration as explained below. A double-conical nanopore is present through the center of the entire stack, with a shape typical of that resulting from ultra-bright electron lithography processing [95], and a smallest diameter of 2.4 nm, at the
Figure 4.15: Schematic diagram of a 4 layer device containing a two graphene layers (black) to control the translational motion of DNA through the nanopore. The top graphene layer ($V_{C1}$) controls the translational speed of the DNA, while the second ($V_{C2}$) controls the lateral confinement of the DNA within the nanopore. The third graphene layer ($V_{DS}$) measures the sheet current. Finally, a heavily-doped back gate (green) lies underneath the sheet current layer to control the carrier concentration. Oxide barriers (transparent) between different graphene layers provide electrical isolation. Taken from ref [3]. (See figure C.7 in the Appendix for a cross-sectional schematic diagram).
When an oxide comes into contact with an aqueous salt solution, a chemical reaction occurs, between its surface atoms and the electrolytic solution, creating a static layer of charge on the oxide surface [96, 97]. We take this into account by including a small, 1 nm-thick layer of charge, \( \sigma = 10^{12} \text{ cm}^{-2} \) in units of \( e \), the electronic charge. Because the magnitude of the charge is strongly dependent on particular choice of oxide, salt, and solution pH, we treat \( \sigma \) as an adjustable parameter which can be optimized for the particular device application.

### 4.2.2 Conductance Sensitivity Enhancement with Tunable Gate Electrode

We first investigate the carrier concentration response due to changing the bias of an external gate electrode in the multilayer structure described above. The bottom gate bias was set to values between \( V_G = -4 \text{ V} \) to \( 4 \text{ V} \) in 1 V intervals. For each gate bias value, the potential of the entire system was calculated from eq. 2.39, and inserted into the Hamiltonian. It is assumed that the source and drain leads are held at 0 V.

Figure 4.17a (above) shows the local electrical potential in the graphene layer at \( V_G = -4 \text{ V} \),
0 V, and 4 V. Due to the negative charge layers present on the oxide surfaces in contact with water, the potential in the GNR is less than zero at a $V_G = 0$ V, especially away from the pore. The potential in and around the immediate vicinity of the nanopore remains unchanged by gate bias changes as a result of heavy screening by the electrolytic solution, thereby maintaining a potential value of approximately 0 V inside the nanopore for all gate biases. The effects of screening decrease significantly further inside the GNR, away from the pore. Near the GNR leads ($|x| = 7.5$ nm), the potential increases by over 200 mV as the gate voltage is increased from $V_G = -4$ V to 4 V. This potential change corresponds to a Fermi energy variation of approximately $0.2$ eV, consistent with the magnitude of the Fermi energy parameter changes used in section 4.1.4. This implies that a gate electrode in this configuration can significantly alter the carrier concentration. The electric potential at these three gate biases along the $x$ axis at $y = 0$ is shown in the lower portion of figure 4.17 a.

Figure 4.17b shows the electron (left) and hole (right) concentrations in a g-QPC in the multilayer device as a function of gate potential. For $V_G = -4$ V, far from the nanopore, in the GNR, the large negative local potential ($-150$ mV) pushes the effective Fermi level far below the conduction band, reducing the electron concentration to negligible levels. For the same reason, the hole concentration is largest at this gate voltage, exceeding $5 \times 10^{12}$ cm$^{-2}$ at some locations. Because of ion screening, the effective potential in the GNR near the pore remains slightly below zero at all gate voltages. This produces a very small but nonzero electron concentration around the nanopore edge, which varies negligibly as the gate voltage is changed. Similarly, the hole concentration around the pore varies slightly as the gate voltage is increased and is quite large compared to the electron concentration due to the effect of the oxide surface charge, exceeding $4 \times 10^{12}$ cm$^{-2}$ for $V_G = -4$ V at various locations around the pore. Owing to the boundary conditions imparted by the nonuniform QPC edge as well as by the nanopore, the local density of states varies around the nanopore. As a result, there is a similar variation of the local carrier concentrations around the perimeter of the pore. The QPC in this study has x- and y- axis reflection symmetry about the nanopore center, and as a result, the spatial distribution of the carrier concentration also acquires these reflection symmetries, as described previously in section 4.1.4.

At larger gate biases, the electron concentration away from the pore is significantly increased,
Figure 4.17: (a) (above) Color plots of the local electric potential in the graphene layer at three gate voltages (-4 V, 0 V, 4 V). (below) Potential profile through the center of the nanopore within the graphene plane at three gate voltages. (b) (above) Local electron (left) and hole (right) concentration in the QPC at the same gate voltages. (below) Total carrier concentration profile along the current propagation direction, averaged along the width (y axis) of the nanoribbon. Taken from ref [6].
achieving values of over $2 \times 10^{12} \text{ cm}^{-2}$ at $V_G = 4 \text{ V}$. The hole concentration responds in the opposite way, becoming negligible far from the nanopore at the largest gate voltage, though remaining significant in the vicinity around the nanopore. These large variations in carrier concentration arising from gate voltage modulation show the tunability of the conductance properties of the graphene transistor. The spatial distribution of the electrons depends on the particular geometry used, and can be tailored to the specific application by changing the edge geometry appropriately. The linear carrier density at these three gate biases along the $x$ axis, averaged over the $y$ axis, is shown in the lower portion figure 4.17b.

At all gate biases, the hole concentration is significantly larger than the electron concentration due to the large negative potential arising from the oxide surface charge. In addition, there is an inherent asymmetry between the conduction and valence bands due to the three-orbital basis used in our model[66]. Both of these are consistent with the location of conductance minimum at non-zero gate biases in experimental systems[98].

A vertical cross section of the absolute electric potential of the entire system at $V_G = -4 \text{ V}$ is displayed in figure 4.18a. Because of ion screening, the potential is approximately zero almost everywhere in solution. However, in the center of the nanopore, in the graphene plane, the potential

---

**Figure 4.18:** (a) Vertical cross section of the absolute electric potential of the system through the nanopore center at $V_G = -4 \text{ V}$. (b) Spatial distribution of electrolytic ions in solution at various gate voltages. Taken from ref [6].
is negative due to the close proximity of the nanoribbon to the oxide surface charge. This is indicative of the screening length of the ions, which allows the potential originating from mobile charges in the pore to penetrate significantly into the nanoribbon. On the sides of the multilayer stack, the potential gradually increases from a value of $-4$ V at the gate electrode to $-50$ mV at the top of the upper oxide layer. The double-conical shape of the nanopore allows the potential of the stack resulting from the gate electrode to be focused onto a majority of the graphene layer. The specific geometry of the pore and stack can be adjusted to enhance or weaken the influence of the gate electrode on the graphene potential and thus carrier concentration.

The electrolyte distribution in the center of the nanopore at $y = 0$ at various gate biases is shown in figure 4.18b. For $V_G = -4$ V, the $K^+$ concentration reaches a value over 120 mM in the pore center. Close to the pore wall, the negative surface charge causes an accumulation of $K^+$ ions in excess of 140 mM. The situation is opposite for $Cl^-$ ions, reaching concentrations of 85 mM and 70 mM in the pore center and wall, respectively.

As the potential is increased, the $K^+$ and $Cl^-$ concentrations decrease and increase respectively, as the potential in the center of the nanopore increases. The $K^+$ ion concentration in the center of the pore decreases by almost 20 mM, and decreases by 30 mM near the pore wall. For $Cl^-$ ions, the concentration in the pore center increases by 10 mM, while at the pore wall it increases by 15 mM. The larger changes in concentration at the pore wall are a result of diminished screening at those locations.

There is a vertical asymmetry of the potential in the pore due to the position of the gate electrode, also appearing in the electrolyte distribution. This is most evident for $V_G = 4$ V, where the $Cl^-$ concentration is clearly larger in the lower half of the nanopore. The geometry of the pore could be modified to enhance this asymmetry, especially through the use of an additional gated layer near the graphene plane. This can be used to alter the ionic conductance properties of the nanopore [99].

### 4.2.3 Conductance Modulation from dsDNA Translocation

We calculated the electric potential in the graphene layer due to the presence of a 10 base pair poly-AT double-stranded DNA (dsDNA) molecule in different vertical positions within the nanopore.
For each gate voltage, the potential was calculated with and without a DNA strand in the pore. For the former situation, the DNA center of mass was held at three different positions on the nanopore (z) axis: in the plane of the graphene layer, 1.25 nm below the graphene plane, and 2.5 nm below the graphene plane. The center of mass of the DNA was maintained at the same x and y positions, namely on the axis of the pore. The conductance was calculated assuming that the leads are biased such that they are charge-neutral, offsetting the influence of the charged oxide substrate.

As seen in the upper portion of figure 4.19a, the conductance of the GNR without a DNA strand is enhanced by a gate electrode, because positive (negative) gate voltages induce additional free electrons (holes) in the GNR. However, the conductance is larger for positive gate voltages due to the presence of the oxide surface charge, in addition to the inherent asymmetry between the valence and conduction bands of the QPC.

Because there is a low concentration of carriers near the pore, the conductance is relatively small, ranging from 1 to 3 µS over the gate voltage range. The presence of a DNA molecule in the nanopore significantly enhances the conductance for all gate voltages, because of the emergence of carriers near the pore due to the electrostatic potential of the DNA charges. For positive gate voltages, the multilayer stack acquires a net positive potential, and the K+ concentration is significantly reduced near the pore wall. As a result, the screening of the negative charges on the DNA is mitigated, and the DNA has a stronger effect on the local carrier concentration and thus the conductance. At negative voltages, there is a larger accumulation of K+ ions around the pore wall, reducing the impact of the local gating due to the DNA charge.

As the DNA is translated along the z axis, the potential in the plane of the graphene sheet due to the DNA charges shows the effective rotation of the DNA, as described previously in section 4.1.4. As a result, the local carrier concentration around the nanopore, as well as the conductance, is altered due to the different DNA positions. As seen in figure 4.19a (above), the change in DNA position translates to a conductance difference of nearly 6 µS at $V_G = 2$ V which is nearly six times the conductance difference at $V_G = -4$ V. Thus, changing the gate voltage can significantly alter the sensitivity of the conductance to the positional changes of external charges in the nanopore. The asymmetry in the conductance about the gate voltage can be attributed to the presence of the surface charges on the oxide layers.
Figure 4.19: a) (above) GNR conductance versus gate bias for different DNA positions along the nanopore axis using the expanded three-orbital basis. (below) GNR conductance versus gate bias using the traditional single-orbital tight-binding model of graphene. b) The electron transmission versus energy around the Fermi energy for the expanded three-orbital basis (solid black), the expanded basis without hydrogen passivation (dashed green), and the single orbital basis without hydrogen passivation (dashed red). Taken from ref [6].

In order to compare the expanded basis of our tight-binding model with the traditional, single $p_z$ orbital tight-binding model of graphene, we performed the same calculation with the simpler basis. As seen in the lower portion of figure 4.19a the conductance resulting from the expanded basis is over one order of magnitude larger than that from the traditional model. In addition, in the simpler model, the gate voltage associated with the minimum conductivity for all DNA positions was found to be 2 V, whereas at this gate voltage the use of the expanded basis model results in a very large conductance.

The large differences between these two models can be attributed to two factors, namely hydrogen passivation allowed by the expanded basis model, as well as the more complex boundary conditions introduced by the additional terms in the expanded Hamiltonian. Figure 4.19b shows the transmission functions for the GNR using the expanded basis with hydrogen passivation, the expanded basis without hydrogen passivation, and the single-orbital basis without hydrogen passivation. The effective gap for the GNR with the expanded basis with passivation is much smaller than those gaps without passivation. This is due to the fact that the hydrogen atoms make the effective GNR width slightly larger. In addition, the Fermi energy is closer to the conduction band.
in this basis. As a result, conductances are higher in the case of passivation with the expanded basis. An interesting feature in all three cases is the existence of additional states within the gap, arising from the constricted QPC edge. These manifest themselves as transmission resonances, occurring at very narrow energy ranges, whose exact positions depend on the particular basis used.

The three-orbital basis corrects many deficiencies of the single-orbital model, namely the inability to reproduce the presence of band-gaps in all GNRs, the asymmetry between valence and conduction bands near the Fermi energy, and the ability to incorporate hydrogen-passivation[66]. Further additions to this basis would add minor corrections to the overall electronic structure, but would not change the global properties of the system.

It should be noted that though the expanded basis set imparts significant changes to the electronic structure around the band gap, the fundamental behavior of our device remains unchanged. Because of the complex boundary conditions of the edge and nanopore, conduction channels can open or close within very narrow energy ranges, allowing minor Fermi energy changes, via a gate electrode or external charges, to cause significant variation in the device conductance regardless of the particular basis used. This is the underlying principle behind our device.

4.2.4 Sculpting Electrostatic Landscape for DNA Manipulation

One of the primary obstacles of implementing a successful graphene-based nanopore transistor is the noise in the signal due to stochastic and thermal fluctuations of DNA bases inside the nanopore. The variations in nucleotide conformation and position can impact the nanoribbon conductance even more than the differences between each nucleotide’s structure. In order to combat this issue, controlling the stochastic fluctuations of DNA molecules is imperative.

To this end, we have performed a series of simulations of dsDNA molecules, confined within a cylindrical boundary, under the influence of electric fields, which are applied within a nanopore. These fields simulate a thick gate electrode layer in the nanopore transistor stack, within which is a stochastically fluctuating dsDNA molecule. Though it is highly idealized, observing how the fluctuations of DNA motion are affected by electric fields can guide the design of a multilayer, gated transistor.

The gated nanopore is modeled as a uniform, cylindrical 2.4 nm diameter nanopore, within a
gated layer of the stack. The potential $\phi$ of the layer and the molarity are varied between $-1.5$ V to $1.5$ V and $0.3$ M and $1.0$ M, respectively. The resulting electrostatic potential, obtained from 2.39 in the absence of DNA, is discretized onto a $129 \times 129 \times 129$ point uniform grid.

Figure 4.20 shows the electrostatic potential and electric field in a plane perpendicular to the nanopore axis, at a gate voltage of $+0.5$ V, and molarity of $0.3$ M. The potential is constant within the gated region, and drops rapidly within the pore boundary, due to the high screening from $Cl^-$ ions, attracted to the positive gate. The potential, along a line through the center of the nanopore ($y = 3.0$ nm), is shown in figure 4.20b. The potential is nearly zero in the center of the pore, indicating that the electric field is very strong near the pore edge. This is indeed the case, as the field reaches values of over $35$ MVcm$^{-1}$ very close to the pore wall.

At higher gate voltages, the value of the field near the pore increases to over $140$ MVcm$^{-1}$, though only within a region $< 1$Å near the pore wall. A realistic system would not be able to sustain enough charges in such a small region to create such a large field. Nevertheless, the DNA molecules studied rarely reach these regions of high field, and are repelled away due to the constraint introduced by the cylindrical pore.

At $1.0$ M, as seen in figure 4.21, the field and potential profiles are almost identical. The differences between the two profile is only present very close to the pore wall, and as explained previously, should have no significant effect on the DNA motion. The decay of the potential occurs over a slightly narrower region near the pore wall, and as a result, the electric field, measuring $\sim 38$ MVcm$^{-1}$, is slightly larger. At negative gate voltages, the fields and potentials are identical in magnitude but opposite in sign.

The electric fields are inserted into the MD simulation via the GridForce module performed with NAMD and analyzed with VMD. In order to simplify the complexity of the simulation, the potential is only applied to the DNA molecule. This is justified, because the redistribution of ions and water due to the electric field is already taken into account with the Poisson-Boltzmann formalism, eqn. 2.39. As a result, the DNA molecule can be studied without having to include the response of every ion and water molecule.

Each simulation models $\sim 15$ ns of stochastic fluctuation of 22 base-pair poly-AT dsDNA under the influence of each potential and molarity combination. In figure 4.22, we see the moving average
Figure 4.20: (Above) Electrostatic potential and (Below) electric field, in $xy$ plane and line across nanopore diameter, of a 0.5 V gated cylindrical nanopore, in a 0.3 M solution.
Figure 4.21: (Above) Electrostatic potential and (Below) electric field, in \( xy \) plane and line across nanopore diameter, of a 0.5 V gated cylindrical nanopore, in a 1.0 M solution.
Figure 4.22: a) Center of mass (CM) displacement from center of nanopore, at five gate voltages and 0.3 M ion concentration. The thick line is the moving average over 100 data points. b) Moving standard deviation over 100 data points of CM displacement at 0.3 M. c) and d) are the moving CM displacement and SD at 1.0 M.

and standard deviation (SD) of the \(xy\) center of mass (CM) displacement, from the center of the nanopore, of a dsDNA molecule subjected to one of five gate voltages. The moving average and standard deviation pertain to the 100 nearest values around a particular simulation time, revealing the coarse motion of the DNA strand amongst its fluctuations. At both molarities, the same trajectory is shown for 0.0 V, since the molarity is irrelevant when no gate voltage (0.0 V) is applied.

When 0.0 V is applied, the fluctuations of the CM are large, as indicated by the CM displacement and SD. However, at 0.3 M, when either positive voltage is applied, the SD of the CM is reduced significantly. This can be explained as a result of the positive field attracting the negatively charged DNA backbone toward one position of the pore, and holding it there. This can be clearly seen
Figure 4.23: CM displacement of DNA from center of nanopore in (left) 0.3 M solution and (right) 1.0 M solution.

in figure 4.23, which shows every CM position for the duration of the entire simulation. At no voltage, the DNA CM is almost uniformly spread around the center of the pore, consistent with the fluctuations seen in 4.22. However, at both positive gate voltages, the DNA CM does not move outside of a very small region, indicating that positive gates can indeed stabilize dsDNA.

At negative voltages, the fluctuations of CM of the DNA are not reduced as significantly, though at $-1.5 \text{ V}$ the SD of the CM motion does decrease. At $-0.5 \text{ V}$, the negative field repels the DNA backbone, pushing the DNA around the nanopore. The CM positions as seen in figure 4.23 are located at many positions around the pore, indicating that it fluctuates greatly under the influence of a small, negative potential. However, the nucleotides themselves have a dipole moment due to the presence of hydrogen atoms. These hydrogen atoms can become “locked” to the negative field of the pore wall, reducing the motion of the DNA molecule. Therefore, at $-1.5 \text{ V}$, the DNA motion is restricted, as seen by the localized CM positions in figure 4.23.

While it is difficult to see in figure 4.22, the influence of molarity increase can be clearly seen in figure 4.23. Each “cluster” of CM positions at positive voltages becomes smaller at 1.0M, indicating
that larger electric fields are induced, and tend to reduce the fluctuations of the DNA, albeit not significantly. For the other gate voltages, the effect of molarity is minor.

In each of the above simulations, the DNA molecule was allowed to evolve from an initial, relaxed state to its final conformation. Being able to quickly turn the stabilization of the DNA on and off is crucial for any application where real-time, precise control is required. To this end, we simulated a pulsed, positive 0.5 V gate voltage on the DNA molecule. The DNA initially has a positive voltage applied for 15 ns, then the voltage is pulsed off and on for 10 ns blocks repeatedly.

Figure 4.24 shows the moving average and SD of the CM displacement as the gate voltage is pulsed on and off. The shaded regions indicate when 0.5 V is applied to the gate, and unshaded regions correspond to no gate voltage. Clearly, the fluctuations are significantly reduced when the gate is pulsed on. The SD is suppressed by over 5 times during an on pulse, and stays low throughout the duration of the pulse. As expected, when the pulse is turned off, the fluctuations increase, showing a large and varied SD throughout the off region. When the positive voltage is turned on again, the fluctuations are again suppressed, clearly revealing its ability to stabilize the DNA.
4.3 Concluding Remarks

We have considered the ability of GNR transistors to sense the motion and conformation of DNA molecules. In addition, we explored the impact of nanoribbon geometry and Fermi energy adjustment on the sensitivity of GNR transistors to external charges. We began to address the stochastic fluctuations which prevent the direct detection of single nucleotides, by proposing to utilize gate electrodes around the nanopore to stabilize and control the motion of dsDNA.

In order to develop a complete, real-time DNA sequencing device with electronic sensing membranes, advanced data analysis techniques, such as neural networks, must be employed. Machine learning algorithms such as neural networks have shown the ability to extract unseen patterns from complex data sets. Acquiring MD simulation data becomes the next hurdle.

Additional graphene layers can be added for higher resolution, and exploring alternative pore geometries can open new paths for the design of the ideal nanopore. Other materials, such as molybdenum disulfide, are emerging as additional exotic, low-dimensional systems, enabling the construction of hybrid transistors from both graphene and MoS$_2$. Recent work [100] on ionic filtration and nanopore electrostatics opens up the possibility of analyzing concentration gradients, which can create additional dynamics inside of the pore. The possibilities for nanopore transistors are unlimited.
All-Carbon Spin Logic

In this chapter, we study circuits composed of spintronic GNR transistors, by adding two carbon nanotubes (CNTs) to a GNR to serve as magnetic gates. The resulting device, composed of zigzag nanoribbons, acts as a magnetoresistive spintronic switch, due to the spontaneous magnetization of the electronic states. In order to describe these states, the mean-field Hubbard interaction, as discussed in section B.1, needs to be included into the secular equation.

5.1 Nanoribbon Transistor with Nanotube Control Wires

A zigzag GNR has a spontaneous magnetic ordering as a result of the on-site Hubbard interaction [65]. There are two metastable states, one resistive ground state and a conducting excited state, which can be switched by a magnetic field. If current passes by a zigzag GNR, through an adjacent CNT, the resulting magnetic field can be strong enough to switch the magnetic state, (see figure 5.1). The GNR, then, can be made to conduct, a form of magnetoresistance (MR). The resulting device is an all-carbon spintronic switch.

Each GNR is treated as a two-terminal device, with a static gate voltage and source-drain bias. Because the gate voltage is held constant, a GNR switching event is mediated solely by a magnetic field and, hence, the current in CNT bundles adjacent to the GNR.
5.1.1 Spontaneous Magnetic Ordering in Zigzag Nanoribbons

In a zigzag-edge GNR, the on-site Hubbard interaction (see eq. 2.21 in Methods), between electrons of opposing spin, results in two stable states: an insulating ground state with global AFM ordering and zero net magnetization, and a metastable conducting state at a slightly higher energy with global FM ordering and, thus, a net magnetization (figure 5.2) [38, 42, 65, 67].

Both magnetic states have local AFM ordering and large magnetization at the edge sites, as can be seen for the AFM state pictured in figure 5.2a. Here, the AFM and FM states refer to the orientations of the edge magnetizations to each other rather than the local spin ordering (figure 5.2c). As seen in figure 5.2b, the magnetization quickly decays further into the GNR, becoming negligible at distances greater than 1 nm from the edge, allowing the magnetic field originating from the current in a CNT close to the GNR edge to alter the GNR’s magnetic energy via the Zeeman interaction. If this field is strong enough, it can switch the ground state of the GNR from AFM to FM, thereby altering its electrical state from insulating to conducting.
In figures 5.3a and b, the band diagrams are shown for the AFM and FM states, respectively, for a 12-ZGNR, with zero current in the CNTs, and \( U = 2.7 \text{ eV} \), where \( U \) is the Hubbard parameter appearing in eqn. 2.21. In the AFM state, there is a large gap between the valence and conduction bands, within which lies the Fermi energy. As a result, there are no available conduction modes, and the conductance is zero. This can also be seen in the gap of the transmission function \( \bar{T}(E) \) of the AFM state (figure 5.3e), which defines the number of available conduction modes as well as the probability for an electron to travel across the device. Alternatively, in the FM state, the gap closes, and there is always at least one conduction mode at all energies, as can be seen in the FM transmission function. Thus, when \( E_F \) lies in the gap in the AFM state, the GNR can be made to conduct if its magnetic state is switched from AFM to FM. However, in the FM state, the net spin polarization splits the band structure each spin direction, indicating that at particular Fermi energies a spin-polarized current can arise[101]. Importantly, if the Fermi energy is not in the gap of the AFM state, then the conductance will always be nonzero, and no change in conductance will be observed when the magnetic state is switched. This is one possible explanation for the lack of MR observed by Bai et al. when an in-plane field is applied to a GNR[41].

### 5.1.2 Magnetic Field Driven Phase Transition

The energy difference \( \Delta E \) between the AFM and FM states, also known as the magnetic instability energy, is a function of the on-site Hubbard parameter \( U \) and the current \( I \) flowing through the external CNT wires. Because the AFM state has a continuous local AFM ordering, there is a nonzero polarization at every site. The FM state, however, must have a lattice sites with zero polarization to maintain reflection symmetry across the GNR. The Hubbard interaction maximizes the system energy at zero polarization, and, as a result, the FM state has a slightly higher energy, yielding AFM as the ground state in the absence of a magnetic field. When the current in the CNT surpasses the critical switching current \( I_C \) at a particular \( U \), the energy of the FM state becomes smaller than the AFM state (\( \Delta E < 0 \)), and the FM state becomes the ground state, increasing the GNR conductance by \( G_0 = \frac{4e^2}{h} \) (figure 5.3f). The conductance is then a binary state variable, taken as ‘1’ in its conductive state at high fields and ‘0’ in its resistive state at low fields.

Figures 5.3c and d show the instability energy for two zigzag GNRs measuring 20 nm wide
Figure 5.2: (a) On-site magnetization profile of a zigzag GNR. The color of each circle represents the spin species, while the radius corresponds to the magnitude of the magnetization. (b) The on-site magnetization of each site in a unit cell as a function of distance from the edge. (c) The global magnetic orientation of the AFM (left) state with oppositely oriented edge magnetizations and the FM (right) state with parallel edge magnetizations.

(above) and 35 nm wide (below). The blue region designates a positive instability energy (the insulating AFM state), while the red regions indicate negative instability energies (the conductive FM state). In the narrower GNR transistor, the CNT wires are placed such that their axes are 10 nm away from the GNR edge, while the wider GNR has CNTs placed 1 nm away. The critical switching current, which depends on $U$, is denoted with a dashed line. The 20 nm GNR is insulating at nearly all $U$ when the current is less than 100 mA. Currents must be in excess of 120 mA, corresponding to current densities greater than $10^{10}$ A/cm$^2$ for a CNT with a 10 nm diameter, to switch the GNR for $U > 3$ eV and $U < 1.9$ eV. The critical currents for $U$ within this range are larger, exceeding the investigated region for some $U$. It is clear that very large CNT currents must be passed in order to switch a GNR in this configuration, which is not always possible or practical.
Figure 5.3: (a and b) Band diagrams for the (a) AFM and (b) FM states of a zigzag GNR. In the AFM state, both up and down spins have identical band structures, while in the FM state, each spin species has a unique band structure. (c and d) Magnetic instability energy for zigzag GNRs measuring (c) 20 nm with a CNT to GNR separation of 10 nm and (d) 35 nm with a CNT to GNR separation of 1 nm. The critical switching current which separates the AFM (blue) phase from the FM (red) phase is denoted with a black dashed line. (e) The transmission function around the band gap for a zigzag 12-GNR at $U = 2.7$ eV for the (blue) AFM state and (red) FM state. (f) A typical switching event, where the GNR conductance increases by $G_0$ when the CNT current passes the critical switching current $I_C$.

Multiple factors can reduce the critical switching current, such as increasing the GNR width as well as placing the control wires closer to the GNR edge. When both of these adjustments are made, as shown by the wider GNR, the critical switching current becomes much smaller by almost two orders of magnitude or more for nearly every value of $U$. In fact, at $U = 2.1$ eV, for example, currents below the sample resolution are enough to switch the GNR. At most $U$, however, the critical current is below 4 mA. The supports previous findings of small instability energies of wide zigzag GNRs[42]. In the FM magnetic state, as the width of the GNR increases, the number of sites with no net polarization, a ‘spin-polarization depletion region’, maintains a near-constant size, and becomes small compared to the width of the GNR. Thus, the instability energy deceases with increased width, and a parallel wire can more easily switch the magnetic state in wider GNRs.
In addition, the magnetic field strength from a wire is inversely proportional to the distance from the wire axis, so ensuring a close proximity between the control wire and GNR edge is crucial. The relatively significant discrepancies between neighboring $U$ values, exacerbated at large GNR widths, is due to the discretization of the Brillouin zone. A denser sampling of reciprocal space would alleviate these numerical issues, but this is computationally demanding and requires more resources than were available for this study.

\section*{5.1.3 Transistor Design Considerations}

When a wire passes the critical switching current, the conductance of a properly gated GNR changes by $G_0$. When the Fermi energy is within the bandgap of the AFM state, at a source-drain bias of 1 V, the current of single GNR transistor changes from zero to $\sim 150 \, \mu A$ when sufficiently high fields are applied. As seen in figure 5.3b, in the 35 nm ribbon, the critical currents for a single CNT, a distance of 1 nm away from either side of the GNR, are on the order of 1-5 mA, corresponding to edge fields of 0.2 to 1.0 T. As a result, to achieve the critical switching fields, bundles of CNTs must be used in a single transistor, as well as multiple GNRs, which number the same as CNTs in a single bundle. The field due to a bundle is inversely proportional to the distance of the bundle to the GNR, but the bundle area is quadratic in the bundle radius, implying the field can be made arbitrarily strong solely by increasing the bundle size. Since the majority of spin polarization of each GNR occurs at the edge atoms only, the critical current in the bundle can always be achieved in this fashion. Though these simulations include currents flowing through both CNT wires, the magnetic state can be flipped by a single CNT wire, as the magnetic energy of the GNR would still be reduced, albeit at half the rate as if both CNT wires were passing a current.

When using CNT bundles as control wires, it is important to note there should ideally be a 1-to-1 correspondence between the number of GNRs in a logic gate and the number of CNTs in a bundle, as each CNT is unzipped into a GNR in the cascading logic paradigm. However, the design of any circuit involving bundles must be carefully considered such that each GNR is subjected to a sufficiently strong magnetic field. One way to guarantee that each GNR within a single logic gate can be switched by the critical current is to place the GNRs in sequence, adjacent to a very long CNT bundle, ensuring that each GNR experiences the same field strength. In this scenario, care
Figure 5.4: Half adder with all-carbon spin logic. CNTs are partially unzipped to create GNRs with negative magnetoresistance that perform the half adder logic function. CNT input currents A and B are connected to the output of a GNR elsewhere in the circuit, and flow in parallel alongside XOR1 to compute $A \oplus B$, which outputs the sum $S$. Current $A$ crosses over insulated CNTs without making an electrical connection, flowing opposite $B$ to compute $A + B$ with OR1. The outputs of XOR1 and OR1 flow in the same direction alongside XOR2 to compute $(A \oplus B) \oplus (A + B)$. The current through XOR2 is output as carry $C$. The gate is held at a constant voltage to maximize the GNR magnetoresistance.

must be taken to not short-circuit the source and drain leads as they would be in close proximity to one another. It should be stressed that the bundle current determines the magnetic field strength in the GNR. Many different strategies to increase the field strength, or reduce the critical switching current, are possible. One obvious solution is to increase the bundle size, but as more CNTs, and thus more GNRs, are included in a single transistor, the complexity of the device increases significantly. A smaller number of CNTs/GNRs would be needed in a single transistor if the ribbons are very wide, or if the source-drain bias is large.

### 5.2 Cascaded Spintronic Logic Circuits

The basic logic element in all-carbon spin logic is the OR/XOR gate shown in figure 5.1. This gate has four regions of operation:

1) No current flows through either CNT control wire. There is no magnetic field perpendicular to the graphene layer, causing the GNR to operate in its resistive AFM state. Minimal current flows through the GNR.
II) Current flows through exactly one CNT control wire: there is a large magnetic field perpendicular to the graphene layer, causing the GNR to operate in its conductive FM state. A large current flows through the GNR.

III) Current flows through both CNT control wires in parallel directions and of equal magnitude: the magnetic fields through the graphene layer are anti-parallel, resulting in cancellation of the Zeeman interaction energies in the FM state. The GNR therefore operates in its resistive AFM state, and minimal current flows through the GNR.

IV) Current flows through both CNT control wires in anti-parallel directions: the magnetic fields through the graphene layer are parallel, resulting in a doubly large magnetic field. The GNR therefore operates in its conductive FM state, and a large current flows through the GNR.

As all voltages do not change with time, the current directions and magnitudes are predetermined. Therefore, an OR gate is defined by control currents oriented in anti-parallel directions, as demonstrated by the following logic, where each element of the tuple \((A, B)\) represents the \(A\) and \(B\) current direction, respectively: \\{(0, 0) \rightarrow I; (0, -1) \rightarrow II; (1, 0) \rightarrow II; (1, -1) \rightarrow IV\}\.

Similarly, an XOR gate is defined by control currents oriented in parallel directions, as demonstrated by the following logic: \\{(0, 0) \rightarrow I; (0, 1) \rightarrow II; (1, 0) \rightarrow II; (1, 1) \rightarrow III\}\.

These gates form a complete basis set and can be used to perform any cascaded logic function, such as the half adder demonstrated in figure 5.4. This circuit uses two XOR gates and one OR gate to perform the conventional logic function, shown in figure C.16 of the Appendix. This all-carbon spin logic half adder is shown with traditional symbols in figure C.17 in the Appendix, to compute the logic \(S = A \oplus B\) and \(C = A \cdot B\). Metallic CNTs are used to connect the GNR transistors, with electrical connections between overlapping CNTs [47, 102–104] controlled by selective placement of insulation. Covalent graphene-CNT contacts of the type described by Zhu et al. can be used to form vertical wiring structures for large-scale integration[105]. This allows for connections to the source and drain in addition to input and output signals from the user.

This cascaded all-carbon spin logic family thus performs with three GNRs a function that requires 20 transistors with traditional CMOS. In addition, specialized functions that rely heavily on XOR gates, such as parity generators, can utilize as few as one-tenth the devices required in
Figure 5.5: All-carbon spin logic parity gate, used in error detection and correction, computes $P = (A \oplus B) \oplus (C \oplus D) = A \oplus B \oplus C \oplus D$. Thus, when there is an odd number of ‘1’ inputs, the output is ‘1’; the output is ‘0’ if there are an even number of ‘1’ inputs.

CMOS (figure 5.5).
Symbol Definitions and Numerical Constants

A.1 Numerical Constants

<table>
<thead>
<tr>
<th>Material</th>
<th>$\epsilon_r$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vacuum</td>
<td>1.0</td>
</tr>
<tr>
<td>Si</td>
<td>11.8</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>11.8</td>
</tr>
<tr>
<td>SiN</td>
<td>3.9</td>
</tr>
<tr>
<td>Graphene</td>
<td>6.0 [106]</td>
</tr>
<tr>
<td>Water</td>
<td>78.0</td>
</tr>
</tbody>
</table>

Table A.1: Relative permittivities (dielectric constants) of dielectric materials
<table>
<thead>
<tr>
<th>Name</th>
<th>Symbol</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electron Charge</td>
<td>$e$</td>
<td>$1.602 \times 10^{-19}$ C</td>
</tr>
<tr>
<td>Boltzmann’s Constant</td>
<td>$k_B$</td>
<td>$1.38 \times 10^{-19}$ JK$^{-1}$</td>
</tr>
<tr>
<td>Planck’s Constant</td>
<td>$h$</td>
<td>$6.626 \times 10^{-34}$ Js</td>
</tr>
<tr>
<td>Planck’s Constant</td>
<td>$\hbar \equiv \frac{h}{2\pi}$</td>
<td>$1.054 \times 10^{-34}$ Js</td>
</tr>
<tr>
<td>C-C Bond Length</td>
<td>$a$</td>
<td>1.42 Å</td>
</tr>
<tr>
<td>Fermi Velocity</td>
<td>$v_F$</td>
<td>$8.74 \times 10^5$ ms$^{-1}$</td>
</tr>
</tbody>
</table>

Table A.2: Commonly used symbols and constants.
A.2 Tight-Binding Parameters

<table>
<thead>
<tr>
<th>Matrix Element</th>
<th>Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$t_1$</td>
<td>2.7</td>
</tr>
<tr>
<td>$t_2$</td>
<td>0.2</td>
</tr>
<tr>
<td>$t_3$</td>
<td>0.18</td>
</tr>
</tbody>
</table>

Table A.3: Third Nearest Neighbor Basis Overlap Matrix Elements
<table>
<thead>
<tr>
<th>Matrix Element</th>
<th>Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_p(C)$</td>
<td>1.2057</td>
</tr>
<tr>
<td>$E_d(C)$</td>
<td>24.1657</td>
</tr>
<tr>
<td>$V_{pp\pi}(C-C)$</td>
<td>-3.26</td>
</tr>
<tr>
<td>$V_{pd\pi}(C-C)$</td>
<td>-2.4</td>
</tr>
<tr>
<td>$V_{dd\pi}(C-C)$</td>
<td>-3.6</td>
</tr>
<tr>
<td>$V_{dd\delta}(C-C)$</td>
<td>-7.4</td>
</tr>
<tr>
<td>$E_p(H)$</td>
<td>13.0402</td>
</tr>
<tr>
<td>$E_d(H)$</td>
<td>20.9020</td>
</tr>
<tr>
<td>$V_{pp\pi}(C-H)$</td>
<td>-0.61754</td>
</tr>
<tr>
<td>$V_{pd\pi}(C-H)$</td>
<td>3.4117</td>
</tr>
<tr>
<td>$V_{dd\pi}(C-H)$</td>
<td>10.4466</td>
</tr>
<tr>
<td>$V_{dd\delta}(C-H)$</td>
<td>-13.9634</td>
</tr>
</tbody>
</table>

Table A.4: Expanded Nearest Neighbor Basis Overlap Matrix Elements (Atomic)
<table>
<thead>
<tr>
<th>$\mu/\nu$</th>
<th>$p_z$</th>
<th>$d_{xz}$</th>
<th>$d_{yz}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$p_z$</td>
<td>$V_{pp\pi}$</td>
<td>$n_x V_{pp\pi}$</td>
<td>$n_y V_{pd\pi}$</td>
</tr>
<tr>
<td>$d_{xz}$</td>
<td>$-n_x V_{pd\pi}$</td>
<td>$n_x^2 V_{dd\pi} + n_y^2 V_{dd\delta}$</td>
<td>$n_x n_y (V_{dd\pi} - V_{dd\delta})$</td>
</tr>
<tr>
<td>$d_{yz}$</td>
<td>$-n_y V_{pd\pi}$</td>
<td>$n_x n_y (V_{dd\pi} - V_{dd\delta})$</td>
<td>$n_y^2 V_{dd\pi} + n_x^2 V_{dd\delta}$</td>
</tr>
</tbody>
</table>

Table A.5: Third Nearest Neighbor Basis Overlap Matrix Elements (Hybridized)
B

Numerical Methods

B.1 Iterative Hubbard Mean Field Method

In order to calculate the electronic properties of zigzag nanoribbons using the Hubbard interaction eqn. 2.21, the on-site occupation must be determined. To do so, we iteratively solve the secular equation,

\[
\langle \hat{n}_{i\sigma}^{t+1} \rangle = \sum_j f_F(D_j)|\epsilon_{ij}|^2
\]  

(B.1)

In all of our calculations, we assume that the temperature is zero, so the sum is over the lowest \(N/2\) states, accounting for spin. The procedure is repeated until the error in occupation \(\epsilon = ||\langle n^{t+1} - n^t \rangle||_\infty\) between iterations is less than \(5 \times 10^{-7}\).

At nonzero temperatures, the Fermi energy \(E_F\) needs to be calculated at each iteration, which can become quite a complex task. The correct solution is to normalize the occupation with the transformation \(\hat{n} \rightarrow \hat{n} - \frac{1}{2}\), yielding a new interaction Hamiltonian,

\[
\hat{V}_{\text{e-e}} = U \sum_i \hat{n}_{i\uparrow}(\langle \hat{n}_{i\downarrow} \rangle - \frac{1}{2}) + \hat{n}_{i\downarrow}(\langle \hat{n}_{i\uparrow} \rangle - \frac{1}{2})
\]  

(B.2)

Though the Fermi energy does not need to be calculated for each iteration, the correct constant factors should be added to yield the correct expressions for the energies.

The secular eqn. 2.17 was solved in C++ using Elemental (ver 0.84) linear algebra libraries
B.2 Renormalization-Decimation Algorithm for the Lead Surface Green’s Function

To calculate the surface Green’s function \( g \) for a semi-infinite nanoribbon, we follow the technique described by Dietl [110], initially described by Lopez-Sancho et al. [111].

Consider a semi-infinite graphene nanoribbon, translationally invariant beyond the surface. The transfer matrix \( H \) is in block-tridiagonal form, and each block is identical. Then, the Green’s function can be written,

\[
g_\alpha = [(E + i \eta) I - H_\alpha]^{-1}
\]

where each block represents the interaction between identical unit cells. Written in another form, eqn. B.3 becomes,

\[
\begin{bmatrix}
d & -A & 0 & 0 & \ldots \\
-B & D & -A & 0 & \ldots \\
0 & -B & D & -A & \ldots \\
0 & 0 & -B & D & \ddots \\
\vdots & \vdots & \vdots & \ddots & \ddots \\
\end{bmatrix}
= I
\]

The first column of eqn. B.4 yields the following set of equations,

\[
dg_{11} = 1 + Ag_{21},
\]

\[
Dg_{n1} = Bg_{n-1,1} + Ag_{n+1,1} \quad \forall n \geq 2
\]
Eqn. B.5 says that the Green’s function between the surface and a cell \( n \) is expressed in terms of the interactions of the adjacent cells. Then, for odd \( n \), it can be rewritten in terms of interactions two cells away,

\[
(d - AD^{-1}B)g_{11} = 1 + (AD^{-1}A)g_{31},
\]

\[
(D - AD^{-1}B - BD^{-1}A)g_{n1} = (BD^{-1}B)g_{n-2,1} + (AD^{-1}A)g_{n+2,1}
\]  

This procedure can be iterated repeatedly, where in each step of the iteration, we renormalize eqn. B.5,

\[
d' = d - AD^{-1}B
\]

\[
D' = D - AD^{-1}B - BD^{-1}A
\]

\[
A' = AD^{-1}A
\]

\[
B' = BD^{-1}B
\]

\[
g'_{n1} = g_{2n-1,1}
\]

After \( N \) iterations, the first line of the renormalized eqn. B.5 reads,

\[
d_N g_{11} = 1 + A_N g_{2N+1,1}
\]

describing the interaction the surface and a cell \( 2^N \) cells away, which is negligibly small. Then, we can directly obtain the surface Green’s function, \( g_{11} \approx d_N^{-1} \).
C

Supplementary Figures and Results

C.1 Conductance Variations due to External Charges

Figure C.1 shows the conductance variation of placing an eighth of an electron test charge in the west and south positions of the 2 nm nanopore located at point P (figure C.1 inset). As mentioned in the main text, the variations follow virtually the same trend as for the full electron test charge, except for a scaling by factor $\frac{1}{8}$, as expected due to the linear scaling of the potential with test charge magnitude.

Figure C.2 shows the conductance variation of placing a full electron test charge in the west and south positions of the 2 nm nanopore located at point Q (figure C.2 inset) of each of the four edge geometries. Similar to the case with the pore at P, the variations are strongly dependent on the position of the charge within the nanopore as well as the Fermi level. The magnitudes of the conductance variations in the 5-GNR (figure C.2a) and 8-QPC (figure C.2c) geometries are larger than those of the same geometries with the pore at point P. Here, for the 5-GNR, the largest variations are almost 1.7 $\mu$S for a charge placed in the south position of the pore in the 5-GNR, and are almost 1.3 $\mu$S for a charge placed in the south position of the 8-QPC pore. When the charge is placed in the west position of the pore, on the other hand, the conductance variations are much smaller, being .25 $\mu$S and .2 $\mu$S for the 5-GNR and 8-QPC, respectively. This once again demonstrates the large sensitivity of the conductance to the angular position of the charge within
Figure C.1: Conductance variations of placing an eighth of an electron test charge in the south and west positions of a 2 nm nanopore located at point P (inset) in a) 5-GNR, b) 15-GNR, c) 8-QPC, and d) 23-QPC. Taken from ref [3].
Figure C.2: Conductance variations of placing a full electron test charge in the south and west positions of a 2 nm nanopore located at point Q (inset) in a) 5-GNR, b) 15-GNR, c) 8-QPC, and d) 23-QPC. Taken from ref [3].

For the wider 15-GNR (figure C.2b) and 23-QPC (figure C.2d) geometries, the conductance variations are similar in magnitude for the geometries with the pore at point P. For the 15-GNR, the maximum conductance variations are .45 μS and .18 μS for a test charge placed in the west and south positions of the pore, respectively. For the 23-QPC, the largest variations are .5 μS and .45 μS for a test charge placed in the west and south positions in the pore, respectively. In all four cases, the conductance variations do not follow a strictly increasing relationship with Fermi energy, displaying many regions of negative differential resistance, sometimes of large magnitude. For example, as seen in figure C.2b, the conductance variation drops by .8 μS, a factor of over 200%, when the Fermi energy is changed from .15 eV to .25 eV. As a result, the Fermi energy plays a strong role in determining the sensitivity of these devices to external electric potentials. Figure
Figure C.3: Conductance variations of placing an eighth of an electron test charge in the south and west positions of a 2 nm nanopore located at point Q (inset) in a) 5-GNR, b) 15-GNR, c) 8-QPC, and d) 23-QPC. Taken from ref [3].

C.3 shows the conductance variations for an eighth of an electron test charge placed in a 2 nm pore at point Q (figure C.3 inset) for all four geometries. Similarly to the other case, the charge variations are almost identical to the full electron case, scaled by a factor $\frac{1}{8}$, as expected.

C.2 Additional Figures
Figure C.4: Illustration depicting the precise lattice configuration used to simulate the a) 5-GNR and b) 8-QPC nanoribbons with a 2.4 nm diameter nanopore. Taken from ref [3].

Figure C.5: Cross-sectional schematic diagram through the central axis of the nanopore of the multilayer device illustrated in figure 4.1 showing source ($V_S$) and drain ($V_D$) contacts as well as the back gate ($V_G$). Taken from ref [3].
Figure C.6: Cross-sectional schematic diagram through the central axis of the nanopore of the multilayer device illustrated in figure 4.15 showing source ($V_S$), drain ($V_D$), and control ($V_{C1}$ and $V_{C2}$) contacts, as well as a back gate ($V_G$). Taken from ref [3].

Figure C.7: Cross-sectional schematic diagram through the central axis of the nanopore of the multilayer device illustrated in figure 4.15 showing source ($V_S$), drain ($V_D$), and control ($V_{C1}$ and $V_{C2}$) contacts, as well as a back gate ($V_G$). Taken from ref [3].
Figure C.8: Molecular extension of poly(A-T)$_{15}$ DNA over the course of a 60-ns SMD simulation performed at a constant pulling speed of 1 Å/ns. Taken from ref [4].
Figure C.9: Force-extension curves for poly(G-C)$_{15}$ DNA. Shown are the force-extension curves that resulted from five independent SMD simulations, Sim 1-5, performed at a pulling speed of 1 Å/ns. The force-extension curve begins with a region corresponding to the elastic extension of B-DNA followed by a B-DNA to zip-DNA transition plateau. In the region beyond the plateau the zip-DNA undergoes elastic extension, which is characterized by a sharp linear increase in force. The inset shows the zip-DNA conformation at the end of the transition plateau. Taken from ref [4].
Figure C.10: Evolution of the angle between base pairs P-P’ and Q-Q’ (see figure C.9) for five independent SMD simulations, Sim 1-5, performed on poly(G-C)$_{15}$ DNA; the angle changes from -180° to 0° as the DNA segment between P-P’ and Q-Q’ transitions from helical to zipper form. Taken from ref [4].
Figure C.11: Snapshots of the electrostatic potential profile of B-DNA in the graphene membrane at 1 M KCl concentration. The electrostatic potential profiles (a-i) correspond to translocation of the DNA segment, comprising of base-pairs between P-P’ and Q-Q’, through the nanopore. The B-DNA, due to the helical DNA conformation, rotates by 180° in the plane of the graphene membrane. Along with the DNA rotates the electrical field inside the graphene nanopore, which induces oscillations in the transverse electronic conductance. Taken from ref [4].
Figure C.12: Snapshots of the electrostatic potential profile of zip-DNA in the graphene membrane at 1 M KCl concentration. The electrostatic potential profiles (a-i) correspond to translocation of the DNA segment, comprising of base-pairs between P-P' and Q-Q', through the nanopore. The zip-DNA does not rotate in the plane of the graphene membrane leading to a constant transverse electronic conductance. Taken from ref [4].
Figure C.13: Graphene lattices with pore diameter = 2.4 nm, employed in the calculation of transverse electronic conductance: (a) 5 nm-wide armchair edge nanoribbon (b) 8 nm-wide QPC edge nanoribbon. Taken from ref [4].
Figure C.14: Snapshots of the electrostatic potential profile of B-DNA in the graphene membrane at 0.1 M KCl concentration. The electrostatic potential profiles (a-i) correspond to translocation of the DNA segment, comprising of base-pairs between P-P' and Q-Q', through the nanopore. Due to reduced screening the electrostatic potential profile in case of 0.1 M KCl has a slower spatial decay than in case of 1 M KCl (see figure C.11). Taken from ref [4].
Figure C.15: Radial distribution of electrostatic potential at the nanopore edge under KCl molar concentrations of 1 M and 0.1 M. The potentials correspond to a DNA conformation, where the base pair P-P’ is inside the nanopore. At low molarity (0.1 M) the potential in the vicinity of the pore is much larger (in magnitude) than in case of high molarity (1 M KCl) due to reduced screening. Taken from ref [4].
Figure C.16: Half adder truth table. The one-bit half adder computes binary addition on two inputs, $A$ and $B$, to compute their sum $S$ and an overflow bit $C$ that is carried to the next digital bit. For example, the binary computation of $1 + 0$ is a sum $S$ of ‘1’ and a carry $C$ of ‘0’. Similarly, $1 + 1$ results in a sum $S$ of ‘0’ and a carry $C$ of ‘1’ used for adding the next bit.

<table>
<thead>
<tr>
<th>A</th>
<th>B</th>
<th>S</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>0</td>
<td>1</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>1</td>
<td>0</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>0</td>
<td>1</td>
</tr>
</tbody>
</table>

Figure C.17: All-carbon spin logic half adder symbolic implementation. Shown here with conventional symbols, the all-carbon spin logic one-bit half adder uses inputs $A$ and $B$ are input to XOR1 to compute $S = A \oplus B$, and to OR1 to compute $A + B$. XOR2 performs the XOR function on $A \oplus B$ and $A + B$ to calculate $C = (A \oplus B) \oplus (A + B)$, which is equivalent to $C = A \cdot B$. 

101
References


[18] M.Y. Han, B. Özyilmaz, Y. Zhang, P. Kim, Physical review letters 98(20), 206805 (2007)


[34] M. Puster, J.A. Rodríguez-Manzo, A. Balan, M. Drndić, ACS Nano 7(12), 11283 (2013)


[110] P. Dietl, Karlsruhe Institute of Technology (2009)