ELECTRONIC TRANSPORT IN FUNCTIONALIZED GRAPHENE:
FROM STRONG CHEMISORPTION TO WEAKLY BONDED ADSORBATES

A Dissertation in
Physics
by
Sangzi Liang

© 2016 Sangzi Liang

Submitted in Partial Fulfillment
of the Requirements
for the Degree of

Doctor of Philosophy

May 2016
The dissertation of Sangzi Liang was reviewed and approved* by the following:

Jorge O. Sofo  
Professor of Physics  
Professor of Materials Science and Engineering  
Dissertation Advisor, Chair of Committee

Vincent H. Crespi  
Distinguished Professor of Physics, Materials Science and Engineering, and Chemistry

Jainendra K. Jain  
Evan Pugh University Professor and Erwin W Müller Professor of Physics

Srinivas Tadigadapa  
Professor of Electrical Engineering

Nitin Samarth  
Professor of Physics  
George A. and Margaret M. Downsbrough Department Head of Physics

*Signatures are on file in the Graduate School
Abstract

Graphene is a new two-dimensional material that has many interesting properties due to its low energy excitations which behave as Dirac fermions. To unlock its application potential, it is necessary to study the electronic transport in graphene samples that are disordered or functionalized. This is partly due to the fact that pristine graphene is costly to prepare, but some application aspects also depend on the controlled functionalization of graphene and the resulting change in the electric conductivity, such as graphene gas sensors. This dissertation discusses four topics related to functionalized graphene systems and their electronic transport behavior.

The localization properties of graphene adatoms is studied in chapter 2. Green’s function perturbation theory is applied on a general tight-binding model of graphene with adatoms and the energy and the decay of the wavefunction of the impurity state is calculated both analytically and numerically. It shows that these states are localized with power-laws rather than the traditional exponential localization in the band gaps of semiconductors. The semi-empirical variable range hopping theory of conduction is revisited in view of this result and a new power-law variable range hopping is proposed for functionalized graphene, which fits available experimental data well.

The data of graphene and carbon nanotube gas sensing experiments is analyzed in chapter 3 with the kinetic Langmuir model adapted to include adsorption sites from which the molecule does not desorb. The model reproduces the available experimental data. Its fitting parameters provide information on the microscopic phenomena governing adsorption, and variation of these parameters allows the optimization of the sensitivity, detection limit, and time response of the sensors. The result reveals an optimal operating temperature before
thermal desorption becomes dominant at high temperature, the potential improvement of selectivity by tuning the gate voltage in a field effect transistor configuration, and quantifies the benefits of reducing the density of defects in the sensing materials.

In chapter 4 we explore an alternative mechanism for the conductance change in graphene gas sensing. Charged functional groups and dipolar molecules on the surface of graphene may counteract the effect of charged impurities on the substrate. This leads to significant changes in the transport behavior. A model for the conductivity is established using the random phase approximation dielectric function of graphene and the first-order Born approximation for scattering. The model predicts optimal magnitudes for the charge and dipole moment which maximally screen a given charged impurity. The dipole screening is shown to be generally weaker than the charge screening although the former becomes more effective with higher gate voltage away from the charge neutrality point.

In chapter 5 we explore another possible explanation for this phenomena assuming that NO chemisorbs to vacancies and eventually dissociates. We found that adsorption of NO in graphene vacancies is favorable by 5.3 eV. In order to evaluate the conductivity due to these impurities, we obtain a minimum tight binding model with a Wannier transformation of the Kohn-Sham orbitals obtained by DFT. The conductivity is calculated using the Kubo-Greenwood formula and the kernel polynomial method. The results show that the conductivity stays the same when NO adsorbs into a vacancy, but it increases when the oxygen atom moves away from the nitrogen atom, either leaving or moving to other parts of the surface, with the former giving a larger increase in conductivity.
# Table of Contents

List of Figures ........................................................................................................................................ vii  
List of Tables ........................................................................................................................................ xi  
Acknowledgements ................................................................................................................................. xii  

Chapter 1 Introduction .............................................................................................................................. 1  
  1.1 Graphene ........................................................................................................................................ 1  
  1.2 Functionalized/Disordered Graphene ............................................................................................. 3  
  1.3 Theories of Graphene’s Electronic Structure and Transport ...................................................... 5  
  1.3.1 Tight-Binding Description of Electronic Structure of Graphene ........................................... 5  
  1.3.2 Computational Methods of Conductivity of Graphene .............................................................. 8  
  1.4 Layout of Dissertation .................................................................................................................... 9  

Chapter 2 Resonant Impurities States and Variable Range Hopping Conduction of Graphene .......... 11  
  2.1 Tight-Binding Perturbation Theory with Green’s Functions ...................................................... 11  
  2.2 Impurity States of Graphene from Adatoms ................................................................................ 13  
       2.2.1 Theory ................................................................................................................................... 13  
       2.2.2 Computation Implementation ............................................................................................... 18  
       2.2.3 Results ................................................................................................................................ 20  
  2.3 Variable Range Hopping Theory ................................................................................................. 23  
  2.4 Power-Law Variable Range Hopping of Graphene ..................................................................... 25  

Chapter 3 Analysis of Adsorption-Desorption Kinetics in Graphene Gas Sensing Experiments .... 29  
  3.1 Graphene Gas Sensing Experiments ............................................................................................. 29  
  3.2 Kinetic Langmuir Model of Adsorption ......................................................................................... 33  
  3.3 Normal and Poison Sites and Adsorption-desorption Kinetics ................................................ 34  
  3.4 Improving the sensors ................................................................................................................... 38  

Chapter 4 Modelling the Screening of Graphene Substrate Charged Impurities ............................. 42  
  4.1 Inconsistencies of the Charge Transfer Explanation .................................................................. 42
4.2 Screening of the Charged Impurities in Graphene Substrate ................................................. 44
  4.2.1 The Dielectric Function of Graphene ................................................................................ 45
  4.2.2 Graphene Screening of a Single Static Point Charge ......................................................... 46
  4.2.3 Screening of Substrate Charged Impurities by Adsorbates ............................................. 49
4.3 Impact of the Screening on the Conductivity .......................................................................... 51
  4.3.1 First-order Born Approximation and the Conductivity ..................................................... 51
  4.3.2 Results and Discussions .................................................................................................... 53
4.4 Conclusions ........................................................................................................................... 59

Chapter 5 Computing the Conductivity of Disordered Graphene with Kernel Polynomial Method ......................................................................................................................... 61
  5.1 Wannier Functions from Density Functional Theory ............................................................ 61
  5.2 Kernel Polynomial Method .................................................................................................. 64
  5.3 NO and Carbon Vacancies of Graphene ............................................................................... 67
    5.3.1 NO Chemisorption on Graphene Vacancies ................................................................. 70
    5.3.2 Oxygen Dissociation ..................................................................................................... 75
    5.3.3 Conclusions .................................................................................................................. 77

Chapter 6 Conclusions and Future Projects ..................................................................................... 78

Bibliography .................................................................................................................................. 80
List of Figures

Figure 1.1 Graphene and a unit cell of graphene with lattice vectors \( \mathbf{a}_i \). Sublattices are labeled A and B. \( \delta_i \) are vectors from a carbon in A sublattice to its three neighbors ............................................2

Figure 1.2 \( \pi \) bands of graphene as evaluated from their analytical expressions. The Fermi energy is at 0 eV. Note the linear dispersion relation near the Fermi energy .............................................6

Figure 1.3 The density of states of the Graphene \( \pi \) band. The hopping parameter \( t \) is 2.7 eV. The density of states is normalized to 2..................................................................................................8

Figure 2.1 Comparison between amplitude of the resonant state obtained from direct diagonalization of the Hamiltonian and Green’s functions. The latter is used to approximate the former in this study.............................................................................................................15

Figure 2.2 Carbon atoms in graphene can be labeled in this way to simplify the expression for Green’s functions. See text for details. It is essentially a scaled normal coordinate system. .......16

Figure 2.3 A labeling of carbon atoms in graphene which allows the Manhattan distance to be quickly calculated (\(|i| + |j|\)). The shaded area is the region where the Green’s functions need to be calculated. The others can be obtained using symmetry .................................................................19

Figure 2.4 Amplitude of the resonance state at resonance energy \( \epsilon_r = \frac{t}{6} \). The left panel shows the amplitudes represented by the radii of circles on the graphene honeycomb lattice. The amplitude on the A sublattice has circles drawn with the same color in the lattice, whereas the amplitude of the B sublattice has a line showing the direction it is taken in the lattice. The center dot (blue) is where the adatom is attached. \( a \) is the nearest neighbor carbon-carbon distance. [Copyright (2012) by The American Physics Society] .................................................................................20

Figure 2.5 Amplitude of the resonance state at resonance energy \( \epsilon_r = \frac{t}{300} \). The left panel shows the amplitudes represented by the radii of circles on the graphene honeycomb lattice. The amplitude of the B sublattice has a line showing the direction it is taken in the lattice, whereas the A sublattice has vanishing amplitudes. The center dot (blue) is where the adatom is attached. \( a \) is the nearest neighbor carbon-carbon distance. [Copyright (2012) by The American Physics Society] .................................................................................21

Figure 2.6 The characteristic decay exponents of the two sublattice sites vs. the resonance energy. For the A sites, the exponent is taken from the sites that forms a triangular lattice with the impurity site. For the B sites, the exponent is taken from sites in the armchair direction. [Copyright (2012) by The American Physics Society] .................................................................................23

Figure 2.7 Experimental data of sample resistance vs. temperature of chemically decorated graphene samples plotted in a log-log scale. The circles and diamonds are data from (Elias et al,
2009), and (Matis et al, 2012), respectively, for samples of hydrogen adatoms on graphene. The squares are data from (Hong et al, 2011) for samples of fluorine adatoms on graphene. From top to bottom, the 4 sets of fluorine data and the 2 sets of hydrogen data are taken with increased gate voltage away from the charge neutrality point.

**Figure 3.1** Schematic illustration of the setup of the graphene gas sensing experiment.

**Figure 3.2** Conductance changes during the detection cycles on the single-wall nanotube device. The circles are the experimentally measured data and the solid lines with the same color are their corresponding fits. The concentration of NO during the experiments is (a) 10 ppt for all 5 cycles (b) 10, 20, 50, 100, and 200 ppt. See the text for experimental details.

**Figure 3.3** Conductance changes during the detection cycles on the graphene device. The circles are the experimentally measured data and the solid lines with the same color are their corresponding fits. The concentration of NO during the experiments is (a) 10 ppt for all 5 cycles (b) 10, 20, 50, 100, and 200 ppt. See the text for experimental details.

**Figure 3.4** Illustration of the definitions of sensor sensitivity and detection limit used in this study. The sensitivity is defined as the derivative of the coverage vs. concentration curve. The detection limit is defined as the concentration that creates a signal that is three times as large as the noise.

**Figure 4.1** The polarizability of graphene obtained using the random phase approximation.

**Figure 4.2** The electric potential created by the charged impurity and the screening charge in graphene in the space on the opposite side of the graphene sheet. As shown in the inset, z is the coordinate for the direction perpendicular to the graphene plane. The screening reduces the potential but preserves the direction of the electric field. The screening is more effective when there is a higher carrier density in graphene. The electric field of each case is labeled at a typical distance of the adsorbates. [Copyright (2014) by The American Physical Society]

**Figure 4.3** Induced charge density on a surface calculated considering 4 different types of screening behaviors. The external field is created by a point charge which is 0.3 Å away from the surface.

**Figure 4.4** (a) Schematic illustration of the proposed structures: bare charge impurity, Cl[Graphene]CFG structure (i = Zδ), and Cl[Graphene]Dipole structure (i = Zp), from left to right. (b) The induced charge density in graphene of the same configuration before and after adsorption of the charged functional group and the dipolar molecule. The potential of the charged impurity is partially canceled by the adsorbates and the scattering is reduced. [Copyright (2014) by The American Physical Society]

**Figure 4.5** Ratio of the conductivity of graphene before and after all charged impurities are covered by adsorption of dipolar molecules (black) or charged functional groups (red) vs the dipole moment (bottom axis) or the charge (top axis). The dipole moment of a few common
molecules are marked to show the theoretical prediction of their effect on the conductivity in this parameter regime. The dotted line separates increased conductivity (larger than one) and decreased conductivity (smaller than one). The parameters used in the calculations are: for the dipole screening, \( k_F = 0.05 \, \text{Å}^{-1} \), \( Z = 0.01 \); for the charge screening, \( k_F = 0.01 \, \text{Å}^{-1} \), \( Z = 0.5 \).

[Copyright (2014) American Physical Society]

**Figure 4.6** Calculated results of the carrier density dependence of the conductivity before and after all charge impurities are saturated with adsorbates and transformed into CI|Graphene|Adsorbate scattering centers. The black line is the base conductivity before adsorption, parameters used are \( Z = 0.1 \), \( n_{\text{imp}} Z = 2 \times 10^{14} \, \text{cm}^{-2} \). The red, blue, and brown lines are conductivities after adsorption of charged functional groups (\( \delta = 0.15 \)), weakly dipolar molecules (\( p = 0.5 \, \text{Å} \)), and strongly dipolar molecules (\( p = 2 \, \text{Å} \)), respectively. [Copyright (2014) by The American Physical Society]

**Figure 4.7** The coverage dependent conductivity normalized by the conductivity before adsorption. The dotted line shows the coverage of adsorbates that saturates the charged impurities. The parameters used are \( k_F = 0.05 \, \text{Å}^{-1} \), \( Z = 0.1 \), \( \delta = 0.15 \), and \( p = 0.2 \, \text{Å} \). [Copyright (2014) by The American Physical Society]

**Figure 5.1** Steps required to use the interface between Quantum Espresso and wannier90 to extract tight-binding model from DFT calculations. Each block has a name for the step and the Linux command that needs to be run. The input files are named with the prefix...

**Figure 5.2** Schematic illustration of the three steps of the calculation of the Kubo-Greenwood formula using parallelism. It assumes that 4096 Chebyshev polynomials are used..

**Figure 5.3** The top panel shows the relaxed structure of pristine graphene and the 4 types of defects that are studied here. The computed values of the labeled distances can be found in Table 1. The isosurfaces of the Wannier functions that are important for the electronic bands near the Fermi level are shown in the bottom panel along with labels indicating the name of each Wannier function and which defect it originates from.

**Figure 5.4** The distance between the oxygen and the nitrogen atoms (\( d_{\text{NO}} \), red), the distance between the nitrogen atom and the graphene plane (\( d_{\text{Nz}} \), red), and the total energy (\( E_{\text{DFT}} \), black) as a function of the displacement of the oxygen atom away from its relaxed position in the adsorption of NO on a carbon vacancy site of graphene as obtained through DFT calculations. The displacement is in the direction that is perpendicular to the graphene plane and the systems are relaxed after the oxygen atom and 4 carbon atoms relatively far away from the defect are fixed in position.

**Figure 5.5** The band structures of 2 by 2 graphene unit cells containing one NO substitution obtained from DFT calculations (black, solid), tight-binding Hamiltonian containing hopping terms between all pairs of Wannier functions (red, dotted), and tight-binding Hamiltonian containing hopping terms between nearest neighbors (blue, solid).
**Figure 5.6** Density of states obtained from kernel polynomial calculations for the 4 types of defects studied in this study. The density of states of pristine graphene (black, dotted) is included in each panel for comparison. The panels show the density of states of graphene containing (a) NO substitutions \( E_F = 0.069 \) eV, (b) carbon vacancies \( E_F = 0 \) eV, (c) N substitutions \( E_F = 0.436 \) eV, and (d) N substitutions and bridging O atoms \( E_F = 0.512 \) eV.

**Figure 5.7** The calculated conductivities of pristine graphene and graphene containing 1% defects. (a) The conductivities zoomed in onto the experimentally accessible energy range. The energy is relative to the carbon site energy in the tight-binding calculation. (b) Same as above except the energy is relative to the Fermi energy of each system. (c) The conductivities in the full energy range of the tight-binding calculation.
List of Tables

Table 2.1 The fitting details of available data sets with both the conventional VRH and the power law VRH. \( V_g \) is the gate voltage relative to the charge neutrality point. \( n \) is the charge density calculated with the gate voltage and sample specifics. \( T_0 \) is the characteristic temperature in the conventional VRH and \( \Omega \) is the squared correlation coefficient for the fits on the linearized data. [Copyright (2012) by The American Physics Society] ........................................................................................................27

Table 3.1 The fitting parameters of available data sets .........................................................................................................................38

Table 4.1 Ionization potential (IA) and electron affinities (EA) of NO, NO\(_2\), and NH\(_3\). The work function of graphene is also included which serves as both its IP and EA. ..................................................44

Table 5.1 Notable distances in the defect systems calculated with DFT, and tight-binding parameters obtained through band fitting. ........................................................................................................71
Acknowledgements

I would like to acknowledge my thesis advisor, Dr. Jorge O. Sofo, for his help and guidance throughout the course of my PhD. He has always been encouraging and supportive and I am deeply grateful for the opportunity to learn from him. I would like to extend a special thanks to Dr. Gugang Chen and the Honda Research Institute, USA for supporting me during my last two years of study and for the fruitful collaboration. I am also thankful to my committee members Dr. Crespi, Dr. Jain and Dr. Tadigadapa for their time, suggestions and help.

I would like to thank the members of my research group, Alejandro, Ivan, Nitin, Piali, and Mark, for many useful discussions. I am also grateful to my friends, JD, Renzhong, and Gang, for always being there for me. It is difficult to imagine these wonderful years without them.

Finally, I would like to express my gratitude to my wife and my parents for their love and support.
Chapter 1
Introduction

Graphene is a relatively new material with many interesting properties. In this chapter I will summarize some of the relevant research on graphene and functionalized/defective graphene, and introduce the tight-binding modeling of graphene’s electronic structure by Wallace [1], which is fundamental to all of the later chapters in this dissertation. In the last section, I will briefly discuss the contents of each following chapter and how they are related to each other.

1.1 Graphene

Carbon is the fundamental building block of life and it has many important allotropes due to its flexibility in bonding, including graphite, diamond, fullerene [2], and carbon nanotubes [3]. Graphene has long been known as a single layer of graphite. Its electronic structure has been studied by P. R. Wallace as early as 1947 [1] whose model is still widely used even today. However, as an isolated two-dimensional material, its experimental preparation is only made possible by Novoselov et al. in 2004 [4] by mechanically exfoliating highly oriented pyrolytic graphite. The discovery of each of the newer allotropes of carbon has been groundbreaking for the condensed matter physics community and graphene is no exception. The number of research articles on graphene increased exponentially after 2005 [5] and the Nobel Prize in Physics for 2010 was awarded for the initial experiments on graphene. The research of graphene has given new interest and importance to several other existing or newly synthesized two-dimensional materials in recent years, including bilayer graphene [6], hexagonal boron nitride [7], silicene [8], and
New methods of synthesizing graphene has been developed, such as the chemical vapor deposition (CVD) method [10,11].

Physically, graphene is a two-dimensional arrangement of carbon atoms in honeycomb lattices (Figure 1.1). The bond length between neighboring atoms is 1.42 Å and each unit cell contains two carbon atoms in equivalent positions, separating all the atoms into two sublattices. The carbon atoms bond to each other with sp2-hybridized orbitals, leaving the p$_z$ orbitals with one electron for each atom and the interactions between these p$_z$ orbitals form symmetrical linear bands that are gapless near the Fermi energy which are responsible for the novel properties of graphene. We will discuss this further with tight-binding modelling in section 1.3.

Graphene has exceptional mechanical [12] and optical [13] properties, but it is mostly studied for its interesting behavior in electronic transport. The electron mobility of
the graphene samples are remarkably high, with the Novoselov experiment giving 15,000 cm$^2$V$^{-1}$s$^{-1}$ [4]. The same experiment also confirmed that there is an electron/hole symmetry near the Fermi energy of graphene with the ability to switch the conducting charge carriers by controlling an external gate voltage [4]. The low energy excitations of graphene, which are massless, chiral, Dirac fermions, have rather unconventional behaviors in theory, including chiral tunneling [14] and the so-called Zitterbewegung motion [15]. Graphene nanoribbons have also been prepared and studied which shows different transport behavior for different width and termination [16,17].

1.2 Functionalized/Disordered Graphene

Defects and contaminations are unavoidable in any practical materials and graphene is especially prone to them due to carbon’s flexibility in bonding as well as the 2D nature of graphene. Even the typically used silicon substrate of graphene in experiments has an oxidized layer of silica that is uneven and has dangling bonds which has a net charge and scatters electrons [18,19]. Discovering how the defects and contaminations affect the electronic transport is the first step in understanding the experimental results. Study of graphene functionalization also serves practical purposes. Since graphene does not have a band gap, traditional semiconductor technologies cannot be directly applied to graphene – the field effect transistors made with graphene do not have on/off states that are clearly distinguishable. Applying functional groups to graphene can change the electronic structure of it and reduce graphene to a normal semiconductor. Purposeful and exactly controlled functionalization of graphene has been proposed to be a way to pattern integrated circuits on graphene [20]. Furthermore, the conductance of graphene shifts after the adsorption of certain molecules [21], which allows sensors with extremely low detection limit to be built [22]. The improvement of such sensors also requires theoretical understanding of the
relationship of the adsorbed molecule and the conductivity changed. This point is the motivation of a large part of this dissertation and will be discussed further in chapters 3-5.

There is a great variety of graphene defects and a large amount of research has been conducted to study them [23]. Point defects, such as single carbon vacancies, hydrogen adatoms, and Stone-Wales defects [24], have been shown to create localized states both theoretically [25,26] and experimentally using scanning tunnel microscopy [27]. These states do not completely participate in transport which lowers the conductivity and causes it to plateau near the Fermi energy [28,29]. The resonant point defects have been found to be one of the limiting factors of electron mobility in graphene. Another factor that limits the mobility is charged impurities in the silica substrate of graphene, which are caused by dangling bonds in silica, and models which includes the charged impurities have been able to explain some experimental data very well [18,30]. An experiment which introduces external charged impurities in the form of potassium also shows the expected results from this theory [31]. Exactly which type of defects is more important in limiting the mobility in graphene has been a controversial topic and the current consensus seems to be that it depends on the exact situation of the sample, the substrate, and the experiment. Other than these defects, there can also be one dimensional defects like dislocation-like defects or defects at the edge, which are experimentally observed [32] but with relatively less theoretical study.

Various atomic and molecular species have been used to functionalize graphene. Hydrogenated graphene (graphane) is one of the early examples which was envisioned theoretically [33,34] as a way to create large bandgap semiconductors from graphene. However, despite DFT calculation evidence that graphane has a formation energy larger than any other hydrocarbons with the same hydrogen composition like benzene, hydrogenation of graphene proves difficult and a fully hydrogenated graphene sample has
never been experimentally synthesized, although progresses were made in that
direction [35]. On the other hand, fluorinated graphite has been experimentally realized as
early as 1940 [36] and fluorinated graphite have been exfoliated from it [37]. Plasma fluorine
is also successful in fluorinating graphene [38] which is regarded as a superior method.
Interesting results on fluorinated graphene include experiments which obtained spin half
para-magnetism [39] and optical conductivity computed through large-scale multi-orbital
tight-binding calculations [40]. Other examples of functionalized graphene include graphene
oxide, which can be reduced to pristine graphene [41], graphene with small molecule [21] or
metal-arene compound adsorptions [42].

1.3 Theories of Graphene’s Electronic Structure and Transport

Here I summarize the theoretical tools that are relevant to this dissertation, some of
which will be expanded in later chapters.

1.3.1 Tight-Binding Description of Electronic Structure of Graphene

The sp2 bonding of carbon atoms leaves the p_z orbitals to form bands at the Fermi
energy. The simplest possible model for its electronic structure is a tight-binding model that
takes the p_z orbitals as the basis set. Since there are two atoms in a unit cell and thus two
sublattices A and B (Figure 1.1), the basis set includes two states,

\[ |A\rangle = \frac{1}{\sqrt{N}} \sum_j e^{i\vec{k}\cdot\vec{R}_j} |A, \vec{R}_j\rangle, \]

\[ |B\rangle = \frac{1}{\sqrt{N}} \sum_j e^{i\vec{k}\cdot\vec{R}_j} |B, \vec{R}_j + \delta_1\rangle, \]
where $N$ is the total number of unit cells and $\vec{R}_j$ are the vectors that point to these cells. $\vec{\delta}_i$ ($i = 1, 2, 3$) are the vectors that originate from an A site to its three neighbors. Since the two states are equivalent, both of their site energies can be set to zero and all the other energies will be in reference to the site energy. The hopping energy is only non-zero between nearest neighbors and the tight-binding Hamiltonian can be written as

$$H = -t \sum_{i,j,n.n.} |A_i \vec{R}_i \rangle \langle B, \vec{R}_j + \vec{\delta}_i| + \text{H.c.}$$

with the hopping energy $t = 2.7 \text{ eV}$. The two basis states enable the Hamiltonian to be written into a matrix form

$$H = \begin{pmatrix} 0 & -t(e^{-ik\vec{a}_1} + e^{-ik\vec{a}_2} + 1) \\ -t(e^{ik\vec{a}_1} + e^{ik\vec{a}_2} + 1) & 0 \end{pmatrix}$$

where $\vec{a}_1$ and $\vec{a}_2$ are the lattice vectors, and diagonalizing the Hamiltonian gives the $\pi$-bands of graphene.

**Figure 1.2** $\pi$ bands of graphene as evaluated from their analytical expressions. The Fermi energy is at 0 eV. Note the linear dispersion relation near the Fermi energy.
\[ \epsilon(k) = \pm t \left| e^{-i\vec{k} \vec{a}_1} + e^{-i\vec{k} \vec{a}_2} + 1 \right| = \pm t \sqrt{1 + 4 \cos^2 \left( \frac{\sqrt{3}}{2} k_x a \right) + 4 \cos \left( \frac{\sqrt{3}}{2} k_x a \right) \cos \left( \frac{3}{2} k_y a \right)} \]

The energy bands are plotted in a 3D plot in Figure 1.2. Note that the bands are symmetric about energy \( \epsilon = 0 \), which is the Fermi energy and happens at the K points, corners of a hexagon that is centered at the origin. A Taylor expansion can be done around the K points which obtains a linear dispersion relationship near the Fermi energy

\[ \epsilon(k_F) \approx \hbar v_F k_F \]

where \( v_F = 10^6 \text{ m/s} \) is the Fermi velocity. This linear relationship is special to graphene and the origin of the analogy between the electrons/holes in graphene and Dirac fermions. The density of states from this Hamiltonian can be written as

\[ \rho(\epsilon) = \frac{A}{2\pi} \int_{\text{primitive cell}} d\vec{k} \delta(\epsilon - \epsilon(\vec{k})) \]

which can been analytically integrated [1] and the result is given by

\[ \rho(\epsilon) = \frac{4}{\pi^2 t^2} \frac{|\epsilon|}{ t \sqrt{Z_0}} K \left( \sqrt{\frac{Z_1}{Z_0}} \right) \]

where \( K(z) \) is the complete elliptical integral of the first kind and

\[
Z_0 = \begin{cases} 
(1 + \left|\frac{\epsilon}{t}\right|^2)^2 - \frac{(\epsilon/t)^2 - 1}{4} & |\epsilon| \leq t \\
4 \left|\frac{\epsilon}{t}\right|^2 & t \leq |\epsilon| \leq 3t
\end{cases}
\]

\[
Z_1 = \begin{cases} 
4 \left|\frac{\epsilon}{t}\right|^2 & |\epsilon| \leq t \\
(1 + \left|\frac{\epsilon}{t}\right|^2)^2 - \frac{(\epsilon/t)^2 - 1}{4} & t \leq |\epsilon| \leq 3t
\end{cases}
\]
The density of states is plotted in Figure 1.3, which is also linear near the Fermi energy and it has two Van Hove singularities at $\epsilon = \pm t$.

Defects and functional groups introduce perturbations into the electronic structure of graphene. In chapter 2, I will introduce the Green’s function perturbation method and calculate the amplitude of impurity states as the result of a point defect. In chapter 5, I will discuss a method that extracts a tight-binding model from DFT calculations using Wannier functions, which is simpler and more insightful than first principle calculations. The model can be extended to a large system.

Another relevant theory is the evaluation of graphene’s dielectric function using the random phase approximation [43,44]. This will be discussed further in chapter 4.

1.3.2 Computational Methods of Conductivity of Graphene
Several theories of electronic transport are discussed in this dissertation. Semi-empirical variable range hopping (VRH) theory is a general theory for conduction in materials with disorder. It assumes that there is a temperature and disorder concentration range so that the average distance between defects is much larger than the coherent distance. This causes electronic transport to happen mainly through incoherent “hopping” between localized states and the description is greatly simplified. It has been applied to disordered graphene in several experimental papers [35,45–47] and it will be discussed in chapter 2.

The Boltzmann transport equation or the first-order Born approximation introduces the impurities as scattering centers and the transition rate for each type of disorder is calculated, which leads to the conductivity. It has been used to estimate the effect of substrate charged impurities on the conduction [18,30,48] and my study on how adsorbed molecules can screen the charged impurities follows the same line in chapter 4.

A way to include all impurities in a coherent manner is to evaluate the conductivity using the linear response theory. For non-interacting electrons at zero temperature, the dc-conductivity tensor from linear response theory is known as the Kubo-Greenwood formula [49]

\[
\sigma^{(ab)}(E) = \frac{2\pi\hbar}{A} Tr \left[ j^{(a)} \delta(E - H) j^{(b)} \delta(E - H) \right]
\]

where \( A \) is the area of the sample cell and \( j \) is the current density operator defined through the Heisenberg equation of motion for the polarization operator. The Kubo-Greenwood formula is used in chapter 5 to evaluate the impact of various defects on the conductivity of graphene.

1.4 Layout of Dissertation

The rest of the dissertation are organized as follows. Chapters 2-5 each discusses a published/submitted paper [50–52] that focuses on one research project with the fundamental
methods explained in more detail. In chapter 2, I analyze the localization of impurity states in graphene using the tight-binding model of an adatom-graphene system with Green’s function perturbation methods. This theory does not specify the adatom species and it applies to a wide range of point defects of graphene. The amplitude of the impurity state wave function is determined and the variable range hopping theory is revisited, which shows that the conductivity depends as a power law of the temperature with an exponent related to the localization of the wave function. In chapter 3, I describe a model that connects the microscopic picture of gas adsorption on graphene with the experimental gas sensing data [22,53]. I will use the model to quantify the sensitivity, detection limit, and time response of the sensors and discuss optimal sensor operating conditions. In chapter 4, I will propose an alternative mechanism to graphene’s gas sensing capability and quantify the effect of adsorbed molecules on the charged impurity whose electric field is partially cancelled and the conductivity is changed by the adsorbates. A quantitative estimation of the conductivity change is given based on the random phase approximation (RPA) dielectric function of graphene and the first-order Born approximation. In chapter 5, I study the adsorption of NO into the carbon vacancies of graphene and how this process can affect the overall conductivity of the graphene sample. The adsorption is studied with DFT and I will apply a tight-binding model of the system after NO adsorption through Wannier function calculations and fitting the band structure. Using the kernel polynomial method, the density of states and dc-conductivity as defined by the Kubo-Greenwood formula are calculated for graphene systems that contain NO and derivative defects.

Finally, in chapter 6, I will discuss overall conclusions of this dissertation and propose future directions of research following the lines of works I have done in my graduate study.
Chapter 2
Resonant Impurities States and Variable Range Hopping Conduction of Graphene

Point defects in graphene, such as adatoms, single substitutions, and carbon vacancies, create localized resonant states. In this chapter, I will introduce a general theory that investigates the localization of these states by calculating the amplitude of the wavefunctions with Green’s function perturbation methods. The application of the semi-empirical variable range hopping conduction theory on graphene is examined in view of this result. Section 2.1 and 2.3 will be background introduction of existing theories and section 2.2 and 2.4 are discussions of the applications of these theories to graphene, which are original and have been published in Physical Review Letters [50].

2.1 Tight-Binding Perturbation Theory with Green’s Functions

The time-independent Schrödinger's equation is a homogeneous differential equation

\[(E - H(\vec{r}))\psi(\vec{r}) = 0\]

with certain boundary conditions. If we generalize the parameter E to be a complex number \(z = E + is\), the corresponding Green’s function of this equation satisfies

\[[z - H(\vec{r})]G(\vec{r}, \vec{r}'; z) = \delta(\vec{r} - \vec{r}')\]

with the same boundary conditions. The Hamiltonian possesses a complete set of eigenstates and corresponding eigenvalues. Using the Dirac bra-ket notation, this can be written in an abstract vector space

\[(z - H)G(z) = 1, \quad H|\phi_n\rangle = E_n|\phi_n\rangle, \quad \langle \phi_n|\phi_m\rangle = \delta_{nm}, \quad \sum_n |\phi_n\rangle\langle\phi_n| = 1\]
The Green’s function can be expressed in terms of the eigenfunctions and eigenenergies of the Hamiltonian

\[ G(z) = \frac{1}{z - H} = \sum_n \frac{1}{z - H} |\phi_n\rangle\langle\phi_n| = \sum_n \frac{|\phi_n\rangle\langle\phi_n|}{z - E_n} \]

Writing out the Green’s function for a system often requires diagonalizing the Hamiltonian in the first place. On the other hand, if the Green’s function is known for a system, a lot of information can be extracted from it, such as discreet energy levels and their degeneracy, continuous energy bands and their density of states. A more complete introduction to the Green’s functions can be found in [54].

Defects are introduced in the form of an additive perturbation in the Hamiltonian

\[ H = H_0 + H'. \]

The unperturbed Hamiltonian is assumed to be solvable with the Green’s function given by

\[ G_0(z) = \sum_k \frac{|k\rangle\langle k|}{z - \epsilon(k)} \]

where |k\rangle are the eigenstates and \(\epsilon(k)\) is the band structure. The full Green’s function can be written as, by definition

\[ G(z) = (z - H)^{-1} = [1 - (z - H_0)^{-1}H']^{-1}(z - H_0)^{-1} = [1 - G_0(z)H']^{-1}G_0(z). \]

Expanding the equation into power series, we obtain

\[ G = G_0 + G_0H'G_0 + G_0H'G_0H'G_0 + \cdots \]

which gives the full Green’s function in terms of the known quantities: Green’s function of the unperturbed system and the perturbation Hamiltonian. Alternatively, we can define the T-matrix
\[ T = H' + H'G_0H' + H'G_0H'G_0H' + \cdots \]

then

\[ G = G_0 + G_0T G_0 \]

The full Green’s function has the same branch cuts as the unperturbed one, which means the two system share the same energy continuum, although this does not prevent the eigenstates or the density of states to be different. For an eigenstate in the energy continuum, we have

\[ (\epsilon - H_0)|k\rangle = 0 \]

and the eigenstate of the full Hamiltonian at the same energy has

\[ (\epsilon - H_0)|k'\rangle = H'|k'\rangle \]

which can be treated as a inhomogeneous equation. A general solution is given by

\[ |k'\rangle = |k\rangle + G_0H'|k'\rangle \]

Iterating this equation and we have

\[ |k'\rangle = |k\rangle + G_0H'|k\rangle + G_0H'G_0H'|k\rangle + \cdots = |k\rangle + G_0T|k\rangle \]

which provides a way to calculated the perturbed eigenstates from the unperturbed one. This equation is known as the Lippman-Schwinger equation [55]. In the next section we will apply this equation to the graphene tight-binding system and specifically investigate the wavefunction of the state that is localized around the defect.

2.2 Impurity States of Graphene from Adatoms

2.2.1 Theory

An adatom can be considered as a perturbation to the pristine graphene system. For the simplest case, let |ad\rangle be the only new orbital introduced by the adatom with site energy
\( \epsilon_{\text{ad}} \) and \(|0\rangle\) is the carbon \( p_z \) orbital that is connected to it with hopping energy \( V_{\text{ad}} \). We can write the Hamiltonian as

\[
H = H_0 + H'
\]

where

\[
H_0 = -t \sum_{i,j,\text{n.n.}} |i\rangle \langle j|
\]

\[
H' = \epsilon_{\text{ad}} |\text{ad}\rangle \langle \text{ad}| + V_{\text{ad}} (|0\rangle \langle \text{ad}| + |\text{ad}\rangle \langle 0|)
\]

This model is typically used when studying graphene-adatom systems [56–58]. The T matrix of this perturbation is given by

\[
T = H' + H'G_0 H' + H'G_0 H'G_0 H' + \cdots
\]

\[
= |\text{ad}\rangle \frac{V_{\text{ad}}}{1 - V_{\text{ad}}^2 G_0^{00} G_0^{\text{ad}}} \langle 0| + \text{H. c.} + |\text{ad}\rangle \frac{V_{\text{ad}}^2 G_0^{00}}{1 - V_{\text{ad}}^2 G_0^{00} G_0^{\text{ad}}} \langle \text{ad}|
\]

\[
+ |0\rangle \frac{V_{\text{ad}}^2 G_0^{\text{ad}}}{1 - V_{\text{ad}}^2 G_0^{00} G_0^{\text{ad}}} \langle 0|
\]

where \( G_0 \) is the Green’s function of the unperturbed Hamiltonian and \( G_0^{00} \equiv \langle 0| G_0 |0\rangle \) and \( G_0^{\text{ad}} \equiv \langle \text{ad}| G_0 |\text{ad}\rangle = (E - \epsilon_{\text{ad}})^{-1} \). The perturbed eigenstate in the band continuum is given by the Lippman-Schwinger equation

\[
|\psi(E)\rangle = |\psi_0(E)\rangle + G_0(E) T(E) |\psi_0(E)\rangle = |\psi_0(E)\rangle + \frac{V_{\text{ad}}^2 G_0^{\text{ad}} \langle 0| \psi_0(E) \rangle}{1 - V_{\text{ad}}^2 G_0^{00}(E) G_0^{\text{ad}}(E)} G_0(E) |0\rangle
\]
which is the sum of the unperturbed Bloch state and a term caused by the perturbation. In particular, for a certain energy $E = \epsilon_r$ that satisfies the resonance condition

$$\text{Re}\left[ 1 - V_{ad}^2 G_0^{00}(\epsilon_r) G_0^{ad}(\epsilon_r) \right] = 0$$

the second term would be significantly enhanced and the Bloch function $|\psi_0(E)\rangle$ can be ignored near the impurity site. This means that for the resonant energy $\epsilon_r$, the perturbed wavefunction is proportional to the matrix element of the Green’s function

$$\langle i | \psi(\epsilon_r) \rangle \propto \langle i | G_0(\epsilon_r) | 0 \rangle$$
Similar results have been obtained before [57,59,60]. The proportionality relationship is demonstrated in Figure 2.1 by comparing the Green’s function calculated by definition and the amplitude of the impurity state calculated by direct diagonalization. This resonance state will have larger amplitude near the adatom, but it never decays to zero for large distance because of the contribution of the Bloch function \(|\psi_0(E)\rangle\). Moreover, note that this expression only depends on the resonance energy \(\epsilon_r\), which means the values of \(\epsilon_{ad}\) and \(V_{ad}\) in the Hamiltonian only contribute to determine \(\epsilon_r\) through the resonance condition, and we can study the effects of different adatom species by varying \(\epsilon_r\).

The decay of the wavefunction of the impurity state can be studied by investigating the lattice Green’s functions (GFs). When the sites are labelled with two indices \(l\) and \(m\), like in Figure 2.2, the GF can be written as

\[
G(l, m; E) = \langle l, m | G(E) | 0 \rangle
\]

which can be evaluate by definition after separating the sites into the two sublattices.
\[ G^{AA}(l, m; E) \equiv \langle A, R_{lm} | (E - H)^{-1} | A, 0 \rangle = \sum_k \langle A, R_{lm} | \psi(k) \rangle \frac{1}{E - \epsilon(k)} \langle \psi(k) | A, 0 \rangle \]

\[
\frac{E}{4\pi^2} \int_0^{2\pi} dk_x \int_0^{2\pi} dk_y \frac{e^{i(k_x l + k_y m)}}{E^2 - t^2 \left( 1 + 4 \cos^2 k_x + 4 \cos k_x \cos 3k_y \right)}
\]

and similarly,

\[
G^{AB}(l, m; E) = -\frac{t}{4\pi^2} \int_0^{2\pi} dk_x \int_0^{2\pi} dk_y \frac{e^{i(k_x l + k_y m)} \left[ e^{-i(k_x + k_y)} + e^{i(k_x - k_y)} + e^{i2k_y} \right]}{E^2 - t^2 \left( 1 + 4 \cos^2 k_x + 4 \cos k_x \cos 3k_y \right)}
\]

The denominator shows that both Green’s functions are determined mostly from contributions from the two Dirac points \((K, K')\) in the Brillouin zone when they are evaluated at energies near zero. Thus for an approximation, it is reasonable to integrate around the two Dirac points rather than the whole BZ and assuming a completely linear band, the GFs have been calculated and given in terms of Hankel functions [61–63],

\[
\langle r, A | G_0(E) | 0 \rangle = -i\beta \frac{A_c E}{4v_F^2} H_0^{(1)} \left( \frac{E r}{v_F} \right)
\]

\[
\langle r, B | G_0(E) | 0 \rangle = -\alpha \frac{A_c E}{4v_F^2} H_1^{(1)} \left( \frac{E r}{v_F} \right)
\]

where \(A_c\) is the area of a unit cell in graphene and \(v_F\) is the Fermi velocity. The amplitude of the Hankel functions \(H_0^{(1)}\) and \(H_1^{(1)}\) decay isotropically, but the GFs also depend on the prefactors

\[
\alpha \equiv e^{-i\frac{\pi}{3}} \left( e^{iK \cdot r - \theta_r} - e^{iK' \cdot r + \theta_r} \right)
\]

\[
\beta \equiv e^{iK \cdot r} + e^{iK' \cdot r}
\]

where \(\theta_r = \tan^{-1}(r_y/r_x)\) when the x axis is taken to be along \(K' - K\). The form of the argument of the Hankel function makes two types of approximations feasible. For an
impurity with a small \( \epsilon_{ad} \) or a large \( V_{ad} \) (e.g. a vacancy), the resonance energy \( \epsilon_r \) solved from the resonance condition will be small, which means we can do small argument expansion to the Hankel function. This gives a resonance state that has zero amplitude on the A sublattice sites and decays as \( r^{-1} \) for the B sites \([25,63]\). On the other hand, when \( \epsilon_r \) is not vanishingly small, we are more interested in the long-range decaying behavior, and it is necessary to do large argument expansion, which gives

\[
\left| H^{(1)}_\nu \left( \frac{E_r}{v_F} \right) \right| = \left( \frac{2v_F}{\pi E_r} \right)^{1/2} \left( 1 + \frac{(4v^2 - 1)v_F}{8E_r} + \ldots \right)
\]

Given enough distance, both the A-site and the B-site amplitude will fall off primarily as \( r^{-0.5} \).

### 2.2.2 Computation Implementation

Other than the asymptotic behavior, the GFs can also be evaluated. Direct numerical integration of the GFs is very difficult, since the integrand fluctuates very quickly, especially when the indices \( l \) and \( m \) are large. This is why all the evaluation methods are based on the equation of motion of the GFs, which, since we are using a nearest neighbor Hamiltonian, links the GF on a carbon site with the GFs on its three neighbors

\[
E_G^{AA}(l,m;E) + tG^{BA}(l-1,m+1;E) + tG^{BA}(l+1,m+1;E) + tG^{BA}(l,m-2;E) = \delta_{l0}\delta_{m0}
\]

\[
E_G^{BA}(l,m;E) + tG^{AA}(l-1,m-1;E) + tG^{AA}(l+1,m-1;E) + tG^{AA}(l,m+2;E) = 0
\]

The GFs for the honeycomb lattice is directly related to the GFs of the triangular lattice, which can be expressed in terms of elliptical integrals. In principle, the recursion relations can be used to calculate all the lattice GFs with simple arithmetic. However, this approach is numerically unstable. This is because like many other recursion relations, there are actually two solutions, one exponentially increasing and the other exponentially decreasing.
Although the initial condition has eliminated the increasing one, any numerical error will be amplified and eventually take over and destroy the accuracy [64,65].

The way to go around this problem was done for the square lattice [66] and can be easily moved to the honeycomb lattice, which involves changing the way of labelling the sites (Figure 2.3) and define a “Manhattan distance” which is the number of steps needed to move between two sites along nearest neighbor connections ($|i| + |j|$). Since a site only connects to sites with Manhattan distances to the origin one more or one less, we can put all the Green’s functions of the sites with the same Manhattan distance $n$ into a vector $V_n$, and the equation of motion can be written as

\[ V_n = \alpha_n V_{n-1} + \beta_n V_{n+1} \]

where $\alpha_n$ and $\beta_n$ are sparse matrices with non-zero elements equal to $-t/E$. Furthermore, an equation can be set up between the vectors $V_n$ and $V_{n-1}$

\[ V_n = A_n V_{n-1} \]
Then we have a recursion relation for the $A$ matrices

$$A_n = (1 - \beta_n A_{n+1})^{-1} a_n$$

At a sufficiently large $N$, $A_N$ is approximated by a finite value. All the $A_n$ with $n < N$ can be calculated using this relation and when $n = 0$, $E^{AA}(0,0) + 3tG^{BA}(1,1) = 1$ gives

$$V_0 \equiv G^{AA}(0,0) = \frac{1}{E + 3tA_1}$$

All the other Green’s functions are then retrieved by $V_n = A_n A_{n-1} \cdots A_1 V_0$. The exponentially increasing solution is eliminated in this method because the $A$ matrices are measured coming down from large Manhattan distances. The physical solution is the one that increases exponentially and it will overcome any error in the initial assumption and during the calculations.

2.2.3 Results

Figure 2.4 Amplitude of the resonance state at resonance energy $\varepsilon_r = t/6$. The left panel shows the amplitudes represented by the radii of circles on the graphene honeycomb lattice. The amplitude on the A sublattice has circles drawn with the same color in the lattice, whereas the amplitude of the B sublattice has a line showing the direction it is taken in the lattice. The center dot (blue) is where the adatom is attached. $a$ is the nearest neighbor carbon-carbon distance. [Copyright (2012) by The American Physics Society]
The calculated GFs (proportional to amplitudes of the resonance state) are plotted in Figure 2.4 for the A sublattice and Figure 2.5 for the B sublattice, where in the insets the amplitude of the GF on a certain site is represented by the radius of the circle that is drawn on that site, and the results mostly confirms the asymptotic approximations. Firstly, the amplitude of the resonance state wavefunction depends on the resonance energy $\epsilon_r$, and the energy-dependent behaviors of the two sublattice sites are drastically different. This is clear from a comparison of Figure 2.4 ($\epsilon_r = t/300$) and Figure 2.5 ($\epsilon_r = t/6$). At low $\epsilon_r$, the resonance state is almost exclusively on the B sublattice sites. The amplitudes on the A sites increase quickly while the B sites stay relatively the same with increasing $\epsilon_r$, and the two sublattice sites have comparable amplitudes at $\epsilon_r = t/6$. Secondly, the wavefunction amplitude decays with power law

$$|\psi(r)| = \frac{\psi_0}{r^s}$$

although the exponent $s$ depends on resonance energy, sublattice, and direction. For the A sites (Figure 2.4), the sites that form a triangular lattice with the impurity site (marked with
red) have larger amplitudes than the other sites (marked with black) when they are approximately the same distance to the impurity. This can be explained with the prefactor

$$\beta \equiv e^{iK \cdot r} + e^{iK' \cdot r}$$

which evaluates to 2 for the former group of sites and -1 for the latter. The two groups give almost perfect linear fits in a log-log plot close to the impurity with essentially the same decay exponent \(s\), while the second group of sites deviates from the linear fit at larger distance. For the B sites, the decay is anisotropical and power laws can be seen in many directions when \(\epsilon_r\) is small. This behavior has been obtained with approximations to the GFs previously by Nanda et al. [63], and our calculation confirms their result. At higher \(\epsilon_r\), the decay in the B sites in the armchair direction is the slowest (and thus contributes the most when calculating overlap) and still obeys very good power laws, while the other data sets start to deviate. Deviations from power laws in both the A sites and the B sites are not explained in the approximated GFs, and they happen at a smaller distance for larger \(\epsilon_r\). Therefore, it is possibly a result of nonzero energy and contributions from k points other than the two Dirac points. The decay exponents for the A sites and the armchair direction of the B sites are plotted in Figure 2.6 with several resonance energies. As predicted by the approximations, the B sites’ decay exponent is 1 at zero resonance energy [25,63], and both exponents approach 0.5 with large resonance energy. Finally, we would like to note that the amplitude of the wavefunction calculated with GFs agrees with evaluation of the GFs with elliptic integrals [64], the results in Ref. [58] for vacancies (\(\epsilon_r = 0\)), as well as the amplitude of the eigenfunction near the impurity (\(r \leq 10a\)) obtained from direct diagonalization of the Hamiltonian with periodic boundary conditions.

The power-law decay and the Bloch-wave behavior at large distance both indicate that the impurity state in graphene is not nearly as localized as a typical midgap state in a
semiconductor, which decays exponentially. The resonance states here are not normalizable, and it would be difficult to define a localization length.

2.3 Variable Range Hopping Theory

Consider a system with localized states near the Fermi level (Figure 2.6) at a low temperature. The temperature is low enough that the energy levels the electrons can jump to are limited to a small window, but it is not low to the point that the coherent length is larger than the typical distance between localized states. In such a situation there is a competition between hopping distance and hopping energy difference. The hopping probability may be smaller for a neighboring state which has a large energy difference than for a more remote state which happens to be closer in energy. This is where the theory gets its name variable range hopping (VRH). The range of the hopping is variable rather than always to the nearest neighbor.

Figure 2.6 The characteristic decay exponents of the two sublattice sites vs. the resonance energy. For the A sites, the exponent is taken from the sites that forms a triangular lattice with the impurity site. For the B sites, the exponent is taken from sites in the armchair direction. [Copyright (2012) by The American Physics Society]
Quantitatively, the transition probability between two impurity states can be written as [67]

\[ P_{ij} = P_0 \exp \left[ -\frac{2r_{ij}}{a} - \frac{\epsilon_{ij}}{k_B T} \right] \]

where \( \exp \left[ -\frac{2r_{ij}}{a} \right] \) is the overlap of the exponentially localized states (\( a \) is the localization length) and \( \exp \left[ -\frac{\epsilon_{ij}}{k_B T} \right] \) represents the energy requirements which becomes less important when the temperature increases. The optimal hopping can be found if we can relate the hopping distance \( r_{ij} \) and the hopping energy difference \( \epsilon_{ij} \), which is done by assuming constant density of states \( g(\mu) \) near the Fermi level

\[ r_{ij}^d = 2g(\mu)\epsilon_{ij} \]

Optimizing the hopping probability using this relationship and we obtain what is known as Mott’s law,

\[ \rho(T) = \rho_0 \exp \left[ \frac{T_0}{T} \frac{1}{d+1} \right] \]

where the parameter \( T_0 \) is the characteristic temperature. Its exact form is obtained through a percolation analysis. For \( d = 2 \),

\[ T_0 = \frac{13.8}{k_B g(\mu)a^2} \]

The Mott’s law has been successful in explaining the experimental temperature dependence of the conductance in many disordered materials [67] and it has been applied directly to experiments on functionalized graphene samples [35,45,47].

Note that \( P_0 \) may contain \( r_{ij} \) or \( \epsilon_{ij} \) in power law as well, but as the exponential dependence is much stronger than the power law factors in \( P_0 \), they do not affect the
optimization. The exact form of $P_0$ is controversial. In terms of the final pre-exponential $T$ factor originating from $P_0$, the exponent has been reported to be of $1/4$ [68], $-1/4$ [69], and $(\nu - 2)/(d + 1)$ [67], where $\nu$ is the critical exponent for the size of the percolating cluster. It is ignored in the original VRH derivation because of the weaker dependence, but it becomes important for graphene.

2.4 Power-Law Variable Range Hopping of Graphene

In view of the simplicity and the extensive usage of the VRH theory, it is necessary to investigate the impact of a power-law decaying impurity state on the hopping conductivity result.

Similar to VRH, we will assume that the density of impurities is low enough so that the average distance between impurities is longer than the average distance between impurities is longer than the phase-coherent length and that coherent scattering from multiple centers can be ignored. By simply replacing the overlap with the power-law decaying wavefunction, the hopping probability between two impurity sites $i$ and $j$ can be written as

$$P_{ij} = \gamma_{ij} \frac{1}{r_{ij}^{2\delta}} \exp \left( -\frac{\epsilon_{ij}}{kT} \right)$$

where $r_{ij}$ and $\epsilon_{ij}$ are the distance and energy difference between the two states, respectively. $\gamma_{ij}$ is a prefactor that comes from the coupling between electrons and phonons. It depends on $\epsilon_{ij}$ and $r_{ij}$ with power laws and is thus ignored in the original VRH [67]. Assuming a smooth density of states near the Fermi level ($g(\epsilon_F)$), $\epsilon_{ij}$, and $r_{ij}$ are related by
where $d$ is the dimension of the system. Taking the occupation of the two states into account, we obtain the conductance between two impurities as [67,70]

$$\sigma_{ij} = \frac{e^2}{kT} P_{ij}$$

where $e$ is the charge of an electron. The conductivity of the bulk is assumed to be proportional to $\sigma_{ij}$ between the most conductive pair of impurities, which corresponds to the maximum of $\sigma_{ij}$ when varying $r_{ij}$ or $\epsilon_{ij}$. This leads to a power-law temperature dependence for the conductivity,

$$\sigma \propto T^\eta$$
\( \eta = 2s/d + s' \) and \( s' \) originates from the prefactor \( \gamma_{ij}/T \). For hydrogenic states, it is estimated to be \( (\nu - 2)/(d + 1) \), where \( \nu \) is the critical exponent for the size of the percolating cluster [67]. In two dimensions, \( \nu = 1.34 \) [71] and \( s' = -0.22 \). The analysis that gives this exponent cannot be easily generalized, but we can still assume \( s' \) to be a constant that does not depend on the details of the impurities.

The power-law dependence of the conductivity on the temperature can be used to fit existing experimental data of the systems of hydrogen adatoms [35,45] and fluorine adatoms [47] on graphene (Figure 2.7) and the extracted parameters are shown in Table 2.1, along with fits that uses the original VRH. The fits are done to all the data points presented in the references. The exponents extracted from the fittings are within reasonable range that is expected from this theory. In both experiments where the effect of gate voltage is studied, the exponent decreases

<table>
<thead>
<tr>
<th>Data set</th>
<th>Conventional VRH</th>
<th>Power law VRH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogenated, ( V_g = 0 ) V</td>
<td>0.9857, 284</td>
<td>0.9930, 0.714</td>
</tr>
<tr>
<td>Hydrogenated, ( V_g = 0 ) V</td>
<td>0.9884, 280</td>
<td>0.9975, 0.524</td>
</tr>
<tr>
<td>Hydrogenated, ( V_g = 3 ) V</td>
<td>0.9819, 187</td>
<td>0.9981, 0.459</td>
</tr>
<tr>
<td>Hydrogenated, ( V_g = 9 ) V</td>
<td>0.9621, 107</td>
<td>0.9928, 0.382</td>
</tr>
<tr>
<td>Fluorinated, ( V_g = 0 ) V</td>
<td>0.9843, 450</td>
<td>0.9730, 0.826</td>
</tr>
<tr>
<td>Fluorinated, ( V_g = 0 ) V</td>
<td>0.9990, 270</td>
<td>0.9761, 0.664</td>
</tr>
<tr>
<td>Fluorinated, ( n = 0.7 \times 10^{12} \text{ cm}^{-2} )</td>
<td>0.9985, 130</td>
<td>0.9843, 0.550</td>
</tr>
<tr>
<td>Fluorinated, ( n = 1.4 \times 10^{12} \text{ cm}^{-2} )</td>
<td>0.9889, 33</td>
<td>0.9955, 0.335</td>
</tr>
<tr>
<td>Fluorinated, ( n = 2.5 \times 10^{12} \text{ cm}^{-2} )</td>
<td>0.9599, 5</td>
<td>0.9929, 0.190</td>
</tr>
</tbody>
</table>

\( V_g \) is the gate voltage relative to the charge neutrality point. \( n \) is the charge density calculated with the gate voltage and sample specifics. \( T_0 \) is the characteristic temperature in the conventional VRH and \( \Omega \) is the squared correlation coefficient for the fits on the linearized data. [Copyright (2012) by The American Physics Society]
when the gate voltage moves away from the charge neutrality point, effectively shifting the Fermi energy so that on average impurity states with higher resonance energies participate in the conduction. This is consistent with the behavior of the B sites’ decay exponent, while the amplitudes on the A sites are too small to be relevant in the range of the experimental gate voltage.

The conventional VRH and the power-law VRH have very similar curvatures in this temperature range and all the data can fit both equations fairly well. Comparing the squared correlation coefficients ($\Omega$) for the linear fits, the data for fluorinated graphene at low gate voltage fit the original VRH better, while the power-law dependence describes all the other datasets better. The currently available data cannot convincingly exclude either equation as the conduction mechanism, especially considering the VRH requires low temperature but all the data go up to room temperature. It can be expected that more continuous and accurate experimental data at low temperature can prove our proposal of a power-law temperature dependence.

In summary, we have shown that the impurity state in graphene is a resonance state in the band continuum, and it is localized only as power-law functions with exponents generally below 1. This means that the VRH theory which assumes exponential localization is not directly applicable to disordered graphene. Replacing the overlap term in VRH, a theory for the temperature dependence of conductivity is derived which fits the existing experimental data. However, since the states are largely delocalized, the hopping picture of conduction may not be the most appropriate approach to model the transport properties of these systems. Further investigation into this problem is needed to develop a theory that includes both the impurity states and the extended unperturbed states.
Chapter 3
Analysis of Adsorption-Desorption Kinetics in Graphene Gas Sensing Experiments

It has been discovered that when graphene is exposed to certain types of molecules, even in extremely small concentration and gas phase, its transport behavior and thus conductivity is affected, which can be detected and quantified in experiments. This phenomenon makes it possible to make a graphene-based gas sensor that is much more sensitive than current commercial sensors with detection limits down to part-per-quadrillion level [22,53]. However, despite this relatively well-known phenomenon, there is no consensus for the mechanism of this conductivity change which limits further improvements to these sensors. In this chapter, I will summarize some of the related experiments and the prevailing theory for the conductivity change. I will also present an analysis of the adsorption-desorption kinetics of one of the experiments that obtained particularly high sensitivity and low detection limit for NO. Chapter 4 and 5 will discuss other possible mechanisms for the conductivity change.

3.1 Graphene Gas Sensing Experiments

Carbon nanotubes and graphene have been fabricated into chemiresistors or field effect transistors and tested against various chemically and biologically important molecules since the early days of their respective discovery, and there is a significant body of scientific literature contributed towards this topic [21,22,53,72–79]. Due to their high surface-to-volume ratio and unique electronic properties [5,80], carbon nanotubes and graphene are promising candidates for detecting molecules with ultra-low concentrations. The experiments on graphene by my collaborators Chen et al. [22] is particularly interesting
because they used a UV light to illuminate the graphene sample and obtained a particularly low detection limit for NO on the part-per-quadrillion (ppq) level. Before doing analysis on their experimental data, I will start by briefly describing the experimental setup since many elements are common among this experiment and others.
Their CVD graphene sample on silicon substrate is placed in a test chamber (Figure 3.1), which is connected to input gases through a mass flow controller. The controller can accurately mix the inert carrier gas (N$_2$) and the sensor target gas (NO, NO$_2$, or NH$_3$). While the test chamber receives a constant flow of the carrier gas, the mass flow controller periodically mixes in the target gas in small concentration, typically on the order of magnitude of part-per-billion. In each test cycle, the target gas is present for 5 minutes and then the whole chamber is flushed with pure N$_2$ for 5 minutes, while the conductance of the graphene sample is constantly measured. The concentration of the target gas in the exhaust is measured which shows that the concentration in the chamber reaches equilibrium in a few seconds. A typical 5-cycle measurement is shown in Figure 3.2(a) for NO with a concentration of 10 part-per-trillion (ppt). During the phase where NO is present, the conductivity increases apparently exponentially towards a certain saturation, and when the chamber is flushed, it recovers exponentially. However, part of the process seems irreversible, as the recovery can never reach the original baseline of the conductivity before
the experiment. We will come back to this point in section 3 of this chapter with data extrapolation and analysis.

Other than the real-time response, the conductivity versus carrier density curve also provides insights into the mechanism of the graphene gas sensor. It is typically measured by building a gate electrode on top so that the charge in the graphene sheet can be controlled with a gate voltage, similar to a capacitor. In this way, graphene samples have been tested against potassium atoms [31], NO₂ [21,76], and NH₃ [76,81]. For the latter two species, the conductivity versus gate voltage curve shifts in voltage from the behavior of pristine graphene after exposure to the target gas, as is best represented by Figure 2 in Ref. [76]. The fact that the slope of the curves near the neutrality point of graphene does not change means that the effect of these molecules on the conductivity is equivalent to charging the graphene sheet. Therefore, the most straightforward explanation for the conductivity change is that there is charge transfer between the molecules and the graphene sheet. The molecule either takes electrons away from graphene (in the case of NO₂), or adds electrons to it (in the case of NH₃), without affecting any other aspects of the electronic transport. The conductivity thus changes as a result of changes in the carrier density.

This explanation was adopted by the authors of these experimental paper and also used in explaining similar experiments with carbon nanotubes [53,72]. First principle calculations have also shown small amount of charge transfer for these systems [82,83]. However, it is far from the consensus of the scientific community. Experiments have shown that contaminated or polycrystalline graphene is actually more sensitive than intrinsic graphene [78,79]. There are many other proposed mechanisms for the conductivity change. Heinze et al. [84] and Karthygeyan et al. [77] proposed that molecules changes the work function of the contact metal electrodes and thus the Schottky barrier. Hwang et al. [48] noted that the charged impurity in the substrate of graphene may be screened by the
molecules, lessening the scattering of electrons. In the analysis of adsorption-desorption kinetics in this chapter, we will assume that the conductivity change is proportional to the coverage of adsorbed molecules, which is the most natural when charge transfer is considered to be the mechanism. We will discuss alternative mechanisms in the two following chapters.

3.2 Kinetic Langmuir Model of Adsorption

When discussing surface adsorptions, a very common starting point is the Langmuir theory [85,86]. In its original form, the Langmuir model discusses the kinetics of adsorption and desorption of molecules onto a surface, which is reflected in the quantity defined as coverage,

$$\theta = \frac{\text{number of adsorbed molecules}}{\text{number of available adsorption sites}}.$$

A few assumptions are made: 1. There are no interactions between gas molecules or adsorbed molecules. 2. The gas follows the ideal gas law, which means that the rate of gas atoms impinging on the surface is given by \(P[2\pi mk_B T]^{-1/2}\), where \(P\) is the partial pressure of the adsorption gas, \(m\) is the mass of the molecule. 3. The probability of molecules sticking to the surface when they impinge on the surface is a constant \(s\). 4. The adsorption is completely reversible and the desorption happens at a constant rate \(\alpha\). The equation that governs the coverage, combining adsorption and desorption, is given by

$$\frac{d\theta}{dt} = -\alpha \theta + J_{\text{stick}}(1 - \theta)$$

$$J_{\text{stick}} \equiv \frac{P}{n\sqrt{2\pi mk_B T}} \cdot s$$
where \( n \) is the areal density of adsorption sites. The equation can be solved when \( P(t) \) is given. The equilibrium coverage for a given pressure and temperature (the Langmuir isotherm), is obtained by setting the coverage changing rate to zero

\[
\theta(P) = \frac{J_{\text{stick}}}{J_{\text{stick}} + \alpha}.
\]

The Langmuir model is obviously simplistic and interactions between molecules, especially adsorbed molecules, are always present to a certain degree. However, it can be a good starting point in qualitative studies of the surface and the adsorption process.

### 3.3 Normal and Poison Sites and Adsorption-desorption Kinetics

This section discusses the experimental results of Ref. [22,53] and the analysis have been published in Applied Physical Letters [51].

The difference between the graphene/nanotube NO detection results and the Langmuir assumptions is that the adsorption is not completely reversible – the conductivity is changed permanently by some molecules and it does not recover to the baseline. A simple and effective way to model this behavior is to consider two types of adsorption sites. The normal site follows all the assumptions of the Langmuir model, whereas the ‘poison’ sites only receive a molecule but the adsorption is so strong that it is almost impossible for the molecule to leave this site in the time scale of the experiment. In this sense, they behave similarly to poisons of catalysts. Physically, these sites may be defect sites and in the case of nanotubes, sites that are affected by multiple nanotubes that are likely to have a higher adsorption energy. The sticking coefficient of these sites differs from those of the normal sites and the rate of change of the coverage can be written as

\[
\frac{d\theta_n}{dt} = -\alpha \theta_n + J_{\text{stick,n}} (Q_n - \theta_n),
\]
\[
\frac{d\theta_p}{dt} = J_{\text{stick}, p}(Q_p - \theta_p),
\]

where the symbols take the same meaning as in the previous section and the subscript \( i = n \) or \( p \) denotes normal sites and poison sites, respectively. The maximum possible coverage of both species must be normalized (\( Q_p + Q_n = 1 \)), and the two parameters are determined by \( \eta \equiv Q_n/Q_p \). As in the Langmuir theory, \( J_{\text{stick}, i} \) is equal to the number of molecules striking a unit area per unit time multiplied by the sticking coefficient. The former quantity is related to pressure and temperature of the gas. In the gas detection experiments [22,53], the partial pressure of the target gas is either a constant (the exposure segments), or zero (the recovery segments). The coverage rate of change equations can be solved in these two situations (with starting time \( t_0 \)) and the solutions are given by

\[
\theta_n(t) = \left( \frac{J_{\text{stick}, n}Q_n}{\alpha + J_{\text{stick}, n}} - \theta_n(t_0) \right) \left( 1 - e^{-\left(\alpha + J_{\text{stick}, n}\right)(t-t_0)} \right) + \theta_n(t_0)
\]

\[
\theta_p(t) = \left( Q_p - \theta_p(t_0) \right) \left( 1 - e^{-J_{\text{stick}, p}(t-t_0)} \right) + \theta_p(t_0)
\]

for the exposure segment, and

\[
\theta_n(t) = \theta_n(t_0)e^{-\alpha(t-t_0)}
\]

\[
\theta_p(t) = \theta_p(t_0)
\]

for the recovery segment, where the normal sites lose molecules exponentially and the poison sites stay the same.

The coverage changes are detected in the conductance measurements. We assume that the conductance change is proportional to the coverage change, which is consistent with the hypothesis that the conductance changes as a result of charge transfer. Also, without
further experimental data we will assume that poison sites and normal sites contribute to the conductance equally

\[ \Delta G \equiv G - G_0 = \sigma (\theta_n + \theta_p) \]

The relationship between conductivity and charge mobility leads to an expression for the coefficient \( \sigma \)

\[ \sigma = g_0 \mu e (n_n + n_p) \delta \]

where \( g_0 \) groups a few geometric factors, \( \mu \) is the electron mobility, and \( \delta \) is the number of electrons transferred between the molecule and the surface.
In total we have obtained the data for 9 runs of the experiments, including 5 for carbon nanotube sensors and 4 for graphene sensors. The measured data seems critically dependent on the sample and the cleaning procedure, presumably due to molecules trapped on poison sites, which is why the data differs between each experimental run. The fitting is done using the generalized reduced gradient nonlinear solver method implemented in Microsoft Excel. The fitting results are shown in Figure 3.2 for nanotubes and Figure 3.3 for graphene, and the parameters obtained from the fit are in Table 3.1. The nanotube and graphene samples grown using CVD is actually a very complex environment, containing many different types of defects and grain boundaries. Considering the simplicity of the model, it can fit the data relatively well. A few things can be learned from the fitting parameters. Firstly, the desorption rate $\alpha$ is larger for experiments with higher concentration of the target gas in both nanotubes and graphene. This could mean that there are more types of adsorption sites. These sites have higher desorption rates and they become more and more important when the gas concentration is higher and thus the total coverage is higher.

**Figure 3.3** Conductance changes during the detection cycles on the graphene device. The circles are the experimentally measured data and the solid lines with the same color are their corresponding fits. The concentration of NO during the experiments is (a) 10ppt for all 5 cycles (b) 10, 20, 50, 100, and 200 ppt. See the text for experimental details.
Secondly, the sticking coefficient and the areal site density are proportional to each other following

\[ s_i = \sqrt{\frac{k_B T J_{\text{stick,}i}}{2 \pi m n_g^{\gamma}} n_i} \]

where \( n_g \) is the concentration of the target molecule in the gas phase. The proportionality constant can be calculated with the fitting parameters. For carbon nanotube sensors, they are 1.2 Å and 3.2 Å for normal sites and poison sites, respectively. For graphene sensors, they are 0.3 Å and 0.4 Å. A determination of either quantity through experimental or theoretical methods can then provide estimation of the other.

### Table 3.1 The fitting parameters of available data sets.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Experimental Procedure</th>
<th>Data set</th>
<th>( \alpha ) (( 10^{-8} ) s(^{-1} ))</th>
<th>( J_{\text{stick}}/n_g ) (( 10^{9} ) s(^{-1} ) × ppt(^{-1} ))</th>
<th>( J_{\text{stick}}/n_g ) (( 10^{9} ) s(^{-1} ) × ppt(^{-1} ))</th>
<th>( \eta )</th>
<th>( \sigma^g )</th>
</tr>
</thead>
<tbody>
<tr>
<td>SWNT</td>
<td>10 ppt for all cycles</td>
<td>1</td>
<td>8.6</td>
<td>31.0</td>
<td>57.1</td>
<td>8.6(^b)</td>
<td>8.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2</td>
<td>8.6</td>
<td>11.4</td>
<td>22.6</td>
<td>8.6(^b)</td>
<td>6.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3</td>
<td>7.6</td>
<td>38.0</td>
<td>103.9</td>
<td>8.6(^b)</td>
<td>2.1</td>
</tr>
<tr>
<td></td>
<td>Increasing ( n_g )</td>
<td>4</td>
<td>9.2</td>
<td>55.7</td>
<td>88.5</td>
<td>8.6</td>
<td>5.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5</td>
<td>10.2</td>
<td>35.2</td>
<td>229.9</td>
<td>11.0</td>
<td>4.3</td>
</tr>
<tr>
<td>Graphene</td>
<td>10 ppt for all cycles</td>
<td>6</td>
<td>9.8</td>
<td>15.4</td>
<td>15.8</td>
<td>5.2(^c)</td>
<td>2.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>7</td>
<td>6.7</td>
<td>6.6</td>
<td>17.7</td>
<td>5.2(^c)</td>
<td>2.1</td>
</tr>
<tr>
<td></td>
<td>Increasing ( n_g )</td>
<td>8</td>
<td>12.3</td>
<td>4.6</td>
<td>2.6</td>
<td>4.8</td>
<td>1.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>9</td>
<td>11.4</td>
<td>0.8</td>
<td>2.0</td>
<td>5.7</td>
<td>4.8</td>
</tr>
</tbody>
</table>

\(^a\)10\(^8\) Ω\(^{-1}\) for SWNT data sets and 10\(^4\) Ω\(^{-1}\) for graphene data sets.

\(^b\)Because the model is over-determined for these data sets, these values are taken as the same value obtained from the fitting of Data 4.

\(^c\)Fixed as the average value obtained from the fittings of Data 8 and Data 9.

### 3.4 Improving the sensors

The benefits of such a theoretical model is that we can now discuss how various indicators of the sensor performance can be quantified and improved. Here we will review the sensor qualities with all the poison sites occupied to simulate repeated use. This can be considered the worst scenario and real sensors should be able to perform better.
Sensitivity: The model gives a relationship between the saturated conductance change versus the partial pressure of the target gas

\[ \Delta G(t = \infty, P) = \sigma \left( Q_p + \frac{J_{\text{stick},n}(P)Q_n}{\alpha + J_{\text{stick},n}(P)} \right). \]

As shown in Figure 3.4, the sensitivity of the sensor can be defined as the derivative of this relationship - a sensor is more “sensitive” if there is a large conductance change for a small change in the concentration of the gas. For this discussion, we will specify that the derivative to be taken at the lowest concentration limit. Therefore, the model gives

\[
\text{sensitivity} = \frac{g_0\mu e\delta s_n}{G_0\alpha} \sqrt{\frac{k_B T}{2\pi m}}
\]

**Figure 3.4** Illustration of the definitions of sensor sensitivity and detection limit used in this study. The sensitivity is defined as the derivative of the coverage vs. concentration curve. The detection limit is defined as the concentration that creates a signal that is three times as large as the noise.

Detection limit: The detection limit is defined by the concentration of the target gas that creates a signal in the conductance of the sensor that is three times as large as the typical noise levels of the experiment. The noise depends on the experimental setup and we will assume it to be a constant \( \Delta G_{\text{err}} \) here. Inverting the conductance versus gas concentration equation and we obtain
\[
\text{detection limit} = \frac{3\Delta G_{\text{err}}n_\alpha}{s_n(g_0\mu e n_\delta - 3\Delta G_{\text{err}})} \sqrt{\frac{2\pi m}{k_B T}}
\]

Time response: In principle, the concentration of target molecules can be calculated from the slope of the signal immediately after adsorption starts. However, this is not a practical approach since random errors and noise can change the slope of the data significantly. Any realistic sensing can be done only after the conductance has reached some level of saturation. In this model, the saturation time is determined by just the two rate constants, \(\alpha\) for the recovery segments and \(J_{\text{stick},n} + \alpha\) for the exposure segments. Considering that \(\alpha \gg J_{\text{stick},n}\) in all of our fitting results, the time response of the sensor is determined primarily by the desorption mechanism and by the temperature.

Many parameters related to the sample condition, the environment, and the experimental setup can affect these aspects of sensor quality. From the apparent temperature dependences in the above equations, the sensors tend to have better sensitivities and lower detection limits when they are operated at high temperature. However, hidden dependences in the desorption rate constant \(\alpha\) could be important, especially at high temperature where thermal desorption is dominant. The sensor could exhibit an optimal temperature similar to metal oxide gas sensors [87]. Lowering the conductance baseline \(G_0\) and increasing the charge transfer \(\delta\) can improve the sensitivity and the detection limit. Both of these can be achieved by adding a top gate and tuning the gate voltage, which also provides some level of selectivity when multiple molecules are being detected [76]. The fraction of normal sites versus poison sites does not factor into any of the sensor qualities, perhaps surprisingly. However, \(n_n\) and \(s_n\) both increase when there is a larger number of normal sites, which can happen by eliminating poison sites and making pure, defect-free samples.
In conclusion, we have modeled the adsorption-desorption kinetics of the carbon nanotube and graphene gas sensing process by introducing poison sites into the Langmuir model. We have quantified sensors characteristics like sensitivity, detection limit, and time response, and suggested ways to improve sensor performance. To continue further with modeling and extracting more information from the experimental results, the reproducibility of the data needs to be improved. Moreover, as we will discuss in the later chapters, what we have assumed here, that the conductance change is due to charge transfer between the molecule and the sensor, is not necessarily the only possible explanation. More experiments varying the temperature, gate voltage, UV light exposure, and defect density need to be done to test and refine the model.
Chapter 4

Modelling the Screening of Graphene Substrate Charged Impurities

In the previous chapter, we explored the prevalent theory for the conductance change when graphene is exposed to certain gas molecules, which is that it is due to charge transfer between the molecule and the graphene sheet. Under closer scrutiny, there seems to be many inconsistencies with this simple theory, which will be discussed in section 4.1. I will introduce a new possible mechanism for the phenomenon which involves screening of the charged impurities in the substrate of graphene, which is described quantitatively in sections 4.3 and 4.4, along with predictions of how the conductivity changes depending on the dipole moment, the carrier concentration in graphene, and the concentration of adsorbates. The model and its predictions have been published in Physical Review B [52].

4.1 Inconsistencies of the Charge Transfer Explanation

The charge transfer mechanism has many inconsistencies when it is applied to the three gas species in the experiment that we have discussed in chapter 3 by Chen et al. [22], NO, NO₂, and NH₃.

Firstly, DFT calculations of the molecules and graphene could not confirm the charge transfer. The calculations show that the molecules are only weakly adsorbed on graphene [82,83], i.e. there is no covalent bonding between carbon atoms and the molecules. The only way charge can be transferred is then by moving a whole electron, similar to forming an ionic bond. However, the charge transfer obtained by integrating the charge density near the molecule in DFT calculations is much smaller than that. The reported electron gains are 0.017e [82] and 0.03e [83] for NO, 0.1e [82] and -0.06e [83] for NO₂, and -
0.02e [82] for NH₃. These calculations are cited [76] to support the idea that NO and NO₂ are electron acceptors, and NH₃ is an electron donor, but the charge transfer is small and can be mostly ascribed to the delocalization error of DFT, which refers to the tendency of electrons to unphysically disperse rather than localize in DFT calculations and has been a known limitation of DFT [88,89]. A fractional charge transfer without a covalent bond is difficult to justify physically.

Secondly, the energetics suggest that charge transfer is unlikely and inconsistent. For an electron to transfer, the difference between the ionic potential of the source and the electron affinity of the destination needs to be compensated by lowering the energy when the charged source and the destination are brought together (the interaction energy). The ionic potential and the electron affinity of the molecules are listed in Table 4.1 along with the work function of graphene [90]. The interaction energy required for an electron to leave graphene and transfer to NO is 4.6 eV, which is on-par with the interaction energy between a pair of sodium and chlorine atoms in sodium chloride. It is unlikely that interaction between the scattered charge in graphene and the charged NO molecule can be so large. Moreover, the interaction energy required for charge transfer between graphene and NO₂ is 2.3 eV, much smaller than NO, but NO is the species graphene is more sensitive to. Both these facts show that charge transfer in the fashion of an ionic bond is unlikely a significant contribution to the conductance change of graphene when exposed to the sensing target gases.
Finally, the charge transfer should produce a mobility decrease, rather than simply affecting the carrier density. When the molecules adsorb to graphene and accept or donate electrons, they are left charged. The charged molecule contributes carriers to graphene, but at the same time, it is inevitable that its electron field scatters electrons and lowers the electron mobility in transport. It is indeed reflected in an experiment with graphene and potassium [31] by conductance versus gate voltage measurements, in which the conductivity minimum shifts and the slope gradually decreases with more potassium doping. However, similar experiments involving NO$_2$ and NH$_3$ [21,76,81] only shows the shifting minimum, with the slope staying relatively constant. Since the charge carrier increase and the mobility decrease cannot be separated from each other, this experimental result means that a mechanism different from the potassium experiment is responsible for the phenomenon. Given that potassium transfers charge extremely easily to graphene, we should reconsider the mechanism for graphene sensors to detect NO, NO$_2$, and NH$_3$.

The interaction between the electrons in graphene and external localized charges have been studied before. In fact, the charged impurities in the silica substrate of graphene have been shown to be the limiting factor for the conductivity [30] in some graphene samples. Their electric field and by extension their impact on transport can be changed by adsorbed polar molecules, which is the mechanism we are exploring in this chapter. I will start by examining how graphene respond to external electric field, introducing the dielectric function of graphene.

### Table 4.1 Ionization potential (IP) and electron affinities (EA) of NO, NO$_2$, and NH$_3$. The work function of graphene is also included which serves as both its IP and EA.

<table>
<thead>
<tr>
<th></th>
<th>NO</th>
<th>NO$_2$</th>
<th>NH$_3$</th>
<th>Graphene</th>
</tr>
</thead>
<tbody>
<tr>
<td>IP (eV)</td>
<td>9.26</td>
<td>9.6</td>
<td>10.0</td>
<td>4.6</td>
</tr>
<tr>
<td>EA (eV)</td>
<td>0.03</td>
<td>2.3</td>
<td>N/A</td>
<td>4.6</td>
</tr>
</tbody>
</table>
4.2.1 The Dielectric Function of Graphene

The electrons in graphene respond to external electric field and screens static charges. The screening behavior is described by the dielectric function, which can be evaluated using the random phase approximation (RPA). RPA is a mean field theory in which each electron is assumed to experience only the self-consistent field from summing the external field and the induced field. It is the approximation that leads to the famous Lindhard dielectric function of 3D and 2D electron gases. It can be written in general as

$$\varepsilon(q, \omega) = 1 + \frac{2\pi e^2}{\kappa q} \Pi(q, \omega)$$

where \(q\) and \(\omega\) are the spatial and temporal frequencies of the external field, respectively. The 2D polarizability is given by

$$\Pi(q, \omega) = -\frac{g_s g_v}{2L^2} \sum_{kss'} \frac{f_{sk} - f_{s'k'}}{\omega + \epsilon_{sk} - \epsilon_{s'k'} + i\eta} (1 + s^s s^{s'} \cos \theta_{kk'})$$

where \(g_s\) and \(g_v\) are the spin and valley degeneracies, respectively, \(k' = k + q\), and \(\cos \theta_{kk'} = (k + q \cos \phi)/k'\). The \(f_{sk}\) is the Fermi function which reduces to a step function when the equation is evaluated at zero temperature.

The evaluation of the polarizability requires utilization of symmetry and carefully evaluating poles of the function, which can be found in Ref. [43,44]. The final result for the static polarizability (\(\omega = 0\)) is given by

$$\Pi(q) = \frac{g_s g_v E_F}{2\pi v_F^2} \left( \Pi^+(q) + \Pi^-(q) \right)$$

where
\[
\Pi^+(q) = \begin{cases} 
1 - \frac{\pi q}{8k_F}, & q \leq 2k_F \\
1 - \frac{1}{2} \sqrt{1 - \frac{4k_F^2}{q^2} - \frac{q}{4k_F} \sin^{-1} \frac{2k_F}{q}} & q > 2k_F
\end{cases}
\]

\[
\Pi^-(q) = \frac{\pi q}{8k_F}
\]

A plot of the polarizability is shown in Figure 4.1. Note that unlike in 2D electron gas [91], the polarizability of graphene does not have a discontinuity at \( q = 2k_F \) and it increases after \( q = 2k_F \), while for 2D electron gas decreases to zero. The discontinuity is the source of the Friedel oscillations and thus the induced charge in graphene does not oscillate around the charge being screened, as I will show in the next section.

4.2.2 Graphene Screening of a Single Static Point Charge

The screening properties of graphene have been expressed in the RPA dielectric function. As a demonstration of the properties of the dielectric function, we will investigate how a single charge can be screened by graphene. The total potential on the same side and on the opposite side of the graphene sheet and the induced charge density are calculated. The results are also relevant to later discussions.
The charged impurities can be approximated as point charges. Place a unit charge near an infinite graphene sheet, at a distance of \( d \). The two-dimensional Fourier transform of the potential produced by the charge in the graphene plane is given by

\[
V^{\text{ext}}(q) = \frac{2\pi q}{d} e^{-dq}
\]

In the linear response regime, the induced potential \( V^{\text{ind}}(q) \) and the induced charge density \( n(q) \) are related to \( V^{\text{ext}}(q) \) through

\[
V^{\text{ind}}(q) = \left( \frac{1}{\epsilon(q)} - 1 \right) V^{\text{ext}}(q) = \frac{2\pi}{q} n(q)
\]

**Figure 4.2** The electric potential created by the charged impurity and the screening charge in graphene in the space on the opposite side of the graphene sheet. As shown in the inset, \( z \) is the coordinate for the direction perpendicular to the graphene plane. The screening reduces the potential but preserves the direction of the electric field. The screening is more effective when there is a higher carrier density in graphene. The electric field of each case is labeled at a typical distance of the adsorbates. [Copyright (2014) by The American Physical Society]
where \( \epsilon(q) \) is the static dielectric function of graphene, assuming it does not depend on the direction of \( \vec{q} \) (as is the case for the graphene RPA dielectric function). Both the induced charge density and the total potential can be obtained from this equation. The former is given by

\[
n(\rho, d) = -\frac{1}{2\pi} \int_0^\infty dq \, q J_0(\rho q) \left( \frac{1}{\epsilon(q)} - 1 \right) e^{-q d}
\]

after Fourier transformation back to real space. \( \rho \) and \( z \) belong to a cylindrical coordinate system whose origin is at the point charge (inset of Figure 4.2) and \( J_0(x) \) is the zeroth order Bessel function of the first kind. As an example, the induced charges in graphene, in a 2D electron gas, in a perfect metal, and in a dielectric with a constant relative dielectric constant of 4.4 are plotted in Figure 4.3, with the distance between the external charge and graphene is 0.3 Å. Note the presence and the lack of Friedel oscillation in 2DEG and graphene, respectively.

On the other hand, the total potential after screening in three dimensional space is

\[
V_{3D}(\mathbf{r}) = \frac{1}{\sqrt{\rho^2 + z^2}} + \int_0^\infty dq \left( \frac{1}{\epsilon(q)} - 1 \right) e^{-q z} J_0(\rho q)
\]

Particularly, the potential on the \( z \) axis (\( \rho = 0 \)) is given by
\[ V_{3D}(z) = \frac{1}{z} + \int_0^\infty dq \left( \frac{1}{\epsilon(q)} - 1 \right) e^{-zq} \]

The potential is only fully screened in the region \( z > 0 \) for perfect metals when \( \epsilon = \infty \). For graphene at different carrier densities, the screened and unscreened potentials are calculated using the random phase approximation (RPA) dielectric function. The results are shown in Figure 4.2.

The potential on the \( z \) axis is reduced by graphene screening but keeps the monotonic trend, thus the direction of the electric field on the other side of graphene is unchanged and it is determined by the sign of the charged impurity. We can also conclude that graphene with a larger \( k_F \) (higher carrier density) is more effective at screening the potential of the charged impurity, although the difference is only approximately 10% in terms of the electric field at a distance of 6 Å between screening with a high carrier density for normal gate configuration \( (n = 10^{13} \text{ cm}^{-2}) \) and screening with graphene at the charge neutrality point.

4.2.3 Screening of Substrate Charged Impurities by Adsorbates

Charged or dipolar functional groups can appear at the surface of graphene as a result of adsorption. When charge transfer occurs between graphene and the adsorbate, the molecule or atom is left at the surface with a net charge. Charged impurities with opposite sign then become attractive centers for these groups. With the correct energetics and adsorbate coverage, the charged functional groups can stay on top of charged impurities and form a complex structure (hereby referred to as the CI|Graphene|CFG structure). For graphene, a charged functional group anchored on top of a charged impurity alters the local electric field, and thus changes the scattering rate of this particular scattering center, affecting the conductivity. Similarly for dipolar groups, due to the inhomogeneity of the electric field produced by the impurity, a positive impurity would attract the negative end of the dipole and vice versa, forming the CI|Graphene|Dipole structures. The resulting structure also affects the local external field on graphene. This idea is shown schematically in Figure
4.4. The top panel shows the bare charged impurities and the two proposed structures. The bottom panel is a plot of the induced charge density as a result of screening within graphene of the charge and the dipole. For these parameters, the chance of scattering is reduced by the adsorbates.

To estimate the likelihood of such a scenario, we calculated the energy gained from forming these compound structures. Compared with freely oriented adsorbed dipoles, dipoles in a CI|Graphene|Dipole structure gain energy by adjusting its orientation to accommodate the electric field of the charged impurity. As shown in Figure 4.2, the electric field at typical adsorption distance for an impurity with the charge of an electron and graphene at charge neutrality point is calculated using the RPA dielectric function as 0.168 V/Å. Given the typical dipole moments of detectable molecules (~0.02–0.5 eÅ), this gives a rather small energy gain for forming the layered structure. However, the RPA dielectric
function does not include the polarization of the graphene sheet in the perpendicular
direction, which in this case would also create charge distribution in graphene that attracts
and orients the dipole in the same direction. A straightforward density functional theory
(DFT) calculation did not give a reasonable estimate due to its tendency to unphysically
transfer a fraction of an electron when there is no covalent bonding, which is known as the
delocalization error of DFT [88,89,92]. To estimate the effect of the perpendicular
polarization, the response of a big super cell of graphene to uniform perpendicular external
electric fields is calculated using all electron Dmol3 calculations [93], with the local density
approximation [94] and spin unrestricted [95]. A basis set of double-numeric quality
localized wave functions is used with polarization functions (DNP) and an atomic real-space
cutoff of 7 Bohrs. The super cell contains 32 carbon atoms in a rectangular area of 8.52 Å by
9.84 Å and only the Γ point is used. Eight different electric fields are simulated. The dipole
moments are calculated for all fields and their dependence on the magnitude of the field is
linear. A fit gives a polarizability of 6.62 a.u. per unit cell with a correlation coefficient of
\( R^2 = 0.9992 \). Assuming a distance of 3.6 Å between the charged impurity and the graphene
sheet [96], an impurity with the charge of an electron creates a dipole moment of 0.143 eÅ in
a unit cell of graphene which in turn creates an additional field of approximately 0.153 V/Å
(approximated as a point dipole) at 3 Å away in the region of typical adsorbates. This
effectively doubles the field that an adsorbate dipole feels and the total energy gain for
forming the Cl|Graphene|Dipole structure is estimated as 0.06–0.15 eV. This value is
expected to be even larger for charged functional groups since they are attracted more
strongly. These estimates show that there is a large energy gain to form these structures
compared with the room temperature thermal energy, especially for larger dipoles.

4.3 Impact of the Screening on the Conductivity

4.3.1 First-order Born Approximation and the Conductivity
Under the assumption that the Coulomb scattering centers (including charge impurities, free adsorbates, and the complex structures they form) create external potential fields and that they are distributed randomly in the sample without correlation between different species, we calculate the conductivity of graphene using the first-order Born approximation

$$\sigma = \frac{2e_0 \epsilon_F \tau}{\hbar}$$

where $\epsilon_F$ is the Fermi energy and $\tau$ is the scattering time at the Fermi level. At zero temperature, $\tau$ is given by

$$\frac{1}{\tau(k_F)} = \sum_{i,k'} n_{imp}^i \left| u^i(|k_F - k'|) \right|^2 \frac{\epsilon^2 k_F k'}{\epsilon (|k_F - k'|)} \left( 1 - \cos^2 \theta_{kk'} \right) \delta(\epsilon_{k_F} - \epsilon_{k'})$$

where $k_F$ is the Fermi wave vector, $n_{imp}^i$ is the density of the $i$th type of Coulomb impurity, $u^i(q)$ is the corresponding Fourier transformed external potential energy that electrons in graphene experience, and $\theta_{kk'}$ is the scattering angle between $k$ and $k'$. Before the adsorption of the target molecule, charged impurities embedded on the interface of graphene and the substrate are the only type of Coulomb impurities in the system. They are denoted $i = Z$ and

$$u^Z(q) = \frac{2\pi Z e_0^2}{q} e^{-d_2 q}$$

After molecule adsorption, depending on the charge transfer and the formation of CI|Graphene|Adsorbate structures, there are four additional types of Coulomb impurities: $i = \delta$ for a point charge from a charged functional group; $i = p$ for a point dipole oriented randomly near the surface; $i = Z\delta$ for the CI|Graphene|CFG structure, in which the two charges are of the opposite signs; and $i = Zp$ for the CI|Graphene|Dipole structure, in which the dipolar molecule is oriented so that it is attracted to the charged impurity. The $u^i(q)$ for these four types are given by
\[ u^\delta(q) = \frac{2\pi\delta e_0^2}{q} e^{-d\delta q} \]

It is the same form as the charged impurities since they are both treated as point charges. On average, randomly oriented dipoles affect the conductivity like dipoles that have \( \pi/4 \) angles between their dipole moments and the surface normal.

\[ u^p(q) = \sqrt{2\pi}p e_0^2 e^{-d\rho q} \]

\[ u^{Z\delta}(q) = \frac{2\pi Ze_0^2}{q} e^{-d\delta q} - \frac{2\pi\delta e_0^2}{q} e^{-d\delta q} \]

\[ u^{Zp}(q) = \frac{2\pi Ze_0^2}{q} e^{-d\delta q} - 2\pi p e_0^2 e^{-d\rho q} \]

In the above equations, \( Ze_0 \), \( \delta e_0 \), and \( p e_0 \) are the charge on a charged impurity, the charge on a charged functional group, and the dipole moment of an adsorbed molecule, respectively. Note that the parameter \( p \) has dimension of a length. \( d_i \) is the distance between each species and the graphene plane. In reality, they are not always constant due to surface corrugation and the specifics of the adsorbates, but not enough is known about their dependence on these factors and varying them in a reasonable range of \( \pm 1 \) Å has shown only some quantitative effects in our results. Therefore, the distances are kept fixed as \( d_Z = 3.6 \) Å and \( d_\delta = d_\rho = 3 \) Å in all the results shown here. Applying the RPA dielectric function and taking \( \kappa = 2.5 \) for the silica-graphene interface, the scattering time equation can be simplified to

\[ \frac{1}{\tau} = \sum_i \frac{4n^{i_{imp}}k_F}{\pi\hbar^2 v_F} \int_0^1 dx \left( \frac{1 + 1.76}{x} \right)^{-2} x^2 \sqrt{1 - x^2} |u^i(2k_Fx)|^2 \]

which is then numerically evaluated for the conductivity.

4.3.2 Results and Discussions
In the case where substrate charged impurity is the only type of scattering center (no adsorbates) and \( d_z = 0 \), the integral in the scattering time equation can be done analytically,

\[
\frac{1}{\tau} = \frac{4\pi n_{imp}^Z Z^2 e_0^4}{\hbar \varepsilon_F} \int_0^1 dx \left( 1 + \frac{1.76}{x} \right)^{-2} \sqrt{1 - x^2} = \frac{0.135 \pi n_{imp}^Z Z^2 e_0^4}{\hbar \varepsilon_F}
\]

So the carrier mobility

\[
\mu = \frac{\sigma}{n e_0} = \frac{2e_0 \varepsilon_F \tau}{\hbar n \hbar} = \frac{7.49 \times 10^{15}}{n_{imp}^Z Z^2} \text{ V}^{-1} \cdot \text{s}^{-1}
\]

Considering that the charged impurities are created by dangling bonds of silicon and oxygen atoms, the case where \( Z = 1 \) was discussed in the original charge impurity theory in graphene [18,30]. However, screening effects by silica itself and surface undulations can change the effective charge magnitude. Since it is likely that \( Z \) is a parameter of sample quality and depends on the method of preparation, it is included in this model as a free parameter. The value of \( n_{imp}^Z Z^2 \) is determined by the carrier mobility, which is often available through experiment. For
example, a typical mobility of $\mu = 2.5 \text{ m}^2\text{V}^{-1}\text{s}^{-1}$ for a high quality exfoliated graphene sample and an effective charge impurity magnitude of $Z = 0.8$ gives an estimated impurity density of $n_{imp}^Z = 4.7 \times 10^{11} \text{ cm}^{-2}$, on the same order of magnitude as experimentally measured charged impurity density of the silica substrate [97].

It is possible to explore the effects of the magnitude of the adsorbate charge/dipole, gate voltage (carrier density), and adsorbate coverage with this model. We will first discuss the effect of screening by a single adsorbate molecule of varying charge/dipole magnitude with a fixed gate voltage. When an adsorbate molecule is attracted to a substrate charged impurity and forms a CI|Graphene|Adsorbate structure, to the carriers in graphene it effectively transforms an $i = Z$ scattering center to $i = Z\delta$ or $Zp$ for charged or dipolar functional groups, respectively. The degree to which the charged impurity is screened and the conductivity affected depends on the magnitude of the adsorbed charge or dipole moment. The calculated ratio of the scattering times and thus the conductivities of a $Z\delta$ or $Zp$ scattering center to an $i = Z$ impurity is plotted in Figure 4.5 as a function of $\delta$ or $p$ for a fixed $k_F$. In both cases, the conductivity is increased when the magnitude of the adsorbed charge or dipole is small. The conductivity then reaches a peak when the in-plane electric field of the adsorbate almost cancels the field of the charged impurity. In the case of the charged functional groups, the cancellation can be complete which results in a sharp resonance peak. Other scattering mechanisms would become important and soften this peak in experimental measurements and verification of the existence of this peak would be a strong indication of adsorbate screening. After the peak, the conductivity decreases due to increasing net field on graphene. Eventually the magnitude of the added charge or dipole becomes so large that the net field is larger than the original field of the charged impurity, at which point the adsorbed configuration has a lower conductivity than the bare charged impurity and the ratio falls below one. Instead of charge transfer, in the adsorbate screening model, whether an adsorbate increases or decreases the conductivity depends on the magnitude of the charge or dipole moment. As is
shown in Figure 4.5, there exists a parameter regime in which NH$_3$ decreases the conductivity because it has a significantly larger dipole moment (1.47 Debye), compared with NO (0.16 Debye) and NO$_2$ (0.32 Debye) [90], which increase the conductivity. We note here that the magnitude of the adsorbate charge/dipole moment is only meaningful with respect to the effective magnitude of charged impurities $Z$. Increasing $\delta$ or $p$ would have the same effect as decreasing $Z$.

Next, we will consider the effect of the gate voltage or carrier density on the screening ability of a given adsorbate. Unlike the previous case where the magnitude is varied, the charged or dipolar functional groups have very different behavior when the Fermi wavevector $k_F$ is changed by the gate voltage. Namely, a dipole moment $pe_0$ is approximately equally effective at screening as a point charge of $k_F pe_0$. This can be seen in the expressions of $u^{Z\delta}(q)$ and $u^{Zp}(q)$. The Fourier transformed potential of the charge is divided by an additional $q$ compared with the potential of the dipole, which would be evaluated at $2k_F x$ when the scattering time is calculated. The $k_F$ dependence of the effective magnitude of the dipole can be understood by considering the carrier scattering process at different Fermi energy. As the Fermi level of graphene moves away from the charge neutrality point, the Fermi surface becomes larger and more momentum is required to scatter the electron. This means that the more oscillatory component of the external potential would be relevant in the scattering. As the Fourier transformed potential of the dipole decays slower than that of a point charge with increasing $q$, the dipole is more and more effective at scattering the electron at higher $k_F$ compared to both the charged impurities and the charged functional groups. This result has two important implications. First, given the typical magnitude of $k_F$ in experiments ($\sim 0 - 0.06 \text{ Å}^{-1}$) and typical molecular dipole moments ($\sim 0.01 - 0.1 \text{ e}_0\text{Å}$), the dipole screening has a much smaller effect on the conductivity than charged function groups created by charge transfer, e.g. a potassium ion. In other words, to be in the regime of the cancellation peak in Figure 4.5, the effective charged impurity magnitude $Z$ would need to be much smaller for a typical dipolar molecule than for a typical charged functional
group. Second, the dipole has a larger effect on the conductivity when the gate voltage is farther away from the charge neutrality point. The typical calculated results of the conductivity before and after adsorption are shown in Figure 4.6. Adding charged functional groups does not change the mostly linear carrier density dependence of the conductivity, which is a feature of point charge scattering. It modifies the carrier mobility depending on the relative magnitude of the charges. In contrast, dipolar molecules represented by the blue curve increases faster than linear due to the $k_F$ dependence in its effective magnitude mentioned above. When the dipole is large enough, it is even possible to have a peak in the carrier density dependent data, represented by the brown curve. This peak is very similar in nature to the peak in Figure 4.5. It happens when the potential of the charged impurity is mostly cancelled by the potential of the dipole. After that, the large $k_F$ causes the dipole potential to overcome that of the charged impurity, decreasing the conductivity.

The gate voltage dependence of the conductivity of chemically doped graphene on silica substrate has been measured by many experimental groups [31, 76, 81, 98]. The result is not

![Figure 4.6](image-url)
symmetric with respect to the charge neutrality point and it cannot be reproduced by our model. However, many possibilities remain to be explored: for charge transfer processes, altering the work function of graphene by gate voltage changes the transfer amount; graphene surface charged by gate voltage may be attracted or repelled to charged impurities on the interface and it may corrugate; the charged impurities are in the electric field created by the gate voltage and their positions might shift as a result of changing gate voltage. Focused studies on these effects are still needed to build a comprehensive theoretical model of which the screening effect of the adsorbates should be an important part.

Our model also provides results on the coverage dependence of the conductivity. In the previous two parts we calculated the conductivity when there is exactly the same amount of adsorbates and charged impurities. This is unlikely in real experiments; the sample could contain a mixture of scattering centers: bare charged impurities, charged impurities screened by an adsorbate molecule, and adsorbate molecules not associated with a charged impurity. For simplicity we assume that when more and more molecules are adsorbed to the surface, the adsorbates will first seek out the charged impurities and form the CI|Graphene|Adsorbate structures until all of them are occupied. The calculated change of conductivity vs. the adsorbate
coverage is shown in Figure 4.7 for a parameter regime where screening a charged impurity would increase the conductivity. Due to the lack of information, the density of charged impurities is arbitrarily chosen to be 0.4 of the density of all the available adsorption sites for this figure. The coverage $\theta$ is defined as the proportion of adsorption sites that are occupied. For both charge and dipole cases, before the charged impurities are saturated, the conductivity keeps increasing with additional adsorption due to increasing screening of the charged impurities. After the impurities are all covered by adsorbates, additional adsorption creates more scattering centers and the conductivity decreases. Generally, charged functional groups not associated with an impurity decrease the conductivity faster than freely oriented adsorbed dipoles.

4.4 Conclusions

Due to the important role played by charged impurities in the electronic transport properties of graphene, it is necessary to include their interaction with adsorbates when we study the mechanism of conductivity change in graphene gas sensing. I have demonstrated that the electrostatic interplay between the charged impurities in the substrate, graphene, and adsorbate molecules (either charged or dipolar functional groups) determines the transport relaxation time in graphene. I proposed a comprehensive and quantitative model which calculates the effect of adsorbates on the conductivity as a function of the magnitude of the adsorbed charge or dipole, gate voltage, and adsorption coverage. Generally speaking, charged functional groups have a larger effect on the conductivity than dipoles. Both of them increase the conductivity when the magnitude is small, canceling part of the original electric field from the charged impurities. However, when the magnitude is large, they overshadow the substrate impurity and decrease the conductivity. The conductivity calculated by this model is symmetric with positive and negative gate voltages. For charged functional groups, the conductivity is changed by an approximately constant ratio that is independent of gate voltage, whereas dipoles screen more effectively at a higher gate
voltage. Regarding the coverage dependence, the effect of adsorption on the conductivity becomes larger initially with larger amount of adsorbates. However, after all the charged impurities are saturated with adsorbates, further adsorption leaves additional charge or free dipoles on the surface, reducing the conductivity.

Compared with existing experiments, the dependence of the conductivity on the magnitudes of the dipole moment matches the qualitative results observed. Namely, with a low effective magnitude of charged impurities or a high gate voltage, NO and NO₂ increase the conductivity, while NH₃ decreases the conductivity due to its larger dipole moment [22,76]. To the best of our knowledge, no systematic measurement of coverage dependent conductivity exists in the literature. The observed gate voltage dependence includes a shift in the conductivity minimum for the molecules [21,76,81] and an additional effect of lowering the carrier mobility for potassium adsorption [31]. The latter effect can be explained in our model with charged ions that overcome the charged impurities, causing the conductivity to be decreased by a constant ratio, i.e., lower carrier mobility. With k_F as the only parameter related to the gate voltage and thus an electron-hole symmetric conductivity, our model cannot explain the shifted conductivity minimum before and after adsorption in the gate voltage dependent data. Additional mechanisms that remove the symmetry are needed, which could come from the relationship between charge transfer and the graphene-substrate capacitor, shifting charged impurities or graphene positions with gate voltage, or considering the possibility of charged impurities and adsorbates altering the local work function, facilitating charge transfer. Although the model presented here alone cannot explain all the observed features in experiments, the screening effects considered are an important ingredient and should be part of the solution to this problem.
Chapter 5
Computing the Conductivity of Disordered Graphene with Kernel Polynomial Method

We explored the static electrical effect of adsorbates on the substrate charged impurities in the previous chapter and our model cannot fully explain the experimental behavior. In this chapter, we study the interaction between the sensor target gases and defects of graphene itself. To employ density functional theory to this study, it is necessary to narrow down the problem to the most commonly studied defect of graphene – carbon vacancies, and the gas molecule to which graphene is the most sensitive – nitric oxide (NO).

In the process of this study, we have developed procedures and computer codes that extract tight-binding models from DFT calculations, which are then extended to millions of atoms and solved for density of states and dc conductivities. The methodology is very general and it has been detailed as related to our study in sections 5.1 and 5.2. In sections 5.3, I will discuss the results from application of the methods to NO and carbon vacancy of graphene.

5.1 Wannier Functions from Density Functional Theory

Wannier functions are defined as Fourier transformations of Bloch eigenfunctions of a solid state system. For a single band with Bloch functions $\psi_k(r)$, the Wannier functions are

$$\phi_R(r) = \frac{V}{(2\pi)^3} \int_{BZ} \frac{dk}{e^{-i\mathbf{k} \cdot \mathbf{R}}} e^{i\mathbf{k} \cdot \mathbf{R}} \psi_k(r)$$

where $V$ is the real-space volume of the unit cell and $\mathbf{R}$ is a lattice vector. It can be easily proved that Wannier functions with different lattice vectors are associated by a translational shift

$$\phi_R(r) = \phi_{R+R'}(r + R')$$
and one band corresponds to one unique Wannier function centered at various lattice points. Because the Bloch functions are only defined up to an overall phase, the Wannier function defined above is not unique. The phase $\theta(k)$ can be chosen to obtain localized Wannier functions

$$\phi_R(r) = \frac{V}{(2\pi)^3} \int_{BZ} d\mathbf{k} \; e^{-i\mathbf{k} \cdot \mathbf{R}} e^{i\theta(k)} \psi_k(r)$$

When multiple bands and Bloch functions $\psi_{mk}(r)$ are present, the arbitrary choice of phase becomes an arbitrary choice of a unitary transformation. The Wannier functions can be written as

$$\phi_nR(r) = \frac{V}{(2\pi)^3} \int_{BZ} d\mathbf{k} \; e^{-i\mathbf{k} \cdot \mathbf{R}} \sum_m U_{nm}^{(k)} \psi_{mk}(r)$$

which further allows mixing of the multiple Bloch states at the same k point. The transformation can be chosen to obtain the most localized Wannier functions, which are called maximally localized Wannier functions (MLWFs) and the numerical implementation of the process in implemented in the package wannier90 [99] which is interfaced with many DFT packages to use the DFT Kohn-Sham orbitals as inputs. Transforming DFT Hamiltonians and wavefunctions into Wannier function basis can provide insights into atomic bonding, as well as allow simulations of properties near the Fermi energy at a much lower computational cost than DFT.
The steps needed to obtain Wannier functions using Quantum Espresso and wannier90 are illustrated in Figure 5.1. Essentially, a self-consistent DFT calculation is done to obtain the ground state density, which is followed by a non-self-consistent calculation on a probably finer k-mesh for the Bloch state. The Bloch wavefunctions are then used as inputs in the Wannier function calculations. For the convergence of the Wannier function calculations, a few parameters should be tuned, often in a trial-and-error fashion. The first is the initial projection, which alters the starting point of the calculation and is used when the optimization settles into a local minimum rather than a global one. This includes the selections of the total number of Wannier functions, the atoms on which to start projection, symmetry, and similar related considerations. Secondly, the bands to extract the Wannier functions are not always isolated, which will require disentanglement. The wannier90 package uses an outer energy window and an inner (frozen) energy window to help with the disentanglement. The former defines an energy window from which the most localized Wannier functions are selected from a larger number of bands and potentially partial bands, while the latter defines an energy window in which all Bloch states are
used, effective making the Wannier function exactly a transformation of basis from an extended one to a localized one. A typical choice is to incorporate a few bands near the Fermi level into the inner window so that they are represented exactly. The outer window is then chosen to encompass the correct number of bands, and thus Wannier functions.

In this study, a large cell is needed in order to model defects of graphene, especially for defects with low concentration. This requires the model to be simplified from one based on DFT. We use the process described above to obtain the Wannier functions and the Hamiltonian in the basis of the Wannier functions from DFT calculations. For this purpose, we first do a DFT calculation of the defect in a cell of 2 by 2 graphene unit cells. The wannier90 optimization routines are run, and the resulting Wannier functions and Hamiltonian are reviewed. A converged calculation gives a real Hamiltonian and requires adjusting the outer window, the inner (frozen) window, and the initial projections. Each Wannier function is assigned to a local part of the cell (an atom, a bond, several atoms, etc.) and a nearest-neighbor tight-binding Hamiltonian is extracted from the Wannier Hamiltonian. This Hamiltonian is easily extendable in the sense that it can be constructed for a larger cell or any arbitrary concentration and distribution of the defect. Note that by truncating the hopping terms to the nearest neighbor, many terms in the Hamiltonian needs to be dropped and the resulting tight-binding band structure is not able to follow the DFT band structure perfectly. To mitigate this truncation and also to reduce the effects of defect to defect interactions, the band structure of a larger cell with 4 by 4 graphene unit cells and one defect is calculated using DFT and the tight-binding parameters are optimized to fit a few bands near the Fermi level at high symmetry points (Γ, K, M). A k-point grid of 4 by 4 by 4 is used by the wannier90 package in the Wannier function computation for all the systems.

5.2 Kernel Polynomial Method
The tight-binding Hamiltonian with optimized parameters is used to calculate the density of states and conductivity of the constructed systems using the kernel polynomial method (KPM) [100]. The KPM expands the needed function with Chebyshev polynomials of the first kind \( (T_n) \) and provides a way to truncate the infinite series maintaining the positivity and normalization, providing optimal resolution [100]. The tight-binding Hamiltonian can be written generally as

\[
H = \sum_i \epsilon_i c_i^\dagger c_i + \sum_{ij} t_{ij} c_i^\dagger c_j,
\]

where \( \epsilon_i \) is the site energy of the \( i \)th orbital and \( t_{ij} \) is the hopping integral between the \( i \)th and the \( j \)th orbitals. Since the Chebyshev polynomials are only defined on \([-1,1]\), the Hamiltonian needs to be scaled so that all the eigenvalues are within this range.

\[
\tilde{H} = \frac{H}{C}
\]

The Chebyshev expansion coefficients/moments for both the density of states and the conductivity can be expressed as traces. The former can be written as

\[
\tilde{\rho}(E) = \frac{1}{D} \sum_{k=0}^{D-1} \delta(\tilde{E} - \tilde{E}_k),
\]

where the tilde symbol denotes that the density of states and eigenvalues are those of the scaled Hamiltonian, and \( D \) is the dimensionality of the Hamiltonian. The corresponding expansion moments are

\[
\mu_n = \int_{-1}^{1} \tilde{\rho}(E) T_n(E) dE = \frac{1}{D} Tr[T_n(\tilde{H})]
\]

The zero-temperature dc-conductivity tensor is evaluated using the Kubo-Greenwood formula

\[
\tilde{\sigma}^{(ab)}(E) = \frac{2\pi \hbar}{A} Tr[J^{(a)} \delta(\tilde{E} - \tilde{H}) J^{(b)} \delta(\tilde{E} - \tilde{H})],
\]
where $A$ is the area of the sample cell. $J$ is the current density operator defined through the Heisenberg equation of motion for the polarization operator,

$$J^{(a)} = -\frac{ie}{\hbar} \sum_{ij} t_{ij} \left( r^{(a)}_j - r^{(a)}_i \right) c^\dagger_i c_j,$$

where $r^{(a)}_i$ is the $\alpha$-component of the position of the $i$th atom. Treating the two $E_s$ as two different variables, the conductivity can be expanded with a two dimensional KPM. The expansion moments are

$$\mu_{nm} = \int_{-1}^{1} \int_{-1}^{1} \tilde{\sigma}^{(ab)}(E_x, E_y)T_n(E_x)T_m(E_y) dE_x dE_y = \frac{2\pi \hbar}{A} Tr[J^{(a)}T_n(H)]T^{(b)}T_m(H)]$$

The expansion moments can then be evaluated using the recursive relation of Chebyshev polynomials

$$T_{n+1}(x) = 2xT_n(x) - T_{n-1}(x)$$

and stochastic evaluation of traces [101]

$$Tr[A] \approx \frac{1}{R} \sum_{i=1}^{R} \langle r_i | A | r_i \rangle$$

where $|r_i\rangle$ is a random state defined through

$$|r\rangle = \sum_{i=1}^{D} \xi_i|i\rangle$$

where $Re[\xi_i]$ and $Im[\xi_i]$ are independent identically distributed random variables centered at zero.

In the density of states calculation, we use a Hamiltonian representing a cell that is as large as 4096 by 4096 unit cells of graphene containing approximately $10^7$ atoms and the density
is expanded up to Chebyshev order 4096. For such a large matrix, we found that one initial random state is sufficient to achieve convergence. The conductivity calculation is done in three steps, as is illustrated in Figure 5.2. First, the vectors $J^{(b)}T_m(\vec{H})|r\rangle$ are calculated to the highest necessary order using the recursion relation and the results are written to disk. Multiple nodes (up to 512 in our case) are used in the second step. Each node reads in a few of the vectors from the first step and independently compute $T_n(\vec{H})f^{(a)}|r\rangle$. The inner product of each pair of vectors is then calculated and used in the third step, in which a node collects all the inner products and reconstruct the conductivity with

$$\tilde{\sigma}(\vec{E}) = \sum_{n,m=0}^{N-1} \mu_{nm} h_{nm} g_n g_m T_n(\vec{E})T_m(\vec{E}) \pi^2 (1 - \vec{E}^2)^2,$$

where $g_n$ is the Jackson kernel and $h_{nm}$ is a normalization factor which gives a factor of 2 whenever one of its subscript is 0. For the conductivity calculation, $N = 2048$ and the cell is as large as 1024 by 1024 unit cells of graphene. We found that the average of the conductivities computed with 8 different defect distributions and $R = 1$ initial random vector gives a sufficient result for qualitative conclusions.

5.3 NO and Carbon Vacancies of Graphene
As we have discussed in chapter 4, a possible explanation for the sensing capability is that it is not from intrinsic graphene but rather from defects and imperfections, which are abundant in the silica substrate that is typically used for graphene [18,97] as well as in graphene samples prepared with chemical vapor deposition (CVD) [10,11]. We have discussed the substrate impurities in chapter 4. For defects in graphene itself, due to the ability of the carbon atoms to reconstruct and form rings of various sizes, various types of defects have been proposed with carbon vacancies being one of the most commonly studied [23]. It has been shown that vacancies create resonant impurity states that are localized and does not participate effectively in electronic transport, lowering the conductivity [50,102]. NO adsorption into these vacancies may increase the conductivity either directly or by forming other defects such as nitrogen substitution defect or a bridging oxygen. In this section, we investigate this hypothesis by calculating the conductivity using the Wannier function calculation and KPM described above.

Two density functional theory (DFT) packages have been used in various stages of this study. Dmol3 [93] is used to calculate the total energy of various systems. The adsorption energy

![Figure 5.3](image)

**Figure 5.3** The top panel shows the relaxed structure of pristine graphene and the 4 types of defects that are studied here. The computed values of the labeled distances can be found in Table 1. The isosurfaces of the Wannier functions that are important for the electronic bands near the Fermi level are shown in the bottom panel along with labels indicating the name of each Wannier function and which defect it originates from.
of a NO molecule on a carbon vacancy of graphene is derived from the total energies of separate graphene and NO systems, and the total energy of the relaxed structure after adsorption. The calculation is done with generalized gradient approximation (GGA), Perdew-Burke-Ernzerhof functionals (PBE) [103], and spin unrestricted. A basis set of double-numeric quality localized wavefunctions is used with polarization functions (DNP) and an atomic real-space cutoff of 3.7 Å. In relaxation calculations, the initial configuration is compiled by removing a carbon atom from a supercell that contains 4 by 4 unit cells of graphene and replace it with an NO molecule whose nitrogen atom is in the graphene plane. The cell is then relaxed with a geometry optimization calculation which uses a Monkhorst-Pack k-point grid of 12 by 12. Quantum Espresso [104] is used to calculate the band structure of the various graphene systems with defects, and to fit the Wannier functions due to its native integration with the wannier90 package. We performed the calculations with GGA (PBE) ultrasoft pseudopotentials. The Kohn-Sham orbitals are expanded in a plane-wave basis set with cutoffs of 40 Ry and 320 Ry, for the wave

Figure 5.4 The distance between the oxygen and the nitrogen atoms ($d_{NO}$, red), the distance between the nitrogen atom and the graphene plane ($d_{Nz}$, red), and the total energy ($E_{DFT}$, black) as a function of the displacement of the oxygen atom away from its relaxed position in the adsorption of NO on a carbon vacancy site of graphene as obtained through DFT calculations. The displacement is in the direction that is perpendicular to the graphene plane and the systems are relaxed after the oxygen atom and 4 carbon atoms relatively far away from the defect are fixed in position.
function and the charge, respectively. The computation cell is as large as 4 graphene unit cells with 20 Å of vacuum between each layer. The sampling of the Brillouin zone was done using a Monkhorst-Pack grid of 5 by 5 by 10.

5.3.1 NO Chemisorption on Graphene Vacancies

The adsorption energy of a NO molecule on a carbon vacancy site of graphene is studied first using DFT. The relaxed system after NO adsorption is shown in Figure 5.3. The total energy is calculated for this system as well as for the transitional states, which are obtained by displacing the oxygen atom from the relaxed position in the direction perpendicular to the graphene plane and then relax the system with the positions of the oxygen atom and a few carbon atoms fixed. The results are summarized in Figure 5.4. As the oxygen atom moves away from the graphene plane, the nitrogen atom follows, although it is still bonded with the carbon atoms. This causes both the NO bond length and the distance between N and the graphene plane to increase. The process continues until the oxygen atom is about 1.2 Å away from the relaxed position, where the effect of the graphene sheet on the nitrogen atom becomes weak and the NO bond length starts to approach that of an isolated NO molecule (1.15 Å). The NO molecule is essentially desorbed at this distance. This interpretation is corroborated by the DFT total energy results, which shows no energy barrier during the approach and a large increase in energy around 1.2 Å. Subtracting the total energy of the adsorbed system from that of the separated NO molecule and graphene system, we obtain an adsorption energy of 5.3 eV. This means that NO molecules are extremely inclined to be adsorbed into carbon vacancies of graphene and thermal fluctuation is not enough to provide the energy for NO to desorb.

Wannier functions are extracted from DFT calculations. The orbitals responsible for the bands near the Fermi level are obtained and selected as tight-binding basis states, and the tight-binding parameters are readily available and generalizable. This method has been successfully
applied to graphene’s $\sigma$ bands, which obtained pz-like Wannier functions and perfect fit with the DFT bands [105]. The tight-binding parameters obtained through the Wannier function calculation and further fitting can be found in Table 5.1. The carbon vacancies are modeled by the graphene tight-binding model except that hopping between vacancy sites and their neighbors are set to zero. For NO substitutions, we found the most important WFs for the band structure near the Fermi level is one pz-like WF for each carbon atom ($C - p_z$) and three sp2-like WFs centered on the oxygen atom ($O - sp2$), as shown in Figure 5.3. The fitted band structure compared with DFT results are shown in Figure 5.5. The WF tight-binding includes hopping energies between any pair of WFs and it produces bands that are essentially identical to DFT within the inner window. Although the nearest neighbor tight-binding model cannot fit the DFT to the extent of the WFs, it produces bands with similar geometry, especially near the Fermi level and it allows the model to be generalized, in the sense that the tight-binding Hamiltonian can be constructed for any cell size or any defect distribution and concentration. It serves as an effective model for NO substitutions in graphene.

<table>
<thead>
<tr>
<th>Table 5.1</th>
<th>Notable distances in the defect systems calculated with DFT, and tight-binding parameters obtained through band fitting.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Distances (Å)</td>
<td>$d_{cc}$ 1.42</td>
</tr>
<tr>
<td>Site energies (eV)</td>
<td>$\epsilon_{C-pz}$ 0</td>
</tr>
<tr>
<td>Hopping energies (eV)</td>
<td>C-pz, C-pz -2.70</td>
</tr>
</tbody>
</table>


The Hamiltonians of graphene containing 1% (as a proportion to the number of carbon atoms in pristine graphene of the same size) of each type of defects are constructed and the density of states is calculated using the KPM method. Note that when constructing Hamiltonians for all types of defects discussed in this work, we distribute them in the cell randomly and then eliminate defects that are neighboring other defects, so the actual amount of defects is slightly lower (in this case about 500 vacancies are removed from 330000). The calculation results are shown in Figure 5.6, along with comparisons pristine graphene. The density of states of carbon vacancies in graphene agrees with previous results from the literature using similar methods [29]. The peak near the neutrality point consists of resonant impurity states that are localized around the vacancies. The density of states is also symmetric about the neutrality point since the electron-
hole symmetry is not broken by this model. For NO substitutions in graphene, there is hopping between the three \( O - sp^2 \) WFs and a symmetrical linear combination of the three WFs is always an eigenstate of the Hamiltonian and it is completely localized at the oxygen atom, which is reflected in the sharp peak at \( \sim 6.3 \) eV in the density of states. The remaining two linear combinations of these three WFs are connected to the carbon WFs and they create two separate peaks near the neutrality point, which increases in weight when the concentration of NO increases.

For conductivities, two types of graphene samples are considered. When graphene is placed on a substrate, which has a much larger density of states, the Fermi level of the graphene sheet can be considered ‘pinned’. Electron doping into such a graphene system is compensated by

---

**Figure 5.6** Density of states obtained from kernel polynomial calculations for the 4 types of defects studied in this study. The density of states of pristine graphene (black, dotted) is included in each panel for comparison. The panels show the density of states of graphene containing (a) NO substitutions \((E_F = 0.069 \text{ eV})\), (b) carbon vacancies \((E_F = 0 \text{ eV})\), (c) N substitutions \((E_F = 0.436 \text{ eV})\), and (d) N substitutions and bridging O atoms \((E_F = 0.512 \text{ eV})\).
Figure 5.7 The calculated conductivities of pristine graphene and graphene containing 1% defects. (a) The conductivities zoomed in onto the experimentally accessible energy range. The energy is relative to the carbon site energy in the tight-binding calculation. (b) Same as above except the energy is relative to the Fermi energy of each system. (c) The conductivities in the full energy range of the tight-binding calculation.

exchanges with the substrate. Therefore in this case it is reasonable to compare the conductivities with the carbon site energy as the reference energy. Graphene prepared with chemical vapor deposition on silica substrate is normally p-doped [10,11]. Although the position of the Fermi level is not known exactly and supposedly varies between samples, it is not likely to be lower than -0.37 eV, which corresponds to $n = 10^{13} \text{ cm}^{-2}$ in pristine graphene. The second situation is when graphene is isolated. Then it is more appropriate to compare the conductivities by aligning the Fermi level of each system and use it as the reference energy. In our calculation, the Fermi levels are determined by integrating the density of states (Figure 5.6).

Since carbon vacancies does not change the Fermi level and 1% of NO only moves it slightly, their conductivities do not vary much between the two types of graphene samples. The
calculated conductivities are shown in Figure 5.7. In the range that is typically accessible to experiments, NO substitutions in graphene and vacancies in graphene have approximately the same constant plateau of conductivity in the energy range of roughly -0.2 eV to 0.2 eV and they are both lower than the conductivity of pristine graphene, especially away from the charge neutrality point. This reveals the nature of the states in the two peaks of the NO density of states – they are localized states similar to those formed by the vacancies and they do not participate in the conduction.

5.3.2 Oxygen Dissociation

NO adsorbed into vacancies of graphene may create other adsorption species. Our DFT calculations show that dissociative adsorption, effectively converting a NO substitution to a nitrogen substitution and a bridging oxygen adsorption, further lowers the total energy by about 1.4 eV, with a weak dependence on the relative positions of the two defects. The oxygen may diffuse and desorb in the form of oxygen molecules [106,107]. It has also been proposed for boron nitride nanotubes that the oxygen atom which is relatively weakly bonded to nitrogen may react with another NO molecule in the gas, forming NO$_2$ [108]. The same process can also happen for NO in graphene. These processes may be present at the same time and we have studied the conductivity of two extreme cases. One is when all the oxygen atoms have left the surface, either through O$_2$ or NO$_2$, which leaves nitrogen substitutions in graphene. The other is when oxygen is dissociated and diffusing freely, so that there is no correlation between the locations of N substitutions and O adsorptions but the amount of the defects are the same.

To obtain an effective tight-binding model, the two types of defects are calculated with DFT and Wannier function. The resulting structure and the important WFs are shown in Figure 5.3. Both the nitrogen substitution [109] and the bridging oxygen [107,110] relaxed structure are in line with earlier results. The nitrogen atom fits the carbon vacancy very well, causing no significant distortion of the graphene bond lengths. Its p$_z$-like WF is also very similar to that of a
carbon atom. On the other hand, the bridging oxygen raises the two connected carbon atoms out of the graphene plane. Their \( p_z \) orbitals are also removed from the Fermi level by bonding with the oxygen orbitals. The important WFs for this system are found to be: one \( p_z \)-like WF for each carbon atom except the two connected to oxygen, a WF centered on the oxygen atom that has the symmetry of a \( p \)-orbital and is perpendicular to the C-C bond under the oxygen, a WF similar to the above but is parallel to the underlying C-C bond, and a large WF centered near the oxygen atom with significant values around the whole C-O-C region. The tight-binding parameters for these two systems obtained through the band fitting process can be found in Table 5.1.

Hamiltonians with random distributions of these defects are constructed. The density of states and conductivity are calculated using KPM. The results are also shown in Figure 5.6 and Figure 5.7. The nitrogen substitutions act similarly as a carbon atom other than the additional electron. It shifts the Fermi level significantly but only creates a very small increase in the density of states on the positive side of the charge neutrality point. Graphene with nitrogen substitution has a conductivity that is less than pristine graphene since they are still defects and they scatter electrons in conduction, but it is by far the least disruptive to conduction in all the defects considered in this study. It is also similar to results from an earlier study [111]. When an equal amount of bridging oxygen atoms are added in, the density of states in further increases on the negative side of the charge neutrality point. The conductivity is slightly higher than that of graphene with vacancies and graphene with NO substitution in the experimentally accessible energy range, which shows that these additional states around the charge neutrality point are not as localized as the ones formed by vacancies. On the other hand, with both N substitutions and bridging oxygens the system has twice the amount of defects comparing with other systems and it has the lowest conductivity away from the charge neutrality point. To summarize, when the oxygen leaves the nitrogen atom after adsorption into a carbon vacancy, the conductivity increases, which could explain the experimentally measured increase in the conductance of
The presence of UV light in these experiments may facilitate this process through either heating or excitation of the bonding electrons.

5.3.3 Conclusions

In summary, we have studied the interaction between NO and carbon vacancies of graphene, and calculated the impact of NO and various related defects on the conductivity of graphene using a combination of first-principle methods, tight-binding calculations. The orbitals that are important for the physics near the Fermi level are extracted from DFT calculations of the defects, and tight-binding Hamiltonians of cells approaching experimental sizes are constructed and evaluated using the kernel polynomial method. NO molecule is found to adsorb onto carbon vacancies with a high adsorption energy of 5.3 eV in a barrier-less process, but the localized states it creates mean that it behaves similarly to vacancies in electronic transport and does not change the dc-conductivity. However, when the oxygen atom leaves the nitrogen atom, either through reaction with NO in the atmosphere or bonding with carbon directly, the conductivity is increased, especially when only the nitrogen substitutions are left. This could be the reason why experiments have detected partially-reversible increase in the conductance of graphene sensors when they are exposed to NO. The exact mechanism for the oxygen dissociation and the effect of the UV light in this process can be studied in further research.
Chapter 6
Conclusions and Future Projects

To sum up the dissertation, I have studied the transport behavior of graphene with adatoms, adsorbates, and defects using various theories and computational tools. In terms of modeling solid state systems, I used both density functional theory and tight-binding models. In terms of the conductivity, I have used the semi-empirical variable range hopping theory, the decoherent first-order Born approximation, and the Kubo-Greenwood formula which treats the system coherently. Thousands of lines of code are written to either implement these theories or to use existing packages, which are general and can be used in future studies, especially the implementation of the kernel polynomial method.

In chapter 2, we have demonstrated that localization due to point defects in graphene follows power laws, which is different from conventional semiconductors. The variable range hopping which relies on the overlap of localized states is thus also different for graphene and follows a power law as well. However, we should remember that graphene and semiconductors are different in other aspects as well. For example, due to the lack of bandgap, extended Bloch states are present near the Fermi level and should contribute to the conductivity. A model that is really equivalent to VRH in graphene would have to include these states as well. It is also entirely possible that due to the less dramatic localization and no bandgap, semi-empirical models like VRH are not appropriate for graphene.

In chapter 3, 4, and 5, we first assumed charge transfer as the mechanism of the graphene gas sensing experiment and analyzed the experimental data for the adsorption-desorption kinetics from which we proposed possible ways to improve the sensing capabilities. We then reexamined the charge transfer explanation and proposed two new mechanism. The first one includes the
charged impurities in the substrate of graphene into the model, which are then screened by the charges and dipoles of the adsorbates, causing the scattering and thus the conductivity to change. The second one considers interaction between gas molecules and defects of graphene itself, specifically between NO and carbon vacancies. Both models represent physical processes that should have happened during the sensing, but neither could fully explain the experiments independently. Future research in this area could go in several directions. First, partially due to the lack of data, it is unclear how our two mechanisms can work together, which can be studied further with the help of more experimental evidence. Secondly, with a better characterization of the graphene sample used in these experiments, we can expect a better understanding of the population and distribution of defects. The interaction between gas molecules and all types of defects can be calculated and combined. Finally, a large contribution to the conductivity change may be due to the contact, which has been proposed for carbon nanotube gas sensing [77]. When the mechanism of graphene gas sensing is finally clear, we can then move on to investigate why our collaborators have obtained particularly high sensitivity with constant illumination of UV light. We have speculated that its effect may either be helping with transition of electronic states or simply heating, but a more rigorous theoretical model will be required to eventually solve this puzzle.
Bibliography


Vita

Sangzi Liang was born in Haining, Zhejiang province, China, on November 18th, 1986. After attending Haining Senior High School between 2002 and 2005, he studied applied physics at the University of Science and Technology of China in Hefei, Anhui province, China between 2005 and 2009. Since then, he has been working towards his PhD in physics at the Pennsylvania State University.