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Defect-Related Magnetic and Electronic Properties of Graphene

Arash Akbari-Sharbaf

The University of Western Ontario

Supervisor
Michael G. Cottam
The University of Western Ontario

Graduate Program in Physics

A thesis submitted in partial fulfillment of the requirements for the degree in Doctor of Philosophy

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DEFECT-RELATED MAGNETIC AND ELECTRONIC PROPERTIES OF GRAPHENE

(Thesis format: Monograph)

by

Arash Akbari-Sharbaf

Graduate Program in Physics

A thesis submitted in partial fulfillment
of the requirements for the degree of
Doctor of Philosophy

The School of Graduate and Postdoctoral Studies
The University of Western Ontario
London, Ontario, Canada

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ABSTRACT

A fundamental study of the electronic and magnetic properties of graphene modified by defects is presented. This work includes both theoretical and experimental investigations of graphene, graphene-metal composites and related structures, together with edge effects. The theoretical model employed for the description of $\pi$-electrons in graphene is based on the tight-binding Hamiltonian. On the experimental side we place special emphasis on the electron spin resonance technique (ESR).

After describing the theoretical and experimental methods, we first investigate the origin of paramagnetism in graphene nanoribbons (GNRs) using a combination of ESR and other characterisation techniques, corroborated by a theoretical model. We find two paramagnetic species in our GNRs related to structural defects. Subsequently, interactions between magnetic species, introduced in GNRs as impurities are investigated. These are RKKY-type indirect exchange interactions involving the $\pi$-electrons in graphene. The influence of zigzag edges on the RKKY interaction is looked at in detail by using a Green's function method for the bulk and edge modes of GNRs. We also study the influence of metal nanoparticles on the electronic properties of graphene thin films. Specifically, we focus on copper nanoparticles (Cu-NPs), which are expected to form weak bonds with graphene preserving its electronic properties. We introduce a doping mechanism for this system related to the electron-hole symmetry breaking of the electronic band in graphene when its surface is decorated with Cu-NPs. Additional discussion on the paramagnetic nature of other materials, including Au$_{25}^+$ molecular nanoclusters and defects in silicon epilayers are provided. These investigations focus on the ESR techniques and relevant theoretical models for interpreting the data.
Keywords: Graphene, nanoribbons, RKKY interactions, pi-electrons, tight-binding model, graphene-metal composites, electron spin resonance, edge modes, Green's functions.
CO-AUTHORSHIP STATEMENT

The work presented in Chapter 5 was done in collaboration with Sabastine Ezugwu and Dr. Shafiq Ahmed. Dr. Shafiq Ahmed prepared the graphene-thin films. Sabastine Ezugwu did the work involving sputtering, scanning Kelvin probe force microscopy, conductivity, and UV-visible measurements. I did scanning electron microscopy measurements, data analysis, literature review, and theoretical modeling. This work has not been published.

The first section of Chapter 8 is based on a publication with Mahdi Hesari, Mark S. Workentin, Giovanni Fanchini [1]. Some additional discussions on temperature independent Van Vleck paramagnetic nature of Au\textsubscript{25}\textsuperscript{+} while also be presented, which has not yet been published, which was done independently by me. All sample fabrication and characterizations were carried out by Mahdi Hesari under the supervision of Prof. Mark S. Workentin, except for electron spin resonance (ESR) characterization. The theoretical models and simulations for interpreting the ESR spectra was also carried out by.

The second section of Chapter 8 is based on a publication in collaboration with Jean-Mark Baribeau, Xiaohua Wu, and David J. Lockwood at the National Research Council (NRC) of Canada, and Giovanni Fanchini. All sample fabrication and characterization were carried out by the group at NRC, except for electron spin resonance (ESR) characterization. ESR measurements, data analysis, literature survey, and the writing of the manuscript was done by me.
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CHAPTER 1

Introduction

Nature has chosen carbon as the fabric of life, and now it may be possible to make carbon the fabric of technology. Perhaps one of the reasons why carbon has been so successful at forming such complex, functioning, self-reproducing, ever-evolving living structures, such as ourselves, is that carbon is highly versatile. Carbon can support the formation of many structures with immensely different properties. It is this variation in structure and property and the time scales associated with evolutionary processes that have given rise to the bewildering complexity of living organisms. Reflecting on nature, it is clear that we have not even scratched the surface of what is possible, in terms of science and technology developments.

One of the structures that carbon can support is graphene, which is the main subject of this thesis. From theoretical and experimental investigations of graphene and related structures, graphene itself can exhibit a vast variation in properties. In terms of its electronic properties it can be a conductor, a semi-metal, or a semi-conductor. In terms of its magnetic properties it can support magnetic moments, magnetically polarized edges, and spin currents. It is an excellent thermal conductor, highly transparent, extraordinarily robust, flexible, and much more. Interestingly, all these properties can be tailored without the introduction of foreign species (e.g., adatoms). For instance, we will see that the dimension and chirality of graphene has dramatic effects on its properties, while vacancies and edges can produce magnetism. However, the introduction of foreign species will inevitably play an important role in future applications of graphene-based devices.
Even though a vast amount of research has been carried out on graphene and related structures, the developments have not necessarily translated to device applications in technology. Perhaps the major stumbling block in the development of such technologies is the limitation in fabrication techniques.

Most of this thesis is related to the electronic and magnetic properties of graphene when modified by defects. In this introductory chapter we present some of the relevant electronic properties of pristine graphene, and later discuss the nature of defects in graphene. The discussions of defects will cover both intrinsic (i.e., structural defects) and extrinsic (i.e., introduction of foreign species). Special emphasis will be placed on graphene nanoribbons (GNRs), stripes of graphene.

1.1 Overview of pristine graphene and its properties

For a review of the electronic properties of graphene refer to [1, 2]. Pristine graphene is a two-dimensional network of carbon atoms forming a honeycomb lattice. This structure arises because of the nature of bonds between the carbon atoms. Carbon has four valence electrons in the 2s and 2p orbitals. These orbitals are susceptible to mixing when bonds form in order to reduces the cohesion energy of the structure. In the case of graphene an s-orbital electron mixes with two p-orbital electrons forming three strong covalent or sigma (σ) bonds with neighbouring atoms. This is refer to as $sp^2$ hybridization. Since the bonds are in-plane and the angle between bonds are 120° in order to maximize their separation, the bonds produce the two-dimensional honeycomb structure of graphene. The remaining p-orbital valence electrons extend below and above the graphene plane with a vanishing distribution in
the plane of the graphene lattice. These out-of-plane electrons also form bonds with neighbouring atoms, but are much weaker $\pi$-bonds. The $\sigma$- and $\pi$-electrons are effectively decoupled, since they are spatially separated and the scaling of their bond energies are significantly different. Carbon can also form other hybridization schemes. For instance in diamond one $s$-orbital electron mixes with three $p$-orbitals, producing four sigma bonds (i.e., $sp^3$ hybridization) in a three dimensional tetrahedral network. Both $sp^3$ and $sp^2$ hybridizations are shown in Fig. 1.1.

![Diagram of sp$^3$ and sp$^2$ hybridization]

**Fig. 1.1:** Schematic of $sp^3$ and $sp^2$ hybridization of carbon.

Most of the electronic properties of graphene are governed by the out-of-plane $\pi$-electrons. This is because the strong $\sigma$-bonds are highly localized at the carbon sites and generate a wide electronic band gap. The $\sigma$-bonds form an insulating backbone [3]. On the other hand the $\pi$-electrons forming the weaker $\pi$-bonds are more mobile, generating a zero-gap electronic band, as can be calculated using a simple tight-binding model (see Chapter 2).
with nearest neighbour (NN) or next NN hopping [1]. A schematic of both the $\sigma$- and $\pi$-electronic density of states is shown in Fig. 1.2(a). The $\pi$-electronic band falls inside the energy gap of the $\sigma$-electronic band and therefore, the low lying excitations of the system are governed by the $\pi$-electrons.

Fig. 1.2: The $\pi$-electron (a) density of states and (b) dispersion relation for graphene. The density of state shown in panel (a) is a schematic, illustrating a wide-gap $\sigma$-band, and the zero-gap $\pi$-band. The $\pi$-band falls inside the $\sigma$-band energy gap.

The carbons atoms in graphene are arranged in a hexagonal array with NN carbon-carbon distance of $a \approx 1.42\text{Å}$ [1]. In order to assign translational vectors for the hexagonal lattice a bases of two atoms per unit cell must be used. This has dramatic consequences on the properties of graphene, as we will see. The translational vectors are

$$\tilde{a}_1 = \frac{\pi}{2}(3, \sqrt{3}) \text{ and } \tilde{a}_2 = \frac{\pi}{2}(3, -\sqrt{3}),$$

(1.1)

and their reciprocal-lattice counterparts are

$$\tilde{b}_1 = \frac{2\pi}{3a}(1, \sqrt{3}) \text{ and } \tilde{b}_2 = \frac{2\pi}{3a}(1, -\sqrt{3}).$$

(1.2)
Perhaps the most important features of the band structure for graphene are the so called "Dirac points" in reciprocal space given by (for example)

\[
\vec{K} = \left( \frac{2\pi}{3a}, \frac{2\pi}{3\sqrt{3}a} \right) \quad \text{and} \quad \vec{K}' = \left( \frac{2\pi}{3a}, -\frac{2\pi}{3\sqrt{3}a} \right).
\]

The Dirac points coincide with the Fermi level in the \( \pi \)-electronic dispersion relation and therefore govern the nature of propagation of \( \pi \)-electrons in graphene. The form of the dispersion relation for graphene is a consequence of the bipartite nature (2 atoms per unit cell) of the hexagonal lattice, and the decoupling of the \( \pi \)-electrons from the \( \sigma \)-electrons, in the NN tight-binding model.

The \( \pi \)-electronic dispersion relation of graphene using the tight-binding approximation with NN hopping is given by

\[
E = \pm t \sqrt{4 \cos^2 \left( \frac{\sqrt{3}}{2} k_x a \right) + 4 \cos \left( \frac{\sqrt{3}}{2} k_y a \right) \cos \left( \frac{\sqrt{3}}{2} k_x a \right) + 1},
\]

where the + (−) sign corresponds to the conduction (valence) band, \( k_x \) and \( k_y \) are the wavenumbers in \( x \) and \( y \) direction, and \( t \) is the \( \pi \)-electron NN interaction or hopping energy, reported to be \( t \approx 2.8 \text{eV} \) [3]. The dispersion relation is plotted in Fig. 1.2(b). The six points in the plot at zero energy where the valence and conduction bands touch are the Dirac points, with only two adjacent Dirac points being unique. Near a Dirac point the dispersion is linear, as explained later. The linear dispersion relation of \( \pi \)-electrons near the Dirac point corresponds to a non-dispersive propagation of the quasi-electrons with a zero effective mass. The Fermi velocity of these electrons is given by \( v_f = 3ta/2 \approx 10^6 \text{m/s} \) [4]. The non-dispersive nature of these mobile \( \pi \)-electrons, near the Fermi level gives rise to a carrier mobility that tends to infinity. However, since the density of states at the Fermi level (or
density of charge carriers) tends to zero (see Fig. 1.2(a)), the conductivity of graphene is finite with low energy loss. In addition, the non-dispersive nature of the Dirac-electrons gives rise to a non-zero minimum conductivity.

The band structure given by Eq. (1.4) implies perfect electron-hole symmetry at half filling. Because of the linear nature of the dispersion relation, \( \pi \)-electrons in graphene are often treated relativistically, using the 2-D massless Dirac equation [5]. The consequence of the zero effective mass associated with the dispersion of the \( \pi \)-electrons gives rise to a cyclotron mass of \( m^* = \sqrt{n} / v_f \), where \( n \) is the \( \pi \)-electron density, as experimentally verified by Novoselov et al. [6]. Since the \( \pi \)-electronic density of states at the Dirac point tends to zero the cyclotron effective mass also tends to zero at the Dirac point. We now proceed to give an account of defects in graphene.

### 1.2 Defects in graphene

The investigation of defects in graphene and related structures has become a vast area of research [1, 7-35], and can pave the way for the development of advanced materials based on graphene. Here we refer to defects as any type of modification applied to an infinite graphene lattice. In this context, finite graphene flakes, and GNRs are considered defective graphene structures. We begin by discussing some defects reported in the literature for graphene. Here we place defects in two categories: (1) defects related to structural modification of graphene, such as vacancies, disorder and edges, and (2) extrinsic defects such as foreign atoms, and metallic contacts.
1.2.1 Structural defects in graphene

For a review of the many structural defects in graphene see [7]. Structural defects in graphene include, but are not limited to, vacancies, Stone-Wales defects, holes, line defects, and edges.

Among the most important defects in graphene are single vacancies, which have received much attentions in the literature because they are known to be a source of magnetism [8-14]. Unlike single vacancies, di-vacancies (two adjacent carbon atoms missing) are not known to be paramagnetic [7]. We return to the subject of vacancy-induced paramagnetism of graphene shortly, but first will give a brief account of different types of vacancies, lattice distortions and bond reconstructions.

Vacancies have been imaged using high resolution tunnelling electron microscopy (HR-TEM) [15, 36], and scanning tunnelling microscopy (STM) [8]. TEM images of single- and di-vacancies are shown in Fig. 1.3(a)-(d) [7]. Single vacancies have also been detected indirectly using electron spin resonance [14, 37]. When a single carbon atom is removed from the graphene lattice the lattice undergoes a Jahn-Teller distortion, where two of the three dangling bonds generated by the single vacancy form a bond, leave a single dangling bond near the vacancy site. TEM image of the single vacancy after bond reconstruction is shown in Fig. 1.3(a) [7]. In the case of di-vacancies four dangling bonds are generated which pair up leaving no dangling bonds at the di-vacancy site. Di-vacancies can reconstruct into several forms: they can form into two pentagons and one octagon V2(5-8-5) as in Fig. 1.3(b) [7], or three pentagons and three heptagons V2(555-777) as in Fig. 1.3(c) [7], or 5 pentagons, 1 hexagon, and 4 heptagons V2(5555-6-7777), as in Fig. 1.3(d) [7]. Higher order vacancies are also possible with more complicated bond reconstructions.
Reconstruction of the graphene lattice can also take place without the presence of any vacancies. This can happen by the formation of nonhexagonal rings, often grouped in a cluster. There are many structural reconstructions of this type that involve several hexagonal rings which are transformed into pentagons, heptagons and other polygon rings. The simplest example is the Stone-Wales defect, where four hexagons are transformed into two pentagons and two heptagons as in Fig. 1.3(e) [7]. Since these types of defects retain the same number of atoms as the pristine graphene structure no dangling bonds are formed. The abundance of the various vacancies and lattice distortions depend on their formation energies. For a discussion of the formation energies for the various defects refer to [7]. The migration of these defects have also been investigated [7, 16].

We now turn to the discussion of paramagnetism related to single vacancies, which can arise from two sources. Dangling bonds are known to be paramagnetic since they correspond to unpaired electrons in the system. However, typically these dangling bonds are passivated by hydrogen and other functional groups. The second source of paramagnetism is
related to a local imbalance of $\pi$-electron spin density [12]. Since the spin projection associated with the $\pi$-electrons alternate between adjacent sites on a graphene lattice, the absence of a single $\pi$-electron will generate a spin density imbalance in the vicinity of the vacancy. In the case of di-vacancies, where two adjacent atoms of opposite spin projections are missing, the local $\pi$-electron spin density is expected to be zero. This may be broadly generalized to multi-vacancies, where an odd number of missing carbon atoms produces a dangling bond, while the dangling bonds for an even number of missing atoms all pair.

In addition to vacancies and lattice distortions, large holes that extend over many lattice sites have been observed by Zan et al. [38], who generated nanoholes by irradiating graphene using an electron beam at room temperature. Interestingly, they observed spontaneous healing of these holes as shown in the before and after scanning transmission electron microscopy images in Fig. 1.4.

![Fig. 1.4: STEM image of a nanohole in graphene generated by electron irradiated (courtesy of Zan et al., reprint from ref [38]). The smaller holes spontaneously heal, as see in the before (a) and after (b) images.](image.png)
Line defects have also been observed in graphene [39]. These line defects (e.g., see Fig. 1.5) are typically linear sequence of bond-reconstructed point defects similar to those discussed earlier. An important feature of line defects is that they preserve translational symmetry along the line. Line defects have been proposed for applications in valleytronics, acting as a valley filter [40].

![STM image of extended one-dimensional defects in graphene. Image adapted from ref [39] (courtesy of J. Lahiri et al.).](image)

The electronic and magnetic properties of finite graphene structures, such as graphene flakes and GNRs, are dramatically different from the parent graphene structure. In particular, the electronic bands of such structures are significantly modified from pristine graphene. The form of the electronic bands for low-dimensional structures depends on the dimensions and geometry of the structure. In some cases electron correlation effects may play an important role in defining the electronic bands, and so the tight-binding model is inadequate for the description of such structures [41]. For a description of graphene nanoflakes and their
Electronic properties refer to [42]. Since GNRs are a major theme in this thesis we defer discussion of them to a dedicated Section 1.3.

1.2.2 Extrinsic defects in graphene

In addition to having structural defects, graphene can provide an appropriate platform for the introduction of foreign species, such as atoms, and molecules. In particular nitrogen doping has become an intensive area of research. Nitrogen can be incorporated into graphene in three common bonding configurations: pyridinic N, Pyrrolic N, and graphitic N (see Fig. 1.6). For a review of nitrogen doping of graphene and applications refer to [43].

Fig. 1.6: A schematic of graphene doped with nitrogen with bonding configurations: pyridinic N, Pyrrolic N, and graphitic N.

In addition to nitrogen doping a host of other atomic species have been used for doping graphene, including but not limited to, boron [44], potassium atoms [18], transition metals [17] such as Ti, Fe, and Pt, and Si atoms [45].

Another interesting area of research is the doping of graphene with metal contacts [21], and metal nanoparticles (see Chapter 5 for references). This will be an important topic
in Chapter 5, so we will be brief here. Giovannetti et al. [21] illustrated, using density functional theory, that metal contacts absorbed on graphene can form either strong chemical bond or physisorption of the metal contacts depending on the type of metal. For Co, Ni, and Pd strong chemical bonds take place, while for Al, Cu, Ag, Au, and Pt physisorption of the contacts take place. Chemical bonds modify the band structure of graphene, while physisorption of metal contacts preserve the band structure, but can shift the Fermi energy.

1.3 Graphene nanoribbons

A graphene nanoribbon (GNR) is a stripe of graphene, usually considered to be long in one direction, but finite along the width (ranging from a few angstroms up to a few hundred nanometers). Thus GNRs are 1-D structures since they are translationally invariant along the length of the ribbon only. GNRs can be categorized according to their chirality. One can imagine cutting a stripe from a graphene sheet, where the direction of the cut determines the chirality of the ribbon (see Fig. 1.7(a)). If a ribbon is cut such that the edges along the length form a zigzag pattern the ribbon is called a "zigzag" (ZZ) GNR as in Fig. 1.7(b), while a cut at an angle of 30°, 90°, or 120° to the zigzag line produces armchair (A) edges as in Fig. 1.7(c). Other ribbon chiralities are possible, when the cut is made at intermediate angles.

In Fig. 1.7 the alternating light and dark dots represents the two interpenetrating sublattice of graphene. Note that the outer edge of a ZZ-GNR consists of only one sublattice at one edge and the opposite sublattice at the other edge. On the other hand the outer edge of an A-GNR alternates between the two sublattices. This sublattice scheme associated with the
edge has profound consequences on the properties of the different GNRs as we will see throughout this thesis.

In general, GNRs support the same type of intrinsic and extrinsic defects discussed earlier. However, the presence of edges allows for additional type of defects such as edge-functionalization [25-27], and edge disorder [24, 46]. Fig. 1.8 shows a series of different edge defect obtained by HR-TEM [46].

Fig. 1.7: (a) Schematic of the honeycomb lattice geometry showing the zigzag and armchair chirality directions. Schematic of (b) zigzag and (c) armchair graphene nanoribbons.

The chirality and dimensions of GNRs significantly alter their properties (e.g., armchair GNRs can be metallic, or semiconducting depending on its dimensions). *Ab initio* numerical calculations carried out by Son et al. [47] illustrated the dependence of the width of GNRs on its electronic band gap. In the tight-binding approximation, A-GNRs can be
metallic or semiconducting depending on the number of dimer lines along the width of the ribbon. For the semiconducting ribbons the electronic band-gap increases with reducing ribbon width as a consequence of quantum confinement.

Fig. 1.8: HR-TEM images of edge structures for (a) zigzag, (b) armchair, (c) reconstructed zigzag, and (d) Klein edge (courtesy of A. W. Robertson and J. H. Warner, reprint from [46]). Various defect can be noted in the images.

On the other hand, in the tight-binding approximation zigzag GNRs do not exhibit a band gap but instead a sharp Van Hove-type peak appears in the density of states for such structures. This sharp peak is assigned to a peculiar type of edge modes only present for zigzag edges [48]. However, experimentally, narrow ZZ-GNRs with widths below ~20 nm do not typically exhibit a large density of states (as suggested by the tight-binding model) at the Dirac point [41]. Local density of states measurements using STM shows the presence of a gap at the Dirac point across ZZ-edges. Using the Hubbard model in the mean-field approximation, Tao et al. [41] illustrated the splitting of the Van-Hove-type singularity at the Dirac point due to ZZ-edges, and the opening of a band gap. A consequence of this splitting is the spin polarization of the two edges with ferromagnetic coupling of the spins on the same
edge and antiferromagnetic coupling between the two edges. The spin polarization of zigzag edges have been proposed for spintronic applications [49, 50].

We now discuss some of the properties of edge states in GNRs. In subsequent chapters we will explore these edge states in various contexts, such as extend paramagnetic states in GNRs (see Chapter 4), electronic Green's functions of GNRs (see Chapter 6) and the influence of ZZ-edges on the RKKY interaction (see Chapter 7).

1.3.1 Edge states in graphene nanoribbons

As mentioned earlier, using a tight-binding approximation to describe the hopping of π-electrons between nearest-neighbor sites Fujita et al. [48] reported the existence of localized modes along zigzag (ZZ) edges, whereas no such modes are present along armchair (A) edges. These edge modes are peculiar in that they are present even when the interaction energy (hopping) between edge sites is the same as the hopping between interior sites. The dispersion relation associated with this edge mode is a flat band with an energy equivalent to the Fermi energy at half-filling, and they extend only from the Dirac point to the Brillouin zone band edge in k-space [1]. In the density of states (DOS) these edge modes generate a Van-Hove-type singularity at the Dirac point. The relative intensity of this peak in the DOS increases as the number of zigzag edge sites increases relative to the total number of sites (e.g., when the width of a ZZ-GNR is reduced), as we will see in Chapter 4. However, this edge mode is even present for a semi-infinite graphene lattice with a zigzag edge [48], although its DOS becomes negligible compared with the much larger DOS associated with the bulk modes of graphene. If the ZZ ribbon width is reduced these two edges couple
leading to a modified band structure and the opening of an electronic band gap. This is equivalent to the Hubbard model description of narrow ZZ-GNRs [41] discussed earlier.

For the metallic A-GNRs a bandgap can also be generated by the presence of edge modes. These edge modes are of a completely different nature than those discussed for the ZZ-GNRs in [48]. They arise for GNRs when the hopping between edge sites is sufficiently different than those between interior sites. This is expected to be the case for realistic systems since edge sites are under-coordinated and are typically passivated by various functional groups. On the other hand, in a tight-binding approximation no electronic band gaps arise due to confinement for ZZ-GNRs, but instead a sharp peak at the Dirac point appears in the DOS, associated with the two ZZ-edge modes discussed earlier. A coupling between the two edge-modes can split the peak at the Dirac point, and effectively produce a band gap. However, as the ZZ-GNR becomes wider the coupling reduces causing the gap to diminish.

1.4 Motivation and thesis outline

The work presented in this thesis is a fundamental study of defect-related magnetic and electronic properties of graphene structures, treated from both experimental and theoretical points of view. In particular, the class of defects we investigate are those expected to preserve the tight-binding description of π-electrons in graphene.

In Chapter 2, we give a detailed theoretical background of the methodology and techniques used throughout the thesis. These include second quantization and Green's function techniques, the tight-binding model and other complementary models, and an account of paramagnetism with applications to electron spin resonance (ESR). In Chapter 3
we give a description of some of the characterization techniques uses for exploring the properties of our samples experimentally.

Chapters 4 through 8 are based on our research work. Chapter 4 is a combined theoretical-experimental study of paramagnetism in graphene nanoribbons using ESR and a combination of other characterization techniques, with theoretical interpretation based on the tight-binding model. Chapter 5 is also a combined theoretical-experimental study, investigating the electronic properties of graphene decorated with Cu nanoparticles. Chapter 6 is a theoretical study of $\pi$-electron Green's functions for the electronic excitations of a zigzag GNR. The results are obtained using an analytical tridiagonal matrix inversion method. The contributions from two types of zigzag edge excitations (or edge modes) are derived along with contributions from the bulk modes. Then in Chapter 7 we employ these Green's functions to derive a Ruderman-Kittel-Kasuya-Yosida (RKKY)-type interaction between magnetic impurities in zigzag graphene nanoribbon. The RKKY-interaction is mediated by the $\pi$-electron network in graphene. In Chapter 8 we discuss some additional applications of ESR measurements, motivated by investigation of the paramagnetic character of Au$_{25}^+$ molecular clusters and the defect formation mechanism in epitaxially grown silicon epilayers. Finally in Chapter 9 we give some concluding remarks and mention some extensions of this work.
References


CHAPTER 2

Theoretical Methods

In this chapter we describe some of the theoretical methods and physical models to be used throughout this thesis. In Section 2.1 we cover many body techniques. In Section 2.2 we give an account of the models used for calculating the band structure of graphene. In Section 2.3 and 2.4 we cover the theory of paramagnetism both from a microscopic and macroscopic points of view. Some of the discussions in the later sections make reference to applications of electron spin resonance.

2.1 Many body techniques

2.1.1 Second quantization and operator equation of motion

For a many body system, such as a gas of fermions or the π-electrons on a graphene lattice, one can attempt to write down the wave function of the system in terms of the individual particle wave functions. However, this can pose a problem since we often don't know the wave function of the individual particles, and even if we did it would be an intensive numerical task to compute such a wave function due to the enormous number of particles involved in real systems. A powerful tool at our disposal for dealing with such many body problems is the method of second quantization [1, 2]. We start by defining a wave function that is specified by the number of particles in each available single particle state,

$$\Phi = |n_1, n_2, ..., n_i, ..\rangle,$$  \hspace{1cm} (2.1)
where \( n_i \) is the number of particles in state \( i \). We require \( \Phi \) to be orthogonal and normalized. This representation of the wave function is called the occupation number representation. Although this representation can be applied to both bosons and fermions we will discuss the fermion case since the main system under consideration in this thesis consists of the \( \pi \)-electrons in graphene which are fermions. If \( \Phi \) represents the total wave function for a system of fermion particles, it must be antisymmetric with respect to the interchange of co-ordinates of any two particles. Additionally, the Pauli exclusion principle forbids any state to be occupied by more than one particle. As a consequence \( n_i = 0 \) or 1 for any state \( i \). We define two operators, namely creation \( c_i^+ \) and annihilation \( c_i \) operators. When \( c_i^+ \) act on the wavefunction \( \Phi \), it promotes or creates a particle in state \( i \). However, due to the Pauli exclusion principle this is only possible if state \( i \) is unoccupied, therefore we have

\[
c_i^+ |n_1, n_2, ..., n_i, ..\rangle = \begin{cases} (-1)^l |n_1, n_2, ..., n_i + 1, ..\rangle & \text{if } n_i = 0 \\ 0 & \text{if } n_i = 1. \end{cases}
\]

(2.2)

When the operator \( c_i \) act on the wavefunction \( \Phi \), it annihilates a particle in state \( i \). Of course this is only possible if state \( i \) is occupied, thus

\[
c_i |n_1, n_2, ..., n_i, ..\rangle = \begin{cases} 0 & \text{if } n_i = 0 \\ (-1)^l |n_1, n_2, ..., n_i - 1, ..\rangle & \text{if } n_i = 1. \end{cases}
\]

(2.3)

The factor \((-1)^l\) in Eqs. (2.2) and (2.3) is 1 or -1 depending on the value of \( l \), defined by

\[
l_i = \sum_{j=1}^{i-1} n_j = \text{number of particles with } j < i.
\]

(2.4)
Note that $l_i$ depends on the occupation of the available states. This factor ensures that if a sequence of operations on $\Phi$ interchanges the co-ordinates of two fermions the wavefunction reverses signs, as required by the Pauli exclusion principle [1]. Additionally, the form of $l_i$ ensures a simple anticommutation relation between the creation and annihilation operators.

We would like to now find some properties of the operators $c_i^+$ and $c_i$. If we take the sequence of operators $c_i^+c_i$ and apply it to the wave function we get

$$c_i^+c_i|n_1, n_2, ..., n_i, ..\rangle = n_i|n_1, n_2, ..., n_i, ..\rangle.$$

(2.5)

Thus $c_i^+c_i$ gives the occupation of state $i$, and therefore it is commonly called the occupation number operator. Also it can easily be shown that

$$(c_i^+c_j^* + c_jc_i^*)|n_1, n_2, ..., n_i, ..\rangle = \delta_{i,j}|n_1, n_2, ..., n_i, ..\rangle,$$

(2.6)

which leads to the identity

$$\{c_i, c_j^*\} = \delta_{i,j},$$

(2.7)

where we are using the anti-commutation notation $\{A, B\} = AB + BA$ for any two operators, and $\delta_{i,j}$ is the Kronecker-delta.

A sequence of operators $c_i^+c_j$, where $i \neq j$ corresponds to a transfer of a particle from state $j$ to state $i$, provided state $j$ is occupied and state $i$ is unoccupied. If $i$ and $j$
represent spatial co-ordinates, for instance lattice site label, the operator $c^*_i c_j$ acts as a propagation operator in real space.

It is often convenient to associate the time dependence of a system to the operators describing the Hamiltonian rather than the wave function for the system. In the Schrödinger picture the time dependence Schrödinger equation is given by [3, 4]

$$i \frac{\partial}{\partial t} |\phi_s(t)\rangle = H|\phi_s(t)\rangle.$$  \hspace{1cm} (2.8)

It can easily be shown that

$$|\phi_s(t)\rangle = e^{-iHt}|\phi_s(0)\rangle.$$  \hspace{1cm} (2.9)

satisfies the time dependent Schrödinger equation. In this picture the time evolution of the system is imbedded in the wave function of the system. However, if we define a new wave function as

$$|\phi_H(t)\rangle = e^{iHt}|\phi_s(t)\rangle,$$  \hspace{1cm} (2.10)

we get

$$|\phi_H(t)\rangle = e^{iHt} e^{-iHt} |\phi_s(0)\rangle = |\phi_s(0)\rangle.$$  \hspace{1cm} (2.11)

In this representation the wave function becomes time independent. Now suppose an operator $A_s$ in the Schrödinger picture becomes $A_H$ in the new representation (the Heisenberg picture). Since the quantum mechanical matrix elements must be invariant in the two pictures, we must have
\[ \langle \phi_h | A_H(t) | \phi_h \rangle = \langle \phi_S(t) | A_S | \phi_S(t) \rangle. \] (2.12)

This immediately leads to a time-dependent operator of the form

\[ A_H = e^{iHt} A e^{-iHt} \] (2.13)

in the Heisenberg picture. We would like to see how the operator \( A_H \) evolves in time. Taking the time derivative of \( A_H \) we get the relation

\[ \frac{\partial}{\partial t} A_H = i[H, A_H(t)], \] (2.14)

where we have used the commutation notation

\[ [A, B] = AB - BA \] (2.15)

for any operators \( A \) and \( B \). Eq. (2.14) is called the operator equation of motion. In effect, by using the 2nd quantization representation in the Heisenberg picture we have transfers all the information from the wave function to the Hamiltonian operators describing the system.

### 2.1.2 Green's function technique

In addition to 2nd quantization we usually need other techniques to analyze and extract information about many body systems. This brings us to the Green's function technique [5-8], which in a mathematical context is a method for solving differential equations. In the context of quantum and statistical mechanics Green's functions give information about correlations in the system as we will illustrate in this section. These correlations can be used to tackle a host of problems in many body systems including signal propagation.
Here we define the retarded Green's functions [5] for any two quantum operators $A(t)$ and $B(t')$ at time $t$ and $t'$, respectively:

$$\langle \langle A(t), B(t') \rangle \rangle = -i \theta(t - t') \langle [A(t), B(t')] \rangle,$$

(2.16)

where $\theta(t)$ is the unit step function given by

$$\theta(t) = \begin{cases} 
1 & \text{for } t > 0 \\
0 & \text{for } t < 0 .
\end{cases}$$

(2.17)

Two other forms of the Green's function can be defined [5], namely, the advanced and Causal Green's functions, which we will not discuss here. It should be noted that all forms of the Green's function give the same information, and the choice is a matter of convenience.

The operators in the Green's function have a time dependence of the form

$$A(t) = e^{i(H - \mu N)t} Ae^{-i(H - \mu N)t}. $$

(2.18)

The brackets $\langle \rangle$ denote the standard statistical mechanics equilibrium thermal average. The thermal average of operator $A$ is given by

$$\langle A \rangle = \frac{1}{Q} \sum_i \langle i | A | i \rangle e^{-(E_i - \mu_i N_i)/k_B T},$$

(2.19)

where $E_i$ is the energy and $N_i$ is the number of particles in state $i$, $\mu_i$ is the chemical potential, $k_B$ is the Boltzmann factor, $T$ is the temperature, and $Q$ is the grand partition function defined by:

$$Q = \sum_i e^{-(E_i - \mu_i N_i)/k_B T}.$$

(2.20)
Finally, we have defined

\[
[A(t), B(t')] = A(t)B(t') - \epsilon B(t')A(t),
\]

(2.21)

where we set \( \epsilon = 1 \) for a commutation relation and \( \epsilon = -1 \) for an anticommutation relation. Often it is convenient to use Eq. (2.21) in the commutation form for boson operators and anticommutation form for fermion operators.

In the definition of the Green's function there are terms of the form \( \langle A(t)B(t') \rangle \). This term gives us the correlation between operator \( A(t) \) at time \( t \) and operator \( B(t') \) at time \( t' \), and is referred to as the time correlation function. We can define a Fourier transform for the time correlation function by

\[
\langle A(t)B(t') \rangle = \int_{-\infty}^{\infty} \langle AB \rangle_\omega e^{-i\omega(t-t')} d\omega,
\]

(2.22)

where \( \langle AB \rangle_\omega \) is the correlation function in the frequency representation often referred to as the spectral function or spectral intensity. It tells us the strength of correlation associated with each frequency in the Fourier spectrum. Note that we are using units where \( \hbar = 1 \). A simple relation between \( \langle AB \rangle_\omega \) and \( \langle BA \rangle_\omega \) exists. It can be shown that [5]

\[
\langle AB \rangle_\omega = \langle BA \rangle_\omega e^{\omega/k_BT}.
\]

(2.23)

Often the task of solving a many body problem is to derive the spectral function; however, it may be easier to find the Green's function for a system which can then be used to find the spectral function. Here we will derive a relation between the Green's function in the frequency representation and the spectral function. We begin by first using a Fourier transform to write the Green's function in the frequency representation.
\[ G(t - t') = \int_{-\infty}^{\infty} G(E)e^{-iE(t-t')}dE. \]  

(2.24)

The inverse of Eq. (2.24) is given by

\[ G(E) = \frac{1}{2\pi} \int_{-\infty}^{\infty} G(t - t')e^{iE(t-t')}dt. \]  

(2.25)

Substituting Eq. (2.24) into Eq. (2.25) and using Eqs. (2.22) and (2.23) we get

\[ G(E) = \frac{-i}{2\pi} \int_{-\infty}^{\infty} \omega(\omega) \left( e^{\omega t}T - \epsilon \right) \int_{-\infty}^{\infty} \theta(t)e^{i(E-\omega)t}dt. \]  

(2.26)

We can simplify Eq. (2.26) by using an integral representation of the step function [9]:

\[ \theta(t) = \frac{i}{2\pi} \int_{-\infty}^{\infty} e^{-ix}dx dx, \]  

(2.27)

where \( \eta \) is a positive infinitesimal (\( \eta \rightarrow 0 \)), and the identity [9]

\[ \delta(z - z') = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{i(z-z')t}dt. \]  

(2.28)

After some simplification we obtain an expression of the form

\[ G(E) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \omega(\omega) \left( e^{\omega t}T - \epsilon \right) \frac{1}{E - \omega + i\eta}, \]  

(2.29)

relating the Green's function in the frequency representation to the spectral function.

Suppose we have the Green's function for a system and would like to obtain the spectral function. We can find the spectral function by breaking the Green's function into its real and imaginary parts. To do so we use the identity [9]
\[
\frac{1}{x \pm i \eta} = P \left( \frac{1}{x} \right) \mp i \pi \delta(x), \quad \text{(2.30)}
\]

where \( x \) is any real variable, \( \eta \) is a positive infinitesimal, and \( P \) denotes that the principal value is taken in any integration over \( x \). Applying this identity to Eq. (2.29) we can write the real and imaginary parts of the Green's function separately

\[
\text{Re} G_r(E) = \frac{1}{2 \pi} P \int_{-\infty}^{\infty} d\omega \frac{\langle BA \rangle_{\omega} \left( e^{i \omega/\hbar T} - E \right)}{E - \omega},
\]

and

\[
\text{Im} G_r(E) = -\frac{1}{2} \langle BA \rangle_{\omega=E} \left( e^{i \omega/\hbar T} - E \right).
\]

The spectral function can now be expressed in terms of the imaginary part of the Green's function by rearranging Eq. (2.32) as

\[
\langle BA \rangle_{\omega=E} \left( e^{i \omega/\hbar T} - E \right) = \frac{-2}{\text{Im} G_r(E)}.
\]

One of the methods available for solving the Green's function is the Green's function equation of motion, which we will derive here. This can be done in real space or in a frequency representation. We begin by taking the time derivative of Eq. (2.16)

\[
\frac{d}{dt} \langle A(t) B(t') \rangle = -i \left[ \frac{d}{dt} (t - t') \langle [A(t), B(t')] \rangle + \theta(t - t') \left[ \frac{d}{dt} A(t) \right] B(t') - \frac{d}{dt} B(t') \left[ \frac{d}{dt} A(t) \right] B(t') \right]. \quad \text{(2.34)}
\]

Using the operator equation of motion and noting that the second term on the right hand of the above expression is a new Green's function involving the Hamiltonian we can write the above expression in the form
\[
\frac{d}{dt} \langle \langle A(t), B(t') \rangle \rangle = -i \delta(t - t') \langle [A, B]_r \rangle + i \langle [\{H, A(t)\}; B(t')] \rangle.
\]  
(2.35)

To find the Green's function equation of motion in the frequency representation we replace the two Green's functions in Eq. (2.35) by using Eq. (2.24), and replace the delta function using the identity Eq. (2.28). After some straightforward simplification we obtain the Green's function equation of motion in the frequency representation given by

\[
E \langle \langle A; B \rangle \rangle_E = \frac{1}{2\pi} \langle [A, B]_r \rangle - \langle [\{H, A\}; B] \rangle_E.
\]  
(2.36)

2.2 Tight binding and other models for describing graphene

Many of the novel properties of graphene (i.e., ballistic transport, zero effective mass, minimum conductivity, etc.) are a result of its unique electronic band structure. Here we outline some of the theoretical models available for describing properties of graphene, and their advantages and disadvantages. Special emphasis will be placed on the tight binding method due to the ease and accuracy with which it can be applied analytically to graphene.

2.2.1 Tight-binding model

Here we give a brief account of the tight-binding method [10-12]. Imagine forming a lattice with a periodic placement of a basis atom (e.g., in the case of graphene carbon atoms placed in a two dimensional honeycomb pattern). In the vicinity of each lattice site the full Hamiltonian of the lattice can be approximated by the Hamiltonian of the isolated atom \( H_{\text{at}} \) at that site. Therefore, the wave function \( \psi_n \) at each lattice site consists of bound orbitals of the isolated atoms, satisfying the eigenfunction equation
\[ H_{\text{at}} \psi_n = E_n \psi_n, \]  

(2.37)

where \( E_n \) is the energy eigenvalue of the \( n^{\text{th}} \) atomic orbital. In this extreme limit, where the Hamiltonian and wave functions are for individual atoms, a set of \( N \) degenerate energy levels corresponding to the energy of the bound atomic orbital arise, where \( N \) is the number of atoms in the structure. This scenario does not account for the electronic bands associated with solids. To overcome this limitation we introduce a correction potential \( \Delta U(\vec{r}) \) to the Hamiltonian, such that the full Hamiltonian of the crystal becomes

\[ H = H_{\text{at}} + \Delta U(\vec{r}), \]  

(2.38)

where \( \Delta U(\vec{r}) \) is treated as a small perturbation, containing all corrections to the atomic potential required to produce the full period potential of the crystal. If \( \Delta U(\vec{r}) \) vanishes in regions where \( \psi_n \) does not, then the atomic form of the wave function \( \psi_n \) will satisfy the full crystal Hamiltonian. However, for the more realistic case where \( \Delta U(\vec{r}) \) does not vanish but becomes exceedingly small in regions where \( \psi_n \) is non-zero, we expect the wave function to deviate slightly from the atomic form. Using a bases set of the atomic orbitals we can write the modified wave function as

\[ \phi(\vec{r}) = \sum_n a_n \psi_n(\vec{r}), \]  

(2.39)

where \( a_n \) is the coefficient associated with \( n^{\text{th}} \) orbital. The crystal wave function can be written as a linear combination of the wave functions for the \( N \) sites

\[ \psi_k(\vec{r}) = \sum_{i=1}^{N} e^{ik \cdot \vec{R}_i} \phi(\vec{r} - \vec{R}_i), \]  

(2.40)
where \( \vec{k} \) is the wave vector associated with the crystal, and \( \vec{R}_i \) is the position of the \( i^{th} \) lattice site. We note that the form of the crystal wave function preserves Bloch's condition [7, 10], that the eigenfunction of the crystal Hamiltonian should have the form of a plane wave times a function with the periodicity of the Bravais lattice. The time independent Schrödinger equation for the crystal becomes

\[
H\psi(\vec{r}) = [H_{at} + \Delta U(\vec{r})] \psi(\vec{r}) = \varepsilon(\vec{k}) \psi(\vec{r}),
\]

(2.41)

where \( \varepsilon(\vec{k}) \) is energy eigenvalue of the crystal, expected to be dependent on \( \vec{k} \). The contribution from the state \( \psi_m(\vec{r}) \) to the total energy is given by

\[
\int \psi_m^*(\vec{r}) H_{at} \psi(\vec{r}) d\vec{r} + \int \psi_m^*(\vec{r}) \Delta U(\vec{r}) \psi(\vec{r}) d\vec{r} = \int \psi_m^*(\vec{r}) \varepsilon(\vec{k}) \psi(\vec{r}) d\vec{r}.
\]

(2.42)

According to Eq. (2.37) \( H_{at} \) acting on state \( \psi_m \) gives \( E_m \), therefore the above equation reduces to

\[
(\varepsilon(\vec{k}) - E_m) \int \psi_m^*(\vec{r}) \psi(\vec{r}) d\vec{r} = \int \psi_m^*(\vec{r}) \Delta U(\vec{r}) \psi(\vec{r}) d\vec{r}.
\]

(2.43)

Substituting the crystal wave function (Eq. (2.40)) into Eq. (2.43) and using the orthogonality condition

\[
\int \psi_m^*(\vec{r}) \psi_n(\vec{r}) d\vec{r} = \delta_{n,m},
\]

(2.44)

we get

\[
(\varepsilon(\vec{k}) - E_m) \left[ a_m + \sum_n a_n \sum_{\vec{R}_i \neq 0} \alpha_{m,n} (\vec{R}_i) e^{i\vec{k} \cdot \vec{R}_i} \right] = \sum_n a_n \beta_{m,n} + \sum_n a_n \sum_{\vec{R}_i \neq 0} \gamma_{m,n} (\vec{R}_i) e^{i\vec{k} \cdot \vec{R}_i}.
\]

(2.45)

where
Recalling our assumption that the atomic orbitals are well-localized on each lattice site, we expect $\alpha$ and $\gamma$ to be small since they involve a product of two wave functions at different sites. We also expect $\Delta U$ to be small in regions where $\psi$ becomes large and vice versa, and therefore their product is always small. Referring to Eq. (2.45) we see that this would imply $\epsilon(\tilde{k}) \approx E_m$ when the coefficient $a_m$ is large. On the other hand when $\epsilon(\tilde{k})$ is much different than $E_m$, $a_m$ must be small. Consequently only the coefficients $a_m$ corresponding to the orbitals with energy $E_m$, or close to $E_m$ contributes to the crystal wavefunction. If $E_m$ is non-degenerate, as for an s-orbital, Eq. (2.45) reduces to

$$\epsilon(\tilde{k}) = E_m + \beta_{m,m} + \sum_{\delta, \neq 0} \gamma_{m,m} \left( \tilde{R}_i \right) e^{ik\cdot\tilde{R}_i},$$

where we have used the condition $|\alpha_{m,m} (\tilde{R}_i)| << 1$. The above expression is referred to as the s-band dispersion relation. For the case of a p-orbital, $E_m$ would have triple degeneracy leading to three sets of equations, since three coefficients in Eq. (2.45) would contribute.

We now give some physical interpretation of the terms in Eq. (2.47). The first two terms combined correspond to the onsite energy eigenvalue of the full crystal Hamiltonian, where $\beta_{m,m}$ is the correction to $E_m$ due to the potential $\Delta U$. It can be interpreted as the ionization energy or the local work function of the crystal. The last term in Eq. (2.47) is a
propagation term since \( \gamma_{m,m}(\vec{R}_i) \) described the interaction energy between neighbouring lattice sites multiplied by a propagating plane wave.

Eq. (2.47) can be written in a second quantization form [12]. The tight-bind Hamiltonian in the s-band approximation in terms of creation and annihilation operators is

\[
H = \sum_{i,\sigma} \varepsilon_0 c^\dagger_{i,\sigma} c_{i,\sigma} + \sum_{i,j,\sigma} t_{i,j} c^\dagger_{i,\sigma} c_{j,\sigma},
\]

(2.48)

where \( i \) and \( j \) are lattice site labels, \( \varepsilon_0 \) is the ionization energy as described by \( E_m + \beta_{m,m} \), and \( c^\dagger_{i,\sigma} \) and \( c_{i,\sigma} \) are operators that create or annihilate a state at site \( i \), respectively, with spin projection \( \sigma \), and \( t_{i,j} \) is the hopping integral relating to the term \( \gamma_{m,m}(\vec{R}_i) \). Typically \( t_{i,j} \) is nonzero only for nearest-neighbour sites.

As mentioned previously in Chapter 1 graphene is a \( \text{sp}^2 \)-hybridized system of carbon atoms, forming a 2-dimensional honeycomb lattice. The hybridization of the 2s and 2p atomic orbitals generate 3 degenerate \( \sigma \)-bonds and a single non-degenerate \( \pi \)-bond. The \( \sigma \)-bonds are in the graphene plane and are strong covalent bonds, while the \( \pi \)-bond extend out of the graphene plane and form weaker \( \pi \)-bonds. In effect the \( \sigma \)- and \( \pi \)-orbitals are decoupled and can be treated independently. Additionally, the \( \sigma \)-electronic band generates a wide band gap, while the zero gap \( \pi \)-electronic bands fall within \( \sigma \)-electronic band gap (see Fig. 1.2(a)). Due to the non-degenerate nature of the \( \pi \)-orbital we can use the s-band approximation (Eq. (2.47)) for describing the \( \pi \)-electronic bands of graphene.
2.2.2 Relativistic Dirac Fermions

Many properties associated with the electronic bands in a solid depend on states near the Fermi level. Electrons near the Fermi level are the ones that participate in transport and optical phenomenon. As described in the previous chapter, graphene is a zero gap semi-metal with a unique linear dispersion near the Dirac point. Even though the density of electrons at the Dirac point goes to zero, the few electrons that are promoted to the conduction band have extremely high mobility, and zero effective mass. These electrons can be modeled as a two dimensional gas of fermions. This involves expanding the tight-binding Hamiltonian about the Dirac points, leading to the 2D Dirac equation [13]

$$-i v_F \mathbf{\sigma} \cdot \nabla \psi(\mathbf{r}) = E \psi(\mathbf{r}),$$

(2.49)

where $v_F$ is the Fermi velocity, $\mathbf{\sigma} = (\sigma_x, \sigma_y)$ are the Pauli matrices, and $\psi(\mathbf{r})$ is a two component wave function. Eq. (2.49) is a set of two equations. Some of the properties of graphene relating to the relativistic 2D Dirac equation (Eq. (2.49)) are the quantum Hall effect and Berry's phase, which were experimentally observed by Novoselov et al. [14].

2.2.3 Hubbard model

The Hubbard model is an extension to the tight-binding model, where an additional term is added to account for electron correlation effects. Suppose each lattice site on a crystal can support up to two electrons, as for $\pi$-electrons on a graphene lattice. Electrons that are occupying the same lattice site experience a large Coulomb repulsion, compared to electrons occupying different sites. This is a consequence of the fact that the Coulomb energy blows up as $r \to 0$, which is the case for electrons spatially confined on the same lattice site. We designate the energy difference between singly and doubly occupied sites by $U$. Note that
electrons occupying the same site must have opposite spin projections, due to the Pauli exclusion principle. Adding a term to account for this effect in the tight-binding Hamiltonian Eq. (2.48) we get the so-called Hubbard Hamiltonian

$$H = \sum_{i,j,o} \epsilon_{ij,o} c_{ij,o}^+ c_{ij,o} + U \sum_i n_{i,\uparrow} n_{i,\downarrow},$$

(2.50)

where $n_{i,\uparrow}$ and $n_{i,\downarrow}$ are the occupation number with spin projection $\uparrow$ and $\downarrow$ at site $i$. Note that we dropped the first term in Eq. (2.48) since we can choose a the point of reference where $\epsilon_0 = 0$. The correlation term in Eq. (2.50) gives a contribution $U$ if $n_{i,\uparrow} = n_{i,\downarrow} = 1$, which corresponds to the site $i$ being occupied by two electrons of opposite spins. Otherwise the correlation term is zero. For a detailed description of the Hubbard model see [15].

2.2.4 Ab initio and pseudopotential method

There are other methods for calculating band structures. We will note in passing that an ab initio (e.g., density functional theory) approach can be carried out by taking into account the entire electronic structure of the atoms constructing the crystal, and minimizing the formation energy of the crystal through iterative alteration of the wavefunction and crystal parameters. This form of calculation allows for a greater degree of freedom, in the sense that lattice sites can be moved around to minimize the formation energy of the structure. It can be done to account for distortions and lattice relaxation effects. However, this comes at the expense of intensive numerical costs. To overcome some of the computation limitation imposed by ab initio calculation, one can often define a pseudopotential to describe the nuclei and core electrons, while modifying the wavefunction of electrons in the outer shell to minimize the formation energy of the crystal. For a detailed
description of pseudopotential methods see [16, 17]. For density functional theory methods refer to [18, 19].

2.3 Microscopic theory of paramagnetism

Pristine graphene is known to be diamagnetic at $T = 0K$ [20] however, defects can induce paramagnetism [20, 21] in graphene, even at $T = 0K$. In this thesis a comprehensive study of paramagnetism in graphene and graphene related structures will be presented. In addition to graphene, a study of paramagnetism in other molecular and bulk materials will also be made. Here we give an account of the theory of paramagnetism in general and in the context of electron spin resonance (ESR).

At the atomic level paramagnetism can originate from three principal sources. It can arise from the intrinsic spin of an electron, the orbital motion of an electron around a nucleus, and the intrinsic spin of a nucleus. The last case is referred to as nuclear paramagnetism, which is much weaker in comparison to the electronic counterpart. Nuclear paramagnetism is a vast subject area with applications in nuclear magnetic resonance [22] and magnetic resonance imaging [23]. Here we focus on electron paramagnetism with application relating to ESR. Only in the context of hyperfine effects we will refer to nuclear magnetic moments. From this point on we use the term paramagnetism in the context of electron paramagnetism.

Both the intrinsic spin and orbital motion of electrons produce a magnetic moment. However, not all electronic structures are paramagnetic. As an example, a closed shell atomic structure, such as nitrogen has a net zero orbital angular momentum, with all orbitals occupied by pairs of electrons. The pair of electrons have opposite spin projections, which
effectively cancel giving a net zero spin angular momentum. As a consequence there is a net zero magnetic moment associated with the electrons of such structures. However, paramagnetism can be induced by altering the electronic configuration of these non-paramagnetic structures; for instance, by exciting or removing an electron and generating unpaired electrons and hence a net magnetic moment.

If a system has both non-zero spin $\tilde{S}$ and orbital $\tilde{L}$ angular momentum, there are two regimes to consider. If the spin and orbital moments are decoupled they behave independently so we can write the total angular momentum of the system as

$$\tilde{\mu} = \tilde{\mu}_s + \tilde{\mu}_L = -g_L \mu_b \tilde{L} - g_S \mu_b \tilde{S},$$

(2.51)

where $\mu_b = e\hbar/2m$ is the Bohr magneton, $g_L$ is orbital $g$-factor which is exactly unity [24], and $g_S$ is the free electron spin $g$-factor which is approximately 2. More accurately $g_S = 2.00231930419922 \pm \left(1.5 \times 10^{-12}\right)$. On the other hand, if the spin-orbit coupling is strong then $\tilde{L}$ and $\tilde{S}$ are no longer good quantum operators for describing the system. Instead we use the total angular momentum operator $\tilde{J} = \tilde{S} + \tilde{L}$, and it can be shown that [24]

$$\tilde{\mu} = -g \mu_b \tilde{J},$$

(2.52)

where $g$ is given by the Landé equation

$$g = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}.$$  

(2.53)

The form of Eqs. (2.52) and (2.53) is a consequence of the fact that the spin and orbital moments do not precess independently.
Often, the ground state of molecules and paramagnetic centers in solids have zero orbital angular momentum. This implies that the $g$-value for such moments is the free electron $g$-value. However, spin-orbit interactions mix the pure-spin ground state with certain excited states, causing a small amount of orbital angular momentum to appear in the actual ground state and the $g$-value of paramagnetic centers often deviate from the free electron $g$-value. For a detailed discussion refer to [25]. Since the orbital angular momentum is negligible for most cases under consideration we base most of our discussion on the spin angular momentum, and ignore orbital effects, other than for small corrections. These small corrections will be included in terms of local fields of the spin environment as will be discussed later. Transition metals with partially filled $d$ and $f$ shells are an exception, and so the orbital angular momentum and $LS$-couple must be fully taken into account.

2.3.1 Zeeman splitting and the $g$-anisotropy

When an unpaired electron is placed in an external magnetic field $\vec{B} = B\hat{z}$ the spin magnetic moment $\vec{\mu}$ associated with the electron will experience a potential $U = -\mu_z B$, where the $z$-component of $\vec{\mu}$ is given by $\mu_z = g_S \mu_B S_z$, and $S_z$ is the spin projection along the $z$-axis, with eigenvalues $m_z$. For an electron spin $S = \frac{1}{2}$ in the absence of a magnetic field the two quantum states correspond to $m_z = \pm \frac{1}{2}$ and are degenerate. However, when the electron is placed in an external field the degeneracy of the spin states is lifted generating an energy splitting, where $U_\uparrow = -\frac{1}{2} g_S \mu_B B$ and $U_\downarrow = \frac{1}{2} g_S \mu_B B$. Here $U_\uparrow$ and $U_\downarrow$ are the potential energies of the spin projected parallel and antiparallel to the field, respectively. The energy difference is called the Zeeman splitting and is proportional to the external field. In ESR experiments a transition between the Zeeman levels can be induced by pumping the
system with a microwave source, which will be discussed in Chapter 3. Typically in ESR measurements the microwave frequency $\nu$ is kept constant, while the magnetic field is swept. When the resonance condition

$$\hbar \nu = g_s \mu_B B$$  \hspace{1cm} (2.54)

is satisfied the sample absorbs radiation. Since $\nu$ is fixed, the field at which absorption occurs depends on $g_s$.

The $g$-factor in Eq. (2.54) can deviate from the free electron $g$-value due to local magnetic fields present in the medium. These local fields can arise from admixture of the spin and orbital angular momentum (generally small), as discussed previously, or by the induced magnetic polarization of nearby moments due to the external field. The effective magnetic field experienced by a spin can be expressed as $B_{\text{eff}} = B + B_{\text{local}}$, where $B_{\text{local}}$ is the local field at the moment. Eq. (2.54) becomes

$$\hbar \nu = g_s \mu_B \left( B + B_{\text{local}} \right)_Z,$$  \hspace{1cm} (2.55)

where $\left( \right)_Z$ denotes the z-component of the effective field. We can also write the resonant condition in terms of a modified $g$-value

$$\hbar \nu = g \mu_B B$$  \hspace{1cm} (2.56)

since it is often impossible to know $B_{\text{local}}$. Equating Eqs. (2.55) and (2.56) we get

$$g = g_s \frac{\left( B + B_{\text{local}} \right)_Z}{B}.$$  \hspace{1cm} (2.57)
We note that in general \( \vec{B} \) and \( \vec{B}_{\text{local}} \) may be different in direction and/or magnitude. This leads to the possibility of a \( g \)-factor which is not necessarily a constant, and may not only depend on the magnitude but also the orientation of \( \vec{B} \) with respect to the sample. In general we can write a Zeeman Hamiltonian \( H_Z \) taking the above into account. In the principal set of axes the Zeeman Hamiltonian is given by

\[
H_Z = \mu_0 \left( g_x B_x S_x + g_y B_y S_y + g_z B_z S_z \right),
\]

where \( g_x, g_y, \) and \( g_z \) are the \( g \)-values when the field is oriented along \( x, y, \) and \( z, \) respectively. Eq. (2.58) can be written in a matrix notation

\[
H_Z = \mu_0 \mathbf{B}^T \cdot \mathbf{g} \cdot \mathbf{S},
\]

where \( \mathbf{B}^T \) is the transpose of the external field matrix

\[
\mathbf{B}^T = \begin{bmatrix}
B_x & B_y & B_z
\end{bmatrix}
\]

\( \mathbf{g} \) is now a tensor given by

\[
\mathbf{g} = \begin{bmatrix}
g_x & 0 & 0 \\
0 & g_y & 0 \\
0 & 0 & g_z
\end{bmatrix},
\]

in the principal axes, and \( \mathbf{S} \) is the spin matrix

\[
\mathbf{S} = \begin{bmatrix}
S_x \\
S_y \\
S_z
\end{bmatrix}.
\]
The local symmetry at any unpaired electron center can be categorized into 3 groups.

1. **Cubic:** This symmetry group applies to cubic, octahedral and tetrahedral structures. The g-factor is isotropic with all three principle values being equal.

2. **Uniaxial:** Here there is rotational symmetry about a unique axis. The g-tensor consists of one distinct and two identical principle values.

3. **Rhombic:** This is the most general case, with anisotropy for all rotations, giving rise to three unequal principal values in the g-tensor.

### 2.3.2 Hyperfine interaction

Next we discuss the hyperfine interaction between unpaired electrons and the nuclei. This arises in systems where there are non-zero nuclear magnetic moments in the vicinity of paramagnetic centers. The magnetic dipole moments of such nuclei can interact with the dipole moment of an unpaired electron. In the classical picture the potential energy associated with the dipole-dipole interaction is given by [26]

\[
U_{\text{dip}}(\vec{r}) = \frac{\mu_0}{4\pi} \left[ \frac{\vec{\mu}_e \cdot \vec{\mu}_n}{r^3} - \frac{3(\vec{\mu}_e \cdot \vec{r})(\vec{\mu}_n \cdot \vec{r})}{r^5} \right],
\]

where \(\vec{\mu}_e\) and \(\vec{\mu}_n\) are the dipole moments of the electron and nucleus, respectively, and \(\vec{r}\) is the displacement vector between the two dipoles. If these dipoles are placed in a substantially large external magnetic field along the z-axis, the dipoles will align along the field and Eq. (2.63) reduces to
\[
U_{dip}(r) = -\frac{\mu_0}{4\pi} \frac{3\cos^2 \theta - 1}{r^3} \mu_{nz} \mu_{ez},
\] (2.64)

where \( \mu_{ez} \) and \( \mu_{nz} \) are the z-components of \( \vec{\mu}_e \) and \( \vec{\mu}_n \), respectively. In the quantum picture the electron is actually an electron cloud with a distribution depending on the orbital state. To find the interaction energy \( U_{dip} \) we must average over the probability function of the orbital.

For an s orbital with spherical symmetry the average interaction energy at a fixed radial distance \( r \) can be obtained by taking the average of \( \cos^2 \theta \) in Eq. (2.64) over a sphere, which gives a factor \( 1/3 \), and consequently \( U_{dip} = 0 \). This is in contradiction with the experimental observation of hyperfine splitting in the hydrogen atom, where the electron in the 1s orbital experiences the effect of the proton nuclear magnetic moment. Fermi illustrated that for sufficiently large fields the isotropic hyperfine interaction for a one electron system is approximately given by [27]

\[
U_{is} = -\frac{2\mu_0}{3} |\psi(0)|^2 \mu_{ez} \mu_{nz},
\] (2.65)

where \( |\psi(0)|^2 \) is the probability distribution of the electron at the point nucleus \( r = 0 \). \( U_{is} \) is called the isotropic hyperfine interaction and is independent of the field orientation.

In addition to the isotropic hyperfine interaction, which arises from the wave function overlap of the electron and the nucleus, a second form of hyperfine interaction arises as a consequence of the interaction potential defined in Eq. (2.63). This is quite different from the isotropic case since it takes place at a distance. We can express Eq. (2.63) in terms of the quantum operators \( \vec{S} \) and \( \vec{I} \) for the electron and nuclear spins, respectively, using
\[ \tilde{\mu}_e = -\mu_B g_e \tilde{S} \quad \text{and} \quad \tilde{\mu}_n = \mu_n g_n \tilde{I}. \]

Expanding the dot products we can write Eq. (2.63) as matrix spin Hamiltonian of the form

\[ H_{\text{dip}}(\vec{r}) = S^T \cdot A_{\text{Anls}} \cdot I, \quad (2.66) \]

where \( S^T \) is the transpose of the electron spin matrix (Eq. (2.62)), \( I \) is the nuclear spin matrix similar in form to Eq. (2.62), and \( A_{\text{Anls}} \) is given by

\[
A_{\text{Anls}} = \frac{\mu_0}{4\pi} g_e \mu_B g_n \mu_n \begin{bmatrix}
\left\langle \frac{r^2 - 3x^2}{r^5} \right\rangle & \left\langle \frac{3xy}{r^5} \right\rangle & \left\langle \frac{3xz}{r^5} \right\rangle \\
\left\langle \frac{r^2 - 3y^2}{r^5} \right\rangle & \left\langle \frac{-3yz}{r^5} \right\rangle & \left\langle \frac{3z^2}{r^5} \right\rangle \\
\left\langle \frac{r^2 - 3z^2}{r^5} \right\rangle & \left\langle \frac{-3xz}{r^5} \right\rangle & \left\langle \frac{r^2 - 3y^2}{r^5} \right\rangle
\end{bmatrix}. \quad (2.67)
\]

Note that the interaction energy described by Eq. (2.66) depends on the relative orientation of the external field with respect to the displacement vector connecting the two dipole moments. Consequently, Eq. (2.66) is the anisotropic contribution to the hyperfine interaction. We can combine the isotropic and anisotropic contributions and define a hyperfine parameter matrix given by

\[
A = A_0 I_3 + A_{\text{Anls}}, \quad (2.68)
\]

where \( A_0 \) is the isotropic hyperfine parameter which can be extracted from Eq. (2.65) and \( I_3 \) is the 3x3 unit matrix. The hyperfine Hamiltonian \( H_{\text{HF}} \) including both isotropic and anisotropic contributions is given by

\[ H_{\text{HF}}(\vec{r}) = S^T \cdot A \cdot I. \quad (2.69) \]
2.4 Macroscopic theory of paramagnetism

Up to this point we have discussed the theory of paramagnetism at the microscopic level. We now extend our discussion to the macroscopic scale, beginning by replacing the magnetic dipole moment by its macroscopic counterpart, the magnetization, defined as the dipole moments per unit volume. In magnetic resonance experiments we find the magnetic character of a sample by placing it in a magnetic field and see how the sample responds to the field through the magnetization induced by the field. The parameter relating the magnetization $\vec{M}$ of the sample and the external magnetic field $\vec{B}$ is called the magnetic susceptibility $\chi$, defined by

$$\chi = \frac{\partial \vec{M}}{\partial \vec{B}}.$$  \hspace{1cm} \text{(2.70)}

Often $\vec{M}$ is linearly proportional to $\vec{B}$ making $\chi$ a proportionality factor. All the information about the magnetic nature of a sample is imbedded within $\chi$, so if we know $\chi$ then we know how a sample responds to an external field. Here we discuss the various forms of paramagnetism. The temperature dependence of the magnetic susceptibility can give insight about the nature and type of paramagnetism [28], as illustrated in Fig. 2.1.

First let us consider $N$ non-interacting $S=1/2$ magnetic centers imbedded in a sample. When the sample is placed in an external field a Zeeman splitting takes place between spin up and down states. We can use the Boltzmann distribution function to write the population of the two spin states at a finite temperature $T$ as

$$N_\uparrow = \exp\left(\frac{\mu_\uparrow B}{k_B T}\right) \text{ and } N_\downarrow = \exp\left(-\frac{\mu_\downarrow B}{k_B T}\right).$$  \hspace{1cm} \text{(2.71)}
The magnetization of the system is the population difference between the two spin states multiplied by the unit of dipole moment $\mu_z$. Using Eq. (2.71) the magnetization is

$$M = \mu_z (N_\uparrow - N_\downarrow) = \mu_z N \tanh\left(\frac{\mu_z B}{k_B T}\right),$$

(2.72)

where $N = N_\uparrow + N_\downarrow$. In the limit $\mu B / k_B T \ll 1$ Eq. (2.72) reduces to $M = \mu_z^2 NB / k_B T$, which immediately leads to a magnetic susceptibility of the form

$$\chi_{C} = \frac{\mu_z^2 N}{k_B T},$$

(2.73)

where the subscript $C$ refers to Curie paramagnetism (see Fig. 2.1). The above expression for $\chi$ can be generalized to any total angular momentum $J$ [10, 28]. However, the inverse $T$ dependence of $\chi$ is a general feature.

Fig. 2.1: Magnetic susceptibility vs. temperature for Curie, Van Vleck, and Pauli paramagnetism. The diamagnetic susceptibility is also shown.
Next, we discuss paramagnetism associated with itinerant electrons [10, 28]. Itinerant electrons are delocalized in a solid, and therefore many electrons occupy the same spatial coordinates. Consequently we can no longer treat them in terms of Boltzmann statistics, but instead must take into account the Pauli exclusion principal when populating the electronic bands of a solids. Using the Fermi-Dirac distribution function

\[ f(\varepsilon) = \frac{1}{e^{(\varepsilon - \mu)/k_B T} + 1}, \quad (2.74) \]

and the density of states \( g_\sigma(\varepsilon) \) for conduction electrons with spin projection \( \sigma \), we can write

\[ N_\uparrow = \int g_\uparrow(\varepsilon)f(\varepsilon)d\varepsilon \quad \text{and} \quad N_\downarrow = \int g_\downarrow(\varepsilon)f(\varepsilon)d\varepsilon, \quad (2.75) \]

where \( N_\uparrow \) and \( N_\downarrow \) are the number of conduction electrons with spin projection \( \uparrow \) and \( \downarrow \), respectively. In Eq. (2.74) \( \mu_c \) is the chemical potential not to be confused with the magnetic dipole moment. We note that, although \( g_\sigma(\varepsilon) \) depends on the band structure of the material being studied, in the absence of an external field \( g_\uparrow(\varepsilon) = g_\downarrow(\varepsilon) = \frac{1}{2} g(\varepsilon) \) in general. However, when a field is present the energy difference between electrons with spin \( \uparrow \) and \( \downarrow \) lifts this degeneracy leading to

\[ g_\uparrow(\varepsilon) = \frac{1}{2} g(\varepsilon - \mu_z B) \quad \text{and} \quad g_\downarrow(\varepsilon) = \frac{1}{2} g(\varepsilon + \mu_z B). \quad (2.76) \]

Since in general \( \mu_z B \ll \varepsilon \) we can expand \( g_\uparrow(\varepsilon) \) to get the approximate form

\[ g_\uparrow(\varepsilon) \approx \frac{1}{2} g(\varepsilon) - \frac{1}{2} \mu_z B \frac{dg(\varepsilon)}{d\varepsilon}. \quad (2.77) \]

Using Eqs. (2.75) and (2.77) the magnetization associated with the conduction electron is
\[ M = \mu_z (N_+ - N_-) \approx \mu_z^2 B \int \frac{\partial g(\epsilon)}{\partial \epsilon} f(\epsilon) d\epsilon. \] 

(2.78)

Integrating Eq. (2.78) by parts and noting that \( \frac{\partial f(\epsilon)}{\partial \epsilon} = -\delta(\epsilon - \epsilon_F) \), for \( k_B T \ll \epsilon_F \), we get \( M \approx \mu_z^2 g(\epsilon_F) B \), which immediately leads to

\[ \chi_p = \mu_z^2 g(\epsilon_F), \] 

(2.79)

where the subscript \( P \) refers to Pauli paramagnetism. We note that the magnetic susceptibility for conduction electrons (\( \chi_p \)) is temperature independent (see Fig. 2.1), and it is proportional to the density of states at the Fermi level.

Previously we dealt with bulk magnetic susceptibilities. We will now discuss the theory of magnetic susceptibility of individual atoms, ions, or molecules [10, 28]. The Zeeman Hamiltonian of an atom with total magnetic dipole moment \( \mu_S (\hat{L} + g \hat{S}) \) placed in an external field is given by \( \Delta H = \mu_S \left( \hat{L} + g \hat{S} \right) \cdot \vec{B} \). Here we are ignoring diamagnetic effects, spin-orbit coupling, and hyperfine interactions. The Zeeman energy splitting described by \( \Delta H \) is generally small compared to atomic excitation energies, even at high fields, and we can treat it as a perturbation. From second-order perturbation theory [3, 4]:

\[ \Delta E_n = \langle n | \Delta H | n \rangle + \sum_{n' \neq n} \frac{|\langle n | \Delta H | n' \rangle|^2}{E_n - E_n'} \] 

(2.80)

therefore, the energy correction to the atomic excitations is given here by

\[ \Delta E_n = \mu_b \vec{B} \cdot \langle n | \hat{L} + g \hat{S} | n \rangle + \sum_{n' \neq n} \frac{|\langle n | \mu_b (\hat{L} + g \hat{S}) \cdot \vec{B} | n' \rangle|^2}{E_n - E_n'}, \] 

(2.81)

where \( n \) and \( n' \) are the principle quantum numbers. Typically the second term in Eq. (2.81) is
relevant only when the first term vanishes. This is the case for systems with a diamagnetic ground state. For such a system the leading order correction to the ground state energy due to an external magnetic field point along the z-axis is

$$\Delta E_0 = \sum_n \frac{|\langle 0|\mu_B g_z S_z |n\rangle|^2 B^2}{E_0 - E_n},$$  \hspace{1cm} (2.82)

where \( n \) is summed over all excited states of the system. For simplicity we assumed zero orbital angular momentum in Eq. (2.82). The form of Eq. (2.82) indicates that the value of \( \Delta E_0 \) depends on the angular momentum of the excited states for the system. We can find the magnetic dipole moment associated with \( \Delta E_0 \) using the definition

$$\mu = -\frac{\partial \Delta E_0(B)}{\partial B},$$  \hspace{1cm} (2.83)

which immediately gives

$$\mu = -\sum_n \frac{2B|\langle 0|\mu_B g_z S_z |n\rangle|^2}{E_0 - E_n}.$$  \hspace{1cm} (2.84)

For a system of \( N \) atoms or molecules each with a magnetic dipole defined by Eq. (2.84), the magnetization of the system is \( M = \mu(N_\uparrow - N_\downarrow) \). If the energy difference between the ground state and the excited states is much less than \( k_B T \), a fraction of the atoms will be thermally excited leading to a population difference of \( N_\uparrow - N_\downarrow \approx N(E_0 - E_n)/2k_B T \) [28]. The population difference between the spin states of the atoms is temperature dependent, and consequently the magnetization and magnetic susceptibility are also temperature dependent. On the other hand, if \( E_0 - E_n >> k_B T \) [28], then most of the atoms
reside in the ground state, and the population difference is close to $N$. This leads to a temperature independent magnetization and susceptibility

$$
\chi_V = \sum_n \frac{2\left\langle 0 \left| \mu_n \left( L_z + g_0 S_z \right) \right| n \right\rangle^2}{E_0 - E_n} N,
$$

(2.85)

where subscript $V$ refers to temperature independent Van Vleck paramagnetism (see Fig. 2.1).

In the above discussions we considered non-interacting paramagnetic centers. The magnetic interaction effects in paramagnetism, which lead to relaxation times, are described in Appendix A.

References


CHAPTER 3

Experimental Techniques

In this chapter we will discuss some basic concepts and instrumentation related to the main characterization techniques used in this thesis. They include, electron spin resonance (ESR), atomic force microscopy (AFM), Kelvin probe force microscopy (KPFM), scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX), and Raman spectroscopy. The procedures for fabricating samples relevant to each project are discussed in the relevant chapters.

3.1 Electron spin resonance

The theory of paramagnetism was discussed in the previous section. Here we focus on the description of an electron spin resonance (ESR) spectrometer. For a detailed description of the ESR spectrometer refer to [1]. Our ESR measurements were carried out on a Jeol JES-FA200 ESR spectrometer (shown in Fig. 3.1(a)), equipped with a rectangular-TE$_{102}$ dual-compartment resonator, a 200mW X-band microwave generator (9-10 GHz frequency) and a liquid-nitrogen cryostat temperature controller. Major components of an ESR spectrometer are the Helmholtz-coil electromagnet, the above mentioned microwave unit, the resonator, the field modulation system, the power attenuator, able to attenuate the microwave power from 200 mW down to a few nW, and the detection system comprising a locked-in diode. A block diagram showing the components of the ESR spectrometer is shown in Fig. 3.1(b).
ESR operates on the principle of the Zeeman energy splitting as discussed previously. A dc magnetic field generates the Zeeman energy splitting while a microwave source excites spins from an occupied energy level (in which spins are parallel to the dc magnetic field) to an unoccupied energy level (in which spins are anti-parallel to the dc magnetic field) when the Zeeman energy splitting is in resonance with the applied ac microwave field. In commercial ESR spectrometers, these resonance conditions are achieved by varying either the frequency of the microwave source or the intensity of the dc magnetic field. In most ESR spectrometers, the dc magnetic field intensity is varied to attain resonant condition, because it is much simpler to implement.

Fig 3.1: (a) Jeol JES-FA200 ESR spectrometer, and (b) block diagram of the main components of the ESR spectrometer.

**Magnet system**

In order to record an ESR spectrum, the sample is placed between the two Helmholtz coils in the resonant cavity. The magnitude of the field generated by the electromagnets can
be varied between 0 T to 1.7 T in our spectrometer. For \( g \sim 2 \), X-band resonance typically occurs at about 330 mT. For reproducibility and precise measurements of spectral parameters the field must be highly stable and accurate. This is accomplished by using a highly stable regulated power supply and a Hall-effect probe for tracking the field value. The Hall-effect probe plays a crucial role for regulating the field, since the field is typically non-linear and influenced by the hysteresis effect. The voltage reading of the Hall-effect probe must be temperature compensated for an accurate measurement of the field even as the measurement temperature is varied.

**Radiation source and resonator system**

The tuning of the microwave unit is necessary to maximise the fraction of microwave power that is transferred from the generator to the sample placed in the resonator and to minimize the power that is reflected back into the microwave unit. Several degrees of freedom exist to maximise the power absorbed by the sample, which include: i) selecting the appropriate microwave frequency in the range of operation of the X-band generator (approximately 8.75 to 10.15 GHz), ii) adjusting the phase difference between the microwave and the RF modulating field that is used to detect the signal in lock-in mode and iii) adjusting the distribution of the microwave field in the cavity through an iris coupling screw.

The resonator is responsible for enhancing the sensitivity of the ESR spectrometer. Typically, an ESR resonator is a cavity with inner walls coated by a metal with high reflectivity in the microwave range (i.e., gold) and houses the sample during the measurements. The shape of the cavity determines the distribution and polarization of the microwave field that is resonantly enhanced in it and, consequently, the types of ESR transitions that will be excited within the sample. Due to resonant enhancement effects
produced by the cavity, standing waves formed in the resonator have a much larger energy density than traveling waves. A standing wave with a wavelength half of the dimension of the cavity is called the fundamental resonant wavelength. This makes microwave sources in the X-band region convenient since they have wavelengths on the order of centimetres and therefore cavities can be designed with similar dimensions. The fundamental resonant wavelength changes depending on the size, nature and location of the sample within the cavity. Before doing ESR measurement the cavity must be tuned with a sample placed inside. This is done by adjusting the frequency of the microwave source so that a standing wave forms inside the cavity. Once a standing wave is formed power is absorbed by the cavity, and a dip is observed indicating reduced microwave intensity reaching the detector.

Fig 3.2: (a) Schematic of the rectangular-parallelepiped cavity. TE\textsubscript{102} mode (b) electric field, and (c) magnetic field contours supported by the cavity.
There are several criteria for designing a resonant cavity. Electromagnetic modes supported by the resonant cavity should permit a large energy density to be stored, the modes should have a maximum magnetic field and a minimum electric field at the location of the sample, and in most cases the magnetic field component of the microwave source should be perpendicular to the static field generated by the electromagnets. The importance of having a minimum electric field at the location of the sample is to reduce dielectric losses of the microwave field. For instance dipolar molecules such as water absorb microwave energy through the electric field component, which reduces the energy density stored within the resonator and therefore reduces the sensitivity of the instrument. The spin transition occurs through the absorption of the magnetic component of the oscillating microwave field. One of the most common resonators that fulfills these requirements is the rectangular-parallelepiped cavity shown in Fig. 3.2(a). This cavity supports the TE$_{102}$ mode. The nomenclature refers to a transverse electric mode with 1, 0 and 2 half-wavelengths along the $a$, $b$ and $c$ dimensions of the cavity. The electric and magnetic field contours are shown in Fig. 3.2(b) and (c), respectively. From the electric field contours we see that the electric field is a minimum at the center of the cavity. From the magnetic field contours we see that the magnetic field is a maximum and transverse to the static field at the center of the cavity.

Radio-frequency modulation system

In order to enhance the sensitivity of an ESR spectrometer and increase the signal-to-noise (S/N) ratio in an ESR spectrum, a radio-frequency (RF) modulator is employed so that microwave power absorbed by the sample can be measured using a lock-in detection scheme. With this scheme, a small RF modulation is superimposed on the dc magnetic field. This
modulation is accomplished by placing a pair of coils on both sides of the cavity along the axis of the dc field. These coils are driven by an alternating current, typically at 100 kHz, which produces the modulation. Lock-in-amplifiers are current amplifiers that select only a specific frequency of a multi-band ac signal, which corresponds to the frequency of a specific reference signal. This scheme limits the amplification of electrical noise that normally occurs at frequencies that are different from the reference, which leads to dramatic improvements in the signal-to-noise ratio. In addition to increasing the S/N ratio, the RF modulator can be used to attain ESR signal gain. This is done by appropriately increasing the amplitude of the magnetic field produced by the modulation coils. A possible downside of using a detection scheme based on RF modulation is that the modulating field can distort the lineshape of the ESR spectrum, which is critical for extracting information about the nature of paramagnetic centers in a specimen, as discussed in Chapter 2 and Appendix A. This phenomenon occurs because a large modulation amplitude may introduce excessively large fluctuations in the dc magnetic field and broaden the resonance conditions. However, these artefacts can be avoided in an ESR spectrum by using sufficiently low RF modulation amplitudes.

Detection system

Detectors in an ESR spectrometer are Schottky diodes, acting as rectifiers of the incident microwave radiation. This diode in our spectrometer consists of a doped-semiconducting silicon crystal in contact with a tungsten 'cat whisker'. After the signal is detected and rectified by the crystal, the 100-kHz component of the signal undergoes locked-in amplification. The amplified signal is then mixed with the output of the oscillator producing the modulation field. If the two signals are out of phase by 90° the output of the
mixer will be a minimum. The magnitude of the output signal can also be adjusted using a built-in phase shifter between the RF modulator and the RF modulated microwave source. This effectively filters out all components of the signal coming from the resonator except for a narrow band around the modulation frequency. If the amplitude of the modulation field is small enough compared to the linewidth of the ESR spectrum, then the amplitude of the detected current is proportional to the rate of change of the ESR signal per dc magnetic field unit. For this reason, ESR data are typically presented in the literature as the first derivative of the microwave absorption profile vs. the magnitude of dc magnetic field.

**Circulator waveguide system**

The microwave is transmitted from the generator to the resonator and finally to the detector through a system of waveguides incorporating a circulator unit. For X-band microwave sources, the standard waveguide is a brass pipe with rectangular cross section of 12.7 x 25.4 mm-OD. The circulator also acts as an isolator that functions as a non-reciprocal device to avoid backward reflection of microwaves. Any backscattered microwaves can significantly affect and damage the microwave X-band frequency generator. The isolator is typically a 4-port circulator with one of the ports fitted with a terminating load, as depicted in Fig. 3.3. The circulator uses a ferrite rod placed between two small magnets in order to steer the microwave flux in sequence from port 1 to 4, as shown in Fig. 3.3.

Coupling and distribution of the microwave field inside the cavity is achieved using a screw iris with a conducting tip built into the cavity wall (see Fig.3.2(a)). The screw can be adjusted to optimize the impedance matching and is also used to minimize the amount of reflected power.
Fig. 3.3: A schematic of a 4-port circulator with the 4\textsuperscript{th} port fitted with a terminating load. The circulator guides the microwave field from the source to the cavity, where the sample is placed, and onto the detector. The terminating load avoids backscattered radiation that can significantly reduce the sensitivity of the measurement.

\textit{Temperature accessory and controller}

A cryostat and temperature controller unit can be used to adjust the temperature of the sample during measurement. The cryostat unit is a quartz tube that fits vertically into the cavity and is attached to a Dewar filled with liquid nitrogen using a transfer line and includes a calibrated thermocouple for measuring the temperature level. A heating element moderated by the controller unit heats the nitrogen in the Dewar, which causes the pressure in it to rise. This effect pushes cold air into the cavity housing the sample. The thermocouple inside the cavity is connected to the heating element in the Dewar by a computer-automated proportional/integral/differential feedback loop that can be used to stabilize the temperature in the cavity. Specific samples undergoing phase transitions at known temperatures are used by Jeol to calibrate the thermocouple during the maintenance procedure of the spectrometer.
3.2 Atomic force and scanning Kelvin probe force microscopy

The atomic force microscopy (AFM) measurements carried out in the thesis were done using a Witec Alpha 300S atomic force/confocal optical microscope. The AFM unit was modified for Kelvin probe force microscopy (KPFM) measurements by attaching a Stanford DS 345 synthesized function generator, and a Stanford SR844-RF lock-in amplifier that is directly operated by the digital controllers of the Witec system.

3.2.1 Atomic force microscopy

AFM belongs to the group of scanning force microscopy (SFM) techniques and, as such, it works based on the force exerted on an atomically sharp probing tip attached to a cantilever and the sample surface being studied. The origin of the force can be the mechanical contact forces, van der Waals forces, capillary forces, chemical bonding, electrostatic forces, etc. The actual dominant force depends on the tip-sample separation distance. Long-range Coulomb forces arise from induced charges between the tip and the sample, and are mainly attractive. However, signal generation in AFM relies on the extreme short range inter-atomic repulsive forces due to the contact and overlap of the electronic wave functions between the tip and sample. A typical equilibrium separation distance between the tip and samples surface is of the order of a few angstroms, and since the inter-atomic repulsive force is generally influenced by the total electron density around the atom, this force can be used to map the topography of the surface down to atomic dimensions [2].

Our AFM instrument allows for easy control of the probing tip position relative to the sample surface. The basic components of the set up consist of the cantilever, probe tip, laser diode, segmented photodiode detector and the feedback loop. Some of these parts are shown
in Fig. 3.4. In addition, the system is interfaced with a desktop computer for controlling the different components and collecting data. The sample is positioned on a 100 x 100 µm piezoelectric scanner that has a maximum excursion of 10 µm in the z-direction. The mechanical arm on which the confocal microscope is mounted can also be moved in z-direction for optimizing the focal plane at the level of the AFM probe tip.

Fig. 3.4: Schematic representation of an atomic force microscope, showing only the probing tip attached to the cantilever, the laser for tracking the tip position, and the segmented photodiode.

In order to detect the motion of the tip during scan, a laser beam is reflected from the topside of the cantilever into a segmented photodiode, as shown in Fig. 3.4. When the laser is deflected from the calibration point (i.e., center of the segmented photodiode) during sample scan, the vertical position of the scanner is adjusted to maintain the position of the laser beam at
the calibration point. The change in the vertical position during scan is recorded in order to produce a topography image of the sample surface. The driving amplitude as well as the set point is selected to achieve clear and noise free topographic images. The set point indicates the closeness of the tip to the sample surface.

The investigation of sample surface topography can be performed in three different modes as shown in Fig. 3.5. These modes differ mainly by the amount of the interaction force between the probe tip and the sample surface [2].

![Diagram of atomic interaction forces between the AFM tip and the sample surface](image)

**Fig. 3.5:** Atomic interaction forces between the AFM tip and the sample surface, which define the modes of AFM operation into contact, non-contact and tapping modes.

When an AFM tip is within a few angstroms from the sample surface the repulsive force is predominant (F > 0) and the tip is assumed to be in contact with the sample surface, while in the non-contact mode the tip-sample distance is further and the force becomes attractive (F < 0). At the intermediate tip-sample distance the force can fluctuate about F = 0. This is the regime used for tapping-mode AFM measurements. Operation by tapping mode minimizes
the lateral shear forces [2] and can be used to probe the surface topography of loosely bound samples, such as the nanoribbons in Chapter 4.

During a sample scan in tapping mode, the cantilever is set to oscillate at a fixed frequency, close to the natural frequency of the cantilever. The free amplitude (i.e., when the tip is far from sample) of the oscillating cantilever is detected by the segmented photodiode. When the tip is brought in contact with the sample the cantilever is constrained from oscillating at the maximum or free amplitude. The value of this reduced oscillation amplitude is set by the operator, defining the contact distance between the tip and the sample. For optimal measurements the contact amplitude is typically set to ~ 50 – 60% of free amplitude. As the sample is scanned the contact amplitude changes with the surface topography of the sample. The feedback mechanism operates in a way to maintain a constant contact amplitude, by adjusting the vertical position of the piezoelectric scanner on which the sample is mounted. These vertical shifts are recorded producing a topography map of the sample.

3.2.2 Scanning Kelvin-probe force microscopy

AFM is an efficient technique which provides topographic images of samples. However, it cannot be used directly to access the local variation in the work function of materials or contact potential differences between the tip and the sample. These properties are better investigated by scanning Kelvin probe force microscopy (SKPFM), which measures the contact potential difference \( V_{CPD} \) between a conducting AFM tip and a sample, where \( V_{CPD} \) is given by

\[
qV_{CPD} = \varphi_{tip} - \varphi_{sample}.
\]
Here $q$ is the elementary charge, $\varphi_{\text{sample}}$ is the work function of the sample and $\varphi_{\text{tip}}$ is that of the tip. When the AFM tip is brought close to the sample a force exists between them due to the potential difference $V_{\text{CPD}}$. Therefore, the operation of this instrument is based on the small electrostatic force that exists between the conducting tip and the sample. This force is defined in terms of the electrostatic energy $E$ for the tip-sample system, considered as a parallel plate capacitor separated by a distance $Z$:[3, 4]

$$ F = \frac{dE}{dZ} = \frac{1}{2} (\Delta V)^2 \frac{dC}{dZ}, $$ (3.2)

where $C$ is the tip-sample capacitance and $\Delta V$ is their potential difference. To obtain a measurement for $V_{\text{CPD}}$ given in Eq. (3.1), a nullifying voltage is applied between the tip and sample, so that

$$ V = (V_{\text{DC}} - V_{\text{CPD}}) + V_{\text{AC}} \sin(\omega t) $$ (3.3)

gives the total voltage, consisting of a DC-bias voltage and an AC component at angular frequency $\omega$. $V_{\text{AC}}$ generates oscillating electrical forces between the AFM tip and sample surface, and $V_{\text{DC}}$ nullifies the oscillating electrical forces that originated from CPD between tip and sample surface. The expression for the electrostatic force applied to the AFM tip, obtained after inserting Eq. (3.3) into (3.2), is

$$ F_z = \frac{1}{2} \cdot \frac{dC}{dZ} (\Delta \phi)^2 + \frac{1}{4} V_{AC}^2 \cdot V_{AC} \cdot \frac{dC}{dZ} (\Delta \phi) \cdot \sin(\omega t) + \frac{1}{4} \frac{dC}{dZ} V_{AC}^2 \cos(2\omega t) $$ (3.4)

The first term in Eq. (3.4) is the DC component, the second and last terms are respectively the spectral components at $\omega$ and $2\omega$, and $\Delta \phi = V_{\text{DC}} - V_{\text{CPD}}$. 

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In order to zero the electrostatic force, a bias voltage is (in our case) applied to the sample. Provided the substrate is conducting, we obtained stronger signal in this way, by maximizing the signal-to-noise ratio. Since $F_z$ depends on $\Delta \phi$, the value of the bias voltage that minimizes the $\omega$-component corresponds to the contact potential difference. Therefore, if the tip work function is known, the work function of the sample is determined via Eq. (3.1). In order to get an absolute value for the work function of the sample we need to know the work function of the tip. To calibrate the work function of the tip we used a reference bare p-type silicon wafer, for which the work function is well known.

3.3 Scanning electron microscopy and energy dispersive X-ray spectroscopy

The scanning electron microscopy measurements presented in this thesis were carried out using a LEO (Zeiss) 1540XB FIB/SEM, fitted with an Oxford instruments X-ray system for energy-dispersive X-ray elemental analysis, and housed at the nanofabrication facility at the University of Western Ontario.

**Apparatus**

The scanning electron microscope (SEM) produces an image by scanning a narrow beam of electrons over a sample in a raster fashion and detecting the electrons emerging from the sample. As the beam scans over the sample, the number of electrons emerging from the sample changes depending on the composition and topography of the sample. The more irregular the topography of the sample surface the more electrons escape from the surface. The intensity of the scattered electron beam is detected at each point where the beam of
Electrons strike the sample, which is converted to a grey scale based on the number of electrons ejected from that point. The resolution of SEM depends on the diameter of the electron beam. A narrow beam is achieved by sending the electron beam through a sequence of magnetic lenses. Resolutions on the order of 1nm or less can be achieved. For a schematic showing the main components of an SEM see Fig. 3.6.

Fig. 3.6: A schematic representation of a scanning electron microscope.

**Electron beam-specimen interaction**

The electron beam impinging on the sample can partake in both elastic and inelastic scattering with the atoms in the specimen. Elastic events result when a beam electron
interacts with the electric field of nuclei within the specimen. Since nuclei are heavy compared with electrons, the beam electrons deflect without losing much energy. If the beam electron deflects back out of the specimen, the electron is called a backscattered electron, corresponding to an electron escaping the surface of the specimen with an energy greater than 50 eV. Inelastic collisions take place between the beam electrons and the electric field of electrons in the specimen (typically conduction electrons). Since this involves collision between particles of the same mass, energy is transferred to the electrons in the specimen. This transfer of energy to the electrons in the specimen can give them enough energy to overcome the work function of the material allowing them to escape from the surface in order to be detected, as so-called secondary electrons. A secondary electron corresponds to an electron leaving the surface of the specimen with an energy less than 50 eV. Fig. 3.7 is a schematic representation of the energy distribution of the electrons leaving a sample for an electron beam with energy of 30 keV.

Fig.3.7: A schematic of the energy distribution of the secondary and backscattered electrons produced by a electron beam of energy 30keV. Most of the electrons produced have energies of a few electron volts (secondary electrons) or energies equal to or just below the electron beam energy (backscattered electrons). The figure is not to scale.
Whether elastic or inelastic collision is dominant depends on the composition of the sample being investigated. Sample composed of atoms with low atomic numbers such as carbon, undergo significantly more inelastic collisions. The opposite is true for sample composed of species with large atomic numbers. This phenomenon also determines the penetration depth of the electron beam into the sample. Since the angle of deflection is small for an inelastic collision, an incident beam undergoing mostly inelastic collisions penetrates much deeper. The penetration depth of the incident beam must be taken into account, since often we are interested in imaging the surface of samples. For imaging graphene-related materials we typically use incident beams energies on the order of a few keV to avoid deep penetration of the incident beam, because carbon is a relatively light element.

Inelastic scattering of the incident electrons produces not only secondary electrons but also X-rays, Auger electrons, cathodoluminescence and heat. The X-rays emitted from the sample can be used for elemental characterization. This technique is called energy dispersive X-ray (EDX) spectroscopy. When energy from the incident or backscattered electrons is transferred to an inner shell electron of an atom in the sample, the electron can be ejected from the inner orbital leaving a vacant orbital in place. Subsequently, higher shell electrons can transit to the vacant lower orbital by emitting an X-ray or an Auger electron. The energy of the emitted X-ray corresponds to the difference between the energy of the two orbitals involve. Since atoms have distinct energy orbitals, the energy of the emitted X-rays are characteristic of the atoms they originate from. By mapping the intensity vs. energy of the emitted X-rays from a sample we can extract the elemental composition of the samples (see Fig. 3.8). EDX spectrometers use a data base for assigning the various peaks according to their energy to various elements in the periodic table. The relative intensities of the various
peaks can be related to the relative composition of the various elements in the sample. In Fig. 3.8 the source of the continuum X-ray is related to the interaction of the incident beam electrons with the nuclei of the specimen. For a detailed description of SEM and EDX refer to [5].

![Fig. 3.8: Schematic of an energy dispersive X-ray spectra.](image)

### 3.4 Raman spectroscopy

The Raman spectroscopy measurements presented in this thesis were done using a Renishaw In Via spectrometer equipped with a 532-nm diode laser at 100 mW power. Power was normally kept well below that level to limit damage of the sample surface.

Raman spectra are due to inelastic scattering of photons, typically by the collective lattice vibrational modes in a solid or vibrations in molecules. An incoming photon of energy $\omega$ and wavevector $\vec{k}$ scatters with the vibrating lattice producing an outgoing photon of energy $\omega'$ and wavevector $\vec{k}'$. Based on conservation of energy and momentum we must have

$$\omega = \omega' \pm \Omega \quad \text{and} \quad \vec{k} = \vec{k}' \pm \vec{K},$$  

(3.5)
where $\Omega$ and $\vec{K}$ are the energy and momentum imparted to, or withdrawn from, the lattice, in the case of ‘minus’ and ‘plus’ sign respectively. In crystals energy and momentum transfers typically produce quanta of collective and coherent lattice vibrations known as phonons. In molecules the energy and momentum transfer produce localized vibrational excitations. The conservation laws in Eq. (3.5) correspond to a first-order Raman Effect. Higher order Raman effects can also take place, where more than one phonon are annihilated or generated in the inelastic scattering of the photon.

To illustrate the Raman process we give a classical description of Raman scattering by considering the vibrational excitation of a diatomic molecule. Consider a monochromatic electromagnetic (EM) wave, propagating in the $x$-direction and linearly polarized in the $z$-direction, incident on a diatomic molecule placed at the origin of our coordinate system. The time-dependent electric field at the location of the molecule is

$$E_z = E_{z,0} \cos(\omega t),$$  \hspace{1cm} (3.6)

where $E_{z,0}$ is the amplitude and $\omega$ is angular frequency of the oscillating field. We ignore the magnetic component of the field since the excitation we are considering are induced by the electric-field component of the EM wave. The time-dependent displacement vector defining the vibration of the molecule is

$$\vec{D} = \vec{D}_0 \cos(\omega_0 t),$$  \hspace{1cm} (3.7)

where $\vec{D}_0$ is the displacement amplitude and $\omega_0$ is the natural vibration angular frequency of the diatomic molecule. The electric component of the EM wave induces an electric dipole moment $\vec{p}$ given by

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\[ \hat{p} = \alpha \hat{E}, \]  

(3.8)

where the polarizability tensor \( \alpha \) can be expanded in a Taylor series in terms of the displacement vector as \( \alpha = \alpha_0 + \left( \frac{d\alpha}{dD} \right) d + \ldots \), where higher order terms (not shown) correspond to higher order Raman effects. Using Eqs. (3.6)-(3.8), we get

\[ p = \alpha_0 E_{z,0} \cos(\omega t) + \left( \frac{d\alpha}{dD} \right) d_0 E_{z,0} \left\{ \cos[(\omega - \omega_0) t] + \cos[(\omega + \omega_0) t] \right\}. \]  

(3.9)

The induced dipole moment given by Eq. (3.9) involves vibrations at three distinct frequencies. The oscillating dipole will emit light at these frequencies. The first term in Eq.(3.9) produces a photon with energy \( \hbar \omega \) equivalent to the incident photon, and therefore corresponds to elastic scattering (Rayleigh scattering) of the EM wave. The two additional terms correspond to inelastic (Raman) scattering of the incident light producing photons with energies \( (\omega - \omega_0) \hbar \) and \( (\omega + \omega_0) \hbar \). In the first case \( \hbar \omega_0 \) energy is imparted to the dipole (Stokes process), while in the latter case the scattering produces an outgoing photon larger than the incident photon by an amount \( \hbar \omega_0 \) (anti-Stokes process). The intensity of the Stokes and anti-Stokes lines have different temperature dependence. In the anti-Stokes processes where the incident photon gains energy from the material, temperature induced vibrational states need to be present in the material. For this reason the intensity of the anti-Stokes process goes to zero at zero temperature. Fig.3.9 is a generic schematic of a simple Raman spectra, showing some Rayleigh, Stokes, and anti-Stokes peaks.
Although our earlier discussion leading to Eq. (3.9) is an over simplified description, it gives some basic insight about the Raman process. For a quantum mechanical treatment of the Raman process refer to [6]. From Eq. (3.9), we see that the Raman processes occur only when $\frac{d\alpha}{dD} \neq 0$. This condition is usually referred to as a selection rule for the Raman active excitations. Whether or not a vibrational mode is Raman active is intimately related to point groups of molecules and crystals, based on their symmetry. For discussion of point groups refer to [7].

Here we will give a basic description of a standard Raman spectrometer, as depicted in Fig. 3.10. The basic components are an excitation source (usually a laser), microscope objective, lenses, notch filter, spectrometer and a CCD. The laser is guided onto the sample. The scattered light is collected through the microscope objective and is focused into a spectrometer using a focusing lens. Typically a notch filter is used to filter the strong Rayleigh line in order to resolve the much weaker Raman bands. The monochromator uses a
set of gratings and mirrors to guide the scattered light of a selected frequency onto the CCD. As the monochromator scans over the range of frequencies the CCD registers the intensity of the signal.

![Diagram of a standard Raman spectrometer showing the major components.](image)

Fig. 3.10: A schematic of a standard Raman spectrometer showing the major components.

### 3.5 Conclusions

We presented some of the physical concepts related to the main characterization techniques used in this thesis. They included descriptions of electron spin resonance, atomic force microscopy, scanning Kelvin probe force microscopy, scanning electron microscopy, energy dispersive X-ray spectroscopy, and the Raman spectroscopy. Some of the main components of the instruments were also discussed. The electron spin resonance spectrometer was discussed in greater detail since it is a major focus of the thesis.
References


CHAPTER 4

Paramagnetic Centers in Chemically Exfoliated Graphene Nanoribbons

Graphene nanoribbons (GNRs) have attracted significant attention in recent years (see discussion in Section 1.3). One of the more interesting features of GNRs is the tunability of their magnetic [1–5], electronic [4–7], and optical properties [5, 8, 9] based on the ribbon dimensions and chirality. For example, it has been shown that GNRs with zigzag edges may exhibit magnetic ordering and ferromagnetic properties [1], while GNRs with armchair edges do not. In this chapter we present a combined experimental and theoretical study of paramagnetic centers in GNRs of both types.

4.1 Introduction

Understanding the origin of weak and strong magnetism in materials based on GNRs will lead to a host of applications such as high-density data storage and spintronics [1,10]. Specifically, the ability to control the formation of paramagnetic centers, which may act as photon and charge carrier traps [11], can provide improvements in the efficiencies of electronic devices based on GNRs [12]. Nevertheless, the magnetic properties of GNRs are still poorly understood. In most magnetically ordered materials it is the localized $d$ and $f$ electrons of transition metals that give rise to magnetic ordering (see, e.g., [13, 14]). However, in GNRs, no $d$ or $f$ electrons are present and $\pi$-bonded electrons associated with $sp^2$ hybridized carbon atoms are presumed to be responsible for the paramagnetic centres that produce magnetic ordering. In aromatic carbon systems (including graphite, graphene,
graphitic amorphous carbons, carbon nanotubes and GNR) \(\pi\)-electrons tend to be delocalized over a large number of sixfold rings formed by \(sp^2\) hybridized C atoms in order to minimize the formation energy of \(\pi\)-bonds [15]. For GNRs less than \(~20\) nm in width, where the confinement of \(\pi\)-electrons becomes relevant, the electron-electron correlation effects have been suggested to give rise to an electron spin polarization localized along the zigzag edges which reduces the coulombic interaction [16], thereby in effect opening up an energy gap. However, room temperature ferromagnetism has also been observed in graphene sheets where confinement is clearly absent [17] and optical band gaps were also observed in relatively large graphene oxide flakes [18].

In the present study, we have synthesized GNRs using the method developed by Tour and coworkers [19] for longitudinally unzipping multi-wall carbon nanotubes (MWNTs). Advantages of this method lie in the high yield (nearly 100%) of graphene nanoribbons, the large fraction of single-layer GNRs that can be obtained, and the possibility to control the length of GNRs at a relatively constant width that depends on the diameter of the unzipped MWNTs [19]. These widths are significantly larger than those reported for the GNRs which exhibit substantial correlation effects [7, 13]. We have utilized such GNRs to prepare nanoribbon-based paramagnetic thin films using the method developed by Eda et al. [20] for chemically oxidized graphene oxide, which have been studied by electron spin resonance (ESR) spectroscopy. This study will allow us to explore the magnetic properties of GNRs in the absence of electronic correlation effects and, in combination with theoretical calculations, provide us with useful insights into the nature of paramagnetic centres and weak magnetism in GNRs.
4.2 Experiment

GNRs were synthesized from purified MWNTs with diameters 100-170 nm and lengths 5-9 µm purchased from Aldrich Inc. (batch no MKBD9161V). 25 mg of MWNTs were suspended in concentrated sulphuric acid (H₂SO₄) at 1 mg/ml. Afterwards, 500 wt % of oxidizer (potassium permanganate, KMnO₄) was added to the suspension and stirred for one hour, followed by heating and stirring in an oil bath for an additional hour [19]. Seven suspensions were prepared by varying the oxidization temperature in a range from 20°C to 110°C. These suspensions were then centrifuged at 6,000 rpm for 1 hour and the supernatant and sediment separated for characterization and additional processing. For each oxidation temperature, two GNR-based thin films were prepared by vacuum-filrating the supernatant and sediment, respectively, onto 220 nm pore-size membranes (MCE, Millipore) [20] and used for ESR characterization. The membranes were weighted before and after vacuum filtration in order to determine the amount of material deposited. In addition, pieces of (1,0,0) silicon wafers coated with a 300 nm-thick layer of thermally oxidized SiO₂ (University Wafers Inc.) were dip-coated from each of these suspensions in order to prepare GNR samples suitable for direct characterization under optical, electronic and atomic force microscopes. The flow chart used for the synthesis of GNR and preparation of GNR-based thin films is depicted in Fig. 4.1.

Samples prepared on SiO₂-coated Si (1,0,0) wafers were investigated using a Zeiss LEO 1540XB scanning electron microscope (SEM) equipped with an energy dispersive x-ray (EDX) detector for compositional analysis of the specimen. A Witec Alpha 300S atomic force microscope (AFM) was used for tapping-mode characterization of the same samples and a Renishaw InVia spectrometer was used to record the micro-Raman spectra at 633 nm laser excitation and power densities from 200 to 500 W/mm². For each sample a statistical
analysis, based on a number of $10\times10\ \mu m^2$ AFM images recorded on different zones of the substrate, was utilized in order to infer the distribution of the GNR lengths.

Fig. 4.1: Schematic for processing GNRs by oxidation of multi-wall nanotubes, centrifuging the solution and separating the supernatant and sediment, dip coating the solutions onto a Si/SiO$_2$ substrate, and vacuum filtrating the solutions onto MCE filter membranes.

To characterize the paramagnetic centres of GNR-based thin films, we used a Jeol FA-200 ESR spectrometer operating in the X-band (~9.5 GHz). The 100-KHz modulation amplitude of the microwave field used to detect the signal was kept below 30% of the signal line width in order to prevent distortions in the spectral lines. Low microwave power (<1 mW) was used to prevent the saturation of the signal. Preliminary baseline measurements were used to ascertain the negligibility of the ESR signal from the supporting MCE membranes. To calculate the spin density in our samples, we used a built-in Mn$^{2+}$ reference marker installed in the resonator, which was measured simultaneously with the samples and the integrated area of the spectrum was normalized with the weight of the film. ESR measurements below room temperature and down to -170°C were performed using a
computer-controlled liquid nitrogen cryostat. Such measurements are essential to gain insight to the different nature of paramagnetism in GNR-based thin films prepared under different conditions, as will be discussed below. For more detail of the characterization techniques refer to Chapter 3.

4.3 Experimental results

4.3.1 Size distribution and morphological properties of the samples

Fig. 4.2: Samples produced by vacuum filtration onto a MCE filter membrane after centrifuging for all seven oxidation temperatures and (below) schematic of the structural change in the samples with changing oxidation temperature.

A set of magnetic GNR-based thin films prepared at various oxidation temperatures from 20°C to 110°C is illustrated in Fig. 4.2. It is evident that a colour variation of the films is observed with changing oxidation temperature. The pigment of the suspension processed at 20°C and the colour of the films obtained are comparable to the surfactant-assisted dispersions in water of the carbon nanotubes used to prepare our GNRs and similar results can be inferred by more quantitative optical transmission measurements in the visible-near IR
photon energy range (not shown here). Conversely, the pigment of suspensions processed at 40°C and above, gradually becomes lighter until a yellow hue is established at 80°C, a colour typical of graphene oxide [18, 20]. Lighter yellow colours are indicative of the opening of increasingly large optical band gaps in more oxidized materials. Suspensions processed at 90°C and above start to develop a grey charcoal pigment that can be assigned to amorphous carbon (a-C) nanostructures, in which the optical band gap decreases as disorder in the graphene lattice and bond angle distortions become more significant, consistent with the amorphization of the graphene lattice [21].

Fig. 4.3: (a) Scanning electron micrograph of pristine MWNTs dip-coated on a SiO$_2$ coated Si(1,0,0) substrate; (b) corresponding micrographs of GNRs obtained at 40°C, with a partially unzipped MWNT and (c) with a shorter, completely unzipped, GNR obtained at 80°C; (d) entangled GNRs from the same suspension reported in panel c, which is representative of our vacuum-filtrated GNR-based thin films.

Fig. 4.3 reports a set of SEM micrographs elucidating the unzipping process of
MWNTs and the formation of graphene nanoribbons in our samples. Fig. 4.3(a) shows untreated MWNTs, while in panels b and c of Fig. 4.3, partially unzipped MWNTs and unzipped GNRs are visible, with a morphology that can be clearly distinguished from the MWNTs in panel a. It can be observed that the GNRs exhibit a planar, rectangular, shape, while the MWNTs have a tubular shape. Fig. 4.3(d) exhibits a morphology that is representative of our vacuum-filtrated GNR-based thin films. From extensive SEM analysis, we could very seldom observe partially unzipped MWNTs as in Fig. 4.3(b), while fully unzipped GNRs represent an overwhelmingly large fraction of the carbonaceous material in our samples. Such observations are also corroborated by our Raman measurements.

Fig. 4.4: (a) Raman spectra of pristine MWNTs (blue) and GNRs (red) obtained from surfactant oxidized at 80°C. The single 2D peak is consistent with abundant single or few-layer graphene sheets in GNR at the opposite of multiple rolled sheets in MWNTs (which give rise to a composite 2D peak. In the blue spectrum) (b) Detail of the Lorentzian fits of the Raman peaks are discussed in the text (D, G₁, G₂ and D’). The G₁ is related to the polarization direction of the incident light with respect to the ribbon axis, while the G₂ is associated with the E₂g vibrational mode of bulk graphene. is The inset indicates the position of the G₁ and G₂ peaks as a function of the laser power density on the sample. The degeneracy removal of the G-peak at increasing temperature is also an indication of GNRs.

Specifically, Fig. 4.4 shows a Raman spectrum from our pristine MWNTs and the
corresponding spectrum of the film prepared by processing the nanotubes at 80°C. The latter is consistent with the Raman signatures of relatively wide GNRs (> 100 nm) as previously reported in the literature [22, 23]. These spectra were taken at low microscopic resolution (> 50 µm). Our films contain randomly oriented GNR and, therefore, the Raman anisotropy of GNRs [22] cannot be resolved. Apart from this, Fig. 4.4 captures all of the relevant features of the Raman spectrum of GNRs. In Fig. 4.4a, the 2D peak can be simulated by a single Lorentzian, which is consistent with abundant single or few-layer graphene sheets in GNRs, and contrasts with multiple rolled sheets in MWNTs (which give rise of a composite 2D peak). In addition, in Fig. 4.4b, it can be observed that the disorder-related D-peak at 1350 cm⁻¹ (related to defects, impurities and/or graphene edges [23]) is much stronger in GNRs than in MWNTs. In addition, in the spectrum of GNRs shown in Fig. 4.4b, we note the appearance of the D’ peak at 1630 cm⁻¹, which is typically assigned to graphene edges [23] and is not visible in the spectrum of our pristine MWNTs. The appearance of this peak is a signature of GNRs that are approximately 100-150 nm in width [23, 24], and is not consistent with closed MWNTs. Another indication of GNRs can be inferred from the degeneracy removal of the G-peak at increasing temperature [22] which can be clearly observed in the inset of Fig. 4.4a. Finally, all of the Raman peaks of GNRs in Fig. 4.4b are broader than in MWNTs, due to structural disorder introduced during the oxidative process [20] and the removal of degeneracy of the G-Raman peak caused by different thermal response of the ribbons in transversal and longitudinal directions under laser heating [22].

We also corroborated the Raman considerations offered in Fig. 4.4 by AFM studies of our samples, as shown in Figs. 4.5 and 4.6. Fig. 4.5 demonstrates that our GNRs are clearly distinguishable from MWNTs in topographic (height) images. However, in order to perform a more quantitative study of the length and width of the GNRs as a function of the
process temperature, we used the phase images of our tapping-mode AFM micrographs, demonstrated in Fig. 4.6, because they offer a much stronger contrast with the substrate and, therefore, they can be more easily digitally processed. Fig. 4.5(a)-(c) illustrate the quality of GNRs produced between 40°C and 80°C oxidation temperatures. We infer that the width distribution of the GNRs appear to be unaffected by varying the oxidization temperature and are found to be in the range of ~100-200 nm. From AFM topography images (not shown here) we have also observed that an large fraction of the GNRs are single-layer, with thickness ~1 nm or below, and maximum thicknesses up to 20 nm, when stacks are formed by the simultaneous unzipping of a number of shells of a MWNT.

![Fig. 4.5: Atomic force height micrographs of our samples: (a) MWNTs and (b) GNRs obtained from surfactant oxidized at 80°C as in Fig. 4.3. (c) The different height profiles for MWNTs and GNRs obtained through the cross sections drawn in panels a and b are shown.](image-url)
At the relatively low oxidation temperature of 40°C the ribbons have a length distribution [Fig. 4.6(d)] similar to the starting-out MWNTs, with a median length of ~4.5 µm and only a few percent of the GNRs that are longer than 9 µm. However, when the oxidation temperature is increased to 80°C [Fig. 4.6(e)], the ribbons appear to be significantly shortened. Therefore, it is apparent that not only does stronger oxidation cut the nanotubes longitudinally, which is essential for unzipping them, but it is also effective in producing cuts in the direction transverse to the tube axis, leading to median lengths of ~700 nm. Clearly, a fraction of MWNTs is also destroyed during the oxidative process, as demonstrated by the presence of an increasing number of small nanoparticles that are visible in Fig. 4.6(b) at 80°C. At 90°C and above, where films assume the charcoal grey
pigmentation typical of $sp^2$-bonded amorphous carbon, they are entirely formed by such nanoparticles with no ribbon-like features left on the substrate.

A number of EDX spectra (with electron beam at 10keV), analogous to that depicted in Fig. 4.6(f), confirmed that the nanoparticles shown in Fig. 4.6(c), are actually formed by carbon, with no or little amounts of impurities. Specifically, no traces of manganese, a by-product of the oxidation procedure, were observed after appropriate washing of the samples. The absence of Mn is essential for our ESR analysis since Mn ions, if present, are expected to be a relevant source of paramagnetic centres, although such centres can be easily recognized by ESR from the hyperfine modulation of the spectra due to nuclear spins in $^{55}$Mn nuclei. In principle, another possible source of impurity-related paramagnetic centres may be the iron catalyst used for the synthesis of the MWNTs left behind from incomplete purification of the sample. No Fe has been detected by EDX and, in addition, the presence of Fe-related unpaired defects would not account for the $g$-values observed in our ESR investigation, as discussed below.

### 4.3.2 ESR characterization of paramagnetic defects

ESR measurements for most of the supernatant and sediment samples yielded featureless single peaks in the range of $g \sim 2.0026 - 2.0029$. The peaks corresponding to samples prepared at oxidation temperatures of 60°C and below are symmetric and have a Lorentzian profile, as inferred from Fig. 4.7(a) and (b). However, for the sample prepared at 80°C oxidation temperature the ESR spectra exhibit two peaks. The second peak at $g \sim 2.0066$ becomes more apparent in measurements recorded below room temperature, as shown in Fig. 4.7(c), where the spectrum has been simulated using the superposition of two Lorentzian lines. Thus, it is evident that two distinct types of paramagnetic centres, with
different dependences on the oxidation temperature, are present in our samples.

Fig. 4.7: ESR spectra of samples processed at 20°C, 40°C, and 60°C for (a) supernatant and (b) sediment samples. (c) Low-temperature (-160°C) ESR spectrum of the supernatant sample oxidized at 80°C, with two different types of paramagnetic centers.

By recording the intensity of the ESR signal at variable measurement temperatures between 20°C and -180°C, as shown in Fig. 4.8, the origin of paramagnetism in our films can be elucidated for both the supernatant and sediment of samples prepared under different oxidation conditions. Specifically, in paramagnetic solids, the intensity of the ESR signal is proportional to both the spin density and the magnetization. These exhibit different temperature trends, depending on whether they are related to extended or localized paramagnetic centres. For a detailed discussion on the various types of paramagnetism refer to Section 2.4. Specifically, if localized magnetic moments are responsible for the
magnetization, Curie’s Law predicts that the ESR signal is inversely proportional to the measurement temperature (see Eq. (2.73)), while the magnetization and the ESR signal are independent of temperature in the case of Pauli paramagnetism (see Eq. (2.79)) and magnetic moments associated with extended states, such as in metals and semimetals [13, 14].

![Graphs showing ESR signal intensity vs. measurement temperature for supernatant and sediment at different oxidation temperatures.](image)

**Fig. 4.8:** Intensity of the ESR signal vs. measurement temperature for the supernatant at oxidation temperatures of: (a) 20°C, (b) 80°C, (c) 110°C, and sediment at oxidation temperatures of: (d) 20°C, (e) 80°C, and (f) 110°C. The traces in the figures are guides.

For instance, Fig. 4.8(a) and (d) show that, for the samples produced at 20°C, a decreasing trend of peak intensity vs. temperature is observed. We therefore suggest that a major contribution to the magnetization for these cases comes from localized magnetic moments and Curie-type paramagnetism. Conversely, Fig. 4.8(b) and (e) demonstrate that the intensity of the ESR signals for the samples produced at 80°C is independent of the
measurement temperature, with the exception of an anomalous point at -160°C, which coincides with the appearance of the second peak at $g \sim 2.0066$ in the corresponding ESR spectra, shown in Fig. 4.7(c). Here the temperature independence of the peak intensity indicates a large presence of extended states. Finally, at the highest processing temperature (110°C) where no ribbons but only nanoparticles are observed by AFM, Fig. 4.7(c) and (f) suggest that the paramagnetism is, again, mainly Curie-type and attributable to localized states, as can be expected from amorphous carbons [25]. Consequently, Fig. 4.8 leads us to conclude that, in our samples oxidized at different temperatures, three different regimes of paramagnetism are present depending on which type of paramagnetic centre dominates the ESR signal. Curie paramagnetism is associated with MWNTs and long GNRs synthesized at the lowest oxidation temperatures; Pauli paramagnetism is associated with short GNRs synthesized at higher oxidation temperatures, while amorphous carbon nanoparticles produced at the highest temperatures also show Curie paramagnetism. These trends were identified for both the supernatant and sediment samples.

4.4 Theory

As discussed in Chapter 1, for $sp^2$-hybridized carbon systems each carbon atom contributes three $\sigma$-bonded electrons and one $\pi$-bonded electron. $\sigma$-bonded electronic wavefunctions are localized along the axis between two nearest-neighbour carbon atoms and, in graphene and GNRs, the atoms form a planar honeycomb lattice that determines the structural and mechanical properties of these solids [15, 21, 25]. $\pi$-bonded electronic wavefunctions are nonzero only out of plane and are delocalized above and below the lattice formed by $\sigma$-bonded electrons. Due to the negligible overlap between $\pi$-bonded and $\sigma$-bonded electronic wavefunctions, these two electronic systems can be treated independently.
Specifically, $\pi$-bonded electrons possess a much weaker bonding energy than $\sigma$-bonded electrons and, therefore, determine the electronic density of states (DOS) near the Fermi level that, in turn, controls the density of singly-occupied electronic states in $sp^2$-hybridized carbon systems [25].

While doubly-occupied electronic states situated well below the Fermi level are diamagnetic, singly-occupied electronic states sitting near the Fermi level contain unpaired electron spins and therefore can be paramagnetic and ESR active. Simple topological considerations suggest that any $sp^2$-hybridized carbon system comprised of a finite and even number $N$ of carbon atoms forms $N/2$ doubly-occupied $\pi$-electronic states and involves no unpaired spin. Consequently, for an $sp^2$ hybridized carbon system to be paramagnetic and ESR active, one of the following conditions must be satisfied: (a) $N$ is odd and relatively small [26]; (b) $N$ is locally odd, due to the presence of vacancies, interstitials or specific lattice imperfections (including fivefold and sevenfold rings [21]); (c) $N$ tends to infinity or, at least, is large enough for a specific arrangement of $\pi$-electrons (for instance, at the edges of a zigzag GNR) to allow for a nonzero DOS within an interval of energies $\pm k_B T$ about the Fermi level.

Although electron-electron interaction may be important to study quantitatively a number of very small $sp^2$-hybridized carbon systems, it has been reported [13] that only GNRs with width below $\sim 20$ nm exhibit features associated with strong electron correlation effects [7]. These effects become less important for ribbons of larger widths, and in the extreme limit of a large graphene sheet, calculations in the absence of correlation effects are found to give excellent results [27]. From our experiments GNRs produced using MWNTs have widths of the order of hundred nm. In this regime we expect correlation effects to play a minimal role. Thus we will employ the Hückel tight-binding model in order to infer the
electronic structure and formation energies of various GNRs, by analogy with ref. [15] for compact aromatic structures.

The tight-binding Hamiltonian Eq. (2.48) in second-quantized notation can be re-expressed as

$$H = - \sum_{\langle i,j \rangle} t_{i,j} \left( c_i^+ c_j + c_i c_j^+ \right),$$  \hspace{1cm} (4.1)

where $c_i^+$ and $c_i$ are the electronic creation and annihilation operators, respectively, which are associated with out-of-plane $\pi$-orbitals at the lattice site $i$. Also $t$ is the $\pi-\pi$ interaction energy between the nearest-neighbour sites and $\langle i, j \rangle$ denotes that summations are performed only over the nearest-neighbour $\pi$-orbitals. We used $t \sim 2.88$ eV for graphene-based materials [15]. The matrix Hamiltonian for zigzag and armchair GNRs of different dimensions were formulated and diagonalized in order to extract the "valence" and "conduction" electron eigenvalues. The general form of these matrices for both zigzag and armchair GNRs are provided in Appendix B. The density of electronic states for the different GNR structures was numerically calculated by assuming that each energy eigenvalue $E_k$ contributes to the DOS with a Lorentzian peak of width $\Gamma \ll t$. Using this simple procedure the total DOS can be formally written as

$$\text{DOS}(E) = \frac{1}{\pi} \sum_k \frac{\Gamma/2}{(E - E_k)^2 + (\Gamma/2)^2},$$  \hspace{1cm} (4.2)

where the spectrum of eigenvalues $\{E_k\}$ is extracted from the tight-binding Hamiltonian in Eq. (4.1) re-expressed in terms of a matrix representation for the finite GNR lattice provided in Appendix B. The summation in Eq. (4.2) is taken over the entire range of eigenvalues. We assumed $\Gamma = 0.1$ eV, consistent with the amount of disorder that can be expected in a weakly amorphized carbon system [15].
Fig. 4.9: Density of states for (a) zigzag and (b) armchair nanoribbons with a length/width aspect ratio of 11, calculated using the Hückel tight-binding method.

4.4.1. Zigzag edges

The calculated DOS for typical zigzag and armchair GNRs are shown in Fig. 4.9(a) and (b), respectively. The major distinction between the two cases is the peak at the Fermi energy, defined as $E = 0$ on our energy scale. This peak corresponds to an increase in the number of states localized along a zigzag edge. These considerations suggest that zigzag GNRs are ESR active and exhibits Pauli paramagnetism (see Eq. (2.79)) as a consequence of the nature of the paramagnetic centres involved, which extend along the edges of the nanoribbons. On the other hand, no strong peak near the Fermi level is noticed for the armchair case, where the limited DOS at the Fermi level can be assigned to energy states localized at the zigzag ends of the ribbon.

To quantify the contribution from the extended states in terms of the GNR dimensions, the fraction of states in the energy range $E_f \pm k_B T$ was calculated for various
cases of GNR structures, where $E_f$ denotes the Fermi energy. An example of a plot for the fractional density of extended states vs. length/width ($L/W$) aspect ratio is given in Fig. 4.10 for both armchair and zigzag GNRs. From this trend we see that the majority of the extended states arise due to zigzag structures. However, at small aspect ratios (below ~10) the contribution from armchair GNRs start to become comparable.

Fig. 4.10: Fraction of Fermi states in the range of $E_f \pm k_B T$ for both armchair and zigzag nanoribbons plotted in terms of the $L/W$ aspect ratio.

Fig. 4.11: Vacancy-type defect localized near the centre of an armchair GNR. The bond reconstruction and the localized paramagnetic centre arising from it are shown in red.
4.4.2 Vacancies

As discussed in Section 4.3, in addition to Pauli paramagnetism associated with the extended states we have also experimentally observed Curie paramagnetism in our films, which is associated with localized magnetic centres. While Curie paramagnetism cannot be assigned to extended states along a zigzag edge, it has been reported, both experimentally [29] and theoretically [30–32], that single vacancies in graphene, such as those depicted in Fig. 4.11, give rise to localized magnetic moments.

Other common types of defects, such as double vacancies, chemically terminated dangling bonds, and Stone-Wales defects may also be present in our samples, but are not expected to be magnetic [33]. Therefore, it is presumed that the main source of localized paramagnetic centres is vacancies. In order to determine the dominant type of defect in our samples, the formation energy of both vacancies and zigzag edges for GNRs as a function of their length have been calculated and compared. For any given type of nanoribbon with specific length and width, the type of paramagnetic centre with the lower formation energy is expected to be more energetically favoured and, consequently, more abundant.

The defect formation energy per atom for various defective structures, including vacancies and zigzag edges, was calculated by summing over the energy eigenvalues, weighted by their occupation number and divided by the total number of carbon atoms \(N_{\text{tot}}\) in the nanoribbon. The formation energy of defects can be determined as the difference between the formation energies of the non-defective (n-d) and defective (d) structure. In the case of vacancies, we used a GNR with a carbon atom missing at the centre as the defective structure, as shown in Fig. 4.11. With this in mind, the formation energy of vacancies at the centre of a GNR is expressed as
\[ \Delta E_{\text{VAC}}(L, W) = \frac{1}{2N_{\text{tot}}} \left( \sum_k n_{\text{occ}, k} E_k^{(\text{n-d})} - \sum_k n_{\text{occ}, k} E_k^{(\text{d})} \right), \]  

(4.3)

where \( \{E_k^{(\text{n-d})}\} \) and \( \{E_k^{(\text{d})}\} \) represent the spectra of eigenvalues obtained from the tight-binding Hamiltonian in Eq. (4.1), as mentioned before, for a non-defective and defective structure of length \( L \) and width \( W \). Also, \( n_{\text{occ}, k} \) is the occupation number for the \( k \)-th eigenstate of a specific nanoribbon, either armchair or zigzag (i.e., \( n_{\text{occ}, k} = 2 \) for doubly occupied states in the valence band, \( n_{\text{occ}, k} = 0 \) for unoccupied states in the conduction band and \( n_{\text{occ}, k} = 1 \) for singly-occupied paramagnetic states within the energy interval \( E_f \pm k_B T \) in the proximity of the Fermi level).

For comparison, we calculated the corresponding formation energy of zigzag edges given by

\[ \Delta E_{\text{ZZ}}(L, W) = \frac{1}{2N_{\text{tot}}} \left( \sum_k n_{\text{occ}, k} E_k^{(\text{ZZ})} - \sum_k n_{\text{occ}, k} E_k^{(\text{AC})} \right), \]  

(4.4)

where now \( \{E_k^{(\text{ZZ})}\} \) and \( \{E_k^{(\text{AC})}\} \) represent the spectra of eigenvalues for a GNR with zigzag (ZZ) and armchair (AC) edges for structures of length \( L \) and width \( W \). Interestingly, both \( \Delta E_{\text{VAC}} \) and \( \Delta E_{\text{ZZ}} \) appear to be more closely related to the length-to-width (\( L/W \)) aspect ratio, rather than to the simple length, or width, of the nanoribbons. Therefore, we will use \( L/W \) as the relevant parameter for our considerations, even though our GNR films were prepared at a fixed width and varying length.

### 4.5 Discussion

The formation energies for zigzag edges and vacancies at varying aspect ratio are plotted in Fig. 4.12(a). From this plot we see that \( \Delta E_{\text{ZZ}} \) reduces with increasing \( L/W \), making zigzag edges energetically disfavoured for the less compact ribbons (i.e., at a constant width,
for longer ribbons). Conversely, the opposite trend is observed for vacancies that become more favoured with increasing GNR length. The spin densities exhibit an increasing trend for the sediment [Fig. 4.12(c)] and decreasing trend for the supernatant [Fig. 4.12(d)] with increasing GNR length.

These trends are in agreement with the calculated formation energies of vacancies for the sediment and zigzag edge for the supernatant. From Fig. 4.12(d) we see that the spin density is relatively constant for longer ribbons produced at oxidization temperatures of 60°C and below, but starts to increase at 80°C where the median aspect ratio of the ribbons is ~7. At these low aspect ratios the zigzag edge formation energy starts to increases dramatically making zigzag edges more energetically favoured. In fact, Pauli paramagnetism associated with zigzag edges is observed for this sample. In Fig. 4.8(b) we see a deviation from the constant magnetic susceptibility at a measurement temperature of -160°C. This is expected for a mixture of both free carrier states and localized paramagnetic centres where the paramagnetism due to extended states is large. At low enough measurement temperatures the Curie nature of paramagnetism is noticeable, while at higher measurement temperatures where the contribution from localized moments diminishes due to thermal fluctuations, the constant magnetic susceptibility Eq. (2.79) associated with extended states starts to dominate. From Fig. 4.12(a) we see a crossover of the formation energy for zigzag edges and vacancies at a length to width aspect ratio of ~4. From the size distribution of the GNRs shown in Fig. 4.6(e) we expect to have a mixture of vacancies and zigzag edges for this sample.

The combined fraction of extended states, defined as the fraction of states within $\pm k_B T$ of the Fermi energy, for both armchair and zigzag GNRs was calculated in terms of the $L/W$ aspect ratio. Based on the calculated formation energy of the GNRs the Boltzmann distribution function was used to scale the contribution from armchair and zigzag edges for
the different size regimes. A plot of the total fraction of extended states scaled based on the Boltzmann distribution is shown in Fig. 4.12(b). The decreasing trend with increasing aspect ratio is representative of the trend observed for the spin density of the supernatant. The change in magnitude of the extended states for aspect ratios below 20 is small, but it starts to increase significantly for smaller aspect ratios, which corresponds well with the onset of the observed increase in spin density at $L/W \sim 7$.

Fig. 4.12: (a) Formation energy of zigzag edges (triangles) and (b) vacancies (circles and squares) vs. length/width aspect ratio. (b) Total fraction of Fermi states from both armchair and zigzag structures vs. aspect ratio. Spin density of the (c) sediment and (d) supernatant as a function of processing temperature.
For the sediment we note that these structures are expected to be heavier and/or less dispersive, causing them to sink. From the formation energy calculations it is apparent that the larger or heavier structures are more prone to forming vacancies rather than zigzag edges, which explained the increasing spin density with increasing GNR length. As the structures reduce in size vacancies become less energetically favoured causing the spin density to reduce.

The lack of extended states at the highest oxidation temperature (110°C), where no ribbon features were observed is likely due to the fact that an energy gap forms for these small structures where confinement effects become relevant. The increased spin density may be a result of localized odd-numbered carbon clusters in amorphous nanoparticles, in which each odd cluster has a single unpaired electron contributing to the total spin density [26].

4.6 Conclusions

In conclusion, our work represents a thorough study of weak magnetism in GNRs produced by an oxidative method. We found that, by increasing the processing temperature of suspended MWNTs in the presence of an oxidizer, GNRs of reduced lengths and constant widths are produced. ESR measurements of these samples showed very different spin densities and type of paramagnetism dependent on the length distribution of the GNRs. It was shown theoretically that longer ribbons are prone to form vacancies which give rise to localized paramagnetic centres, while shorter ribbons are more prone to form zigzag edges, giving rise to paramagnetism associated with extended states. These findings are in good agreement with the experiment and allow us to assign the paramagnetic centres to zigzag edges in short GNR and to vacancies in longer and less oxidized GNRs.
References

CHAPTER 5

Electronic Properties of Graphene Thin Films Decorated with Copper Nanoparticles

In this chapter we present experiments and theory for the electronic properties of graphene films produced from chemically exfoliated nanographite and decorated with copper nanoparticles (Cu-NPs). Some experiments were done in collaboration with Sabastine Ezugwu and Dr. Shafiq Ahmed.

5.1 Introduction

In order to utilize advanced graphene-based materials in electronic and optoelectronic devices, it is of paramount importance to establish relationships between the fabrication conditions of these materials and their measurable electronic performance properties, by developing physical models. Modeling the effects of incorporating specific heteroatoms and impurities in large-area transparent and conducting graphene films is a typical example of such a requirement. It is well known that the electronic properties of graphene can be tailored via substitutional doping or by chemically bonding specific functional groups to the graphene layer [1-8]. However, substitutional doping and functionalization may also lead to additional undesired effects, because the alteration of graphene through chemical bonding can significantly affect its electronic structure near the Dirac point, which is responsible for the non-dispersive electronic band structure and the exceptional mobility of the carriers in graphene-based materials [9]. Chen et al. demonstrated that the carrier mobility decreases
with increasing dopant density in graphene that was substitutionally doped with potassium as a result of the scattering of $\pi$-electrons in graphene from potassium centers [8].

Controlling the electronic structure of graphene flakes by assembling metallic structures on their surface is another very promising direction of research for tailoring the electronic properties, with significant applications in fabrication of graphene-based batteries [10, 11], supercapacitors [12, 13], fuel cells [14-16] and other devices for electrical and energy applications[17, 18]. Using first principle calculations, Giovannetti et al. showed that the electronic band structure of graphene can be altered by applying metallic layers on its surface [19]. They demonstrated that the effect of metallic structures assembled on graphene is strongly dependent on the specific type of metal being used, with the formation of chemical bonds that may significantly alter the band structure of graphene at the Dirac point in case of some specific metals (such as Co, Ni and Pd). However, for other metals (e.g. Al, Cu, Ag, Au, and Pt) the metallic layers only caused shifts in the Fermi energy of graphene, which resulted in the doping of this material without significantly affecting its band structure. The distinct behaviour of different metals was attributed to differences in their work function relative to graphene [19].

While the work of Giovannetti et al. pointed at an attractive avenue for producing doped graphene thin films while limitedly altering the electronic band structure of graphene near the canonical point, assembling metallic layers on top of graphene sheets is not viable for several practical applications where access to the graphene surface is required [10-18]. To this end, the use of metallic nanoparticles, including specifically gold [20, 21] and copper [22-24], has been extensively studied by experimentalists working in the area of graphene devices. However, the role of the size, shape and concentration of metallic particles in affecting the microscopic properties of these nanocomposite systems has never been
investigated in detail. For instance, it is not clear if the increase in electrical conductivity that has often been observed in graphene layers decorated with metallic nanoparticles [36] is due to some form of substitutional doping, like in crystalline materials, or due to doping by compensation, like in amorphous silicon, or to other effects. Furthermore, it is not clear if the specific location at which a metallic nanoparticle is positioned (e.g. at the center of a graphene flake, or near an edge with a specific conformation) is important in affecting the electronic structure and electrical properties of the system.

In this chapter we investigate at the sub-micron level the electronic structure and the Fermi energy shifts in transparent and conducting graphene thin films formed by collections of flakes with different number of layers when such flakes have been decorated with copper nanoparticles (Cu-NPs) at different diameter and surface area coverage. We develop a theoretical framework based on the tight-binding approximation for understanding the Fermi level shifts and changes in electrical conductivity that we measured by Scanning Kelvin Probe Force Microscopy measurements (SKPFM) and two-point electrical measurements. In our calculations, the presence of Cu-NPs on graphene is accounted for by modifying the local potential for carbon sites in contact with a Cu-NP. This approach is justified assuming that we expect the band structure of graphene to remain mostly intact, since Cu bonds very weakly with graphene and only via Van der Waals interactions. The weak interaction between sp⁴ hybridized carbon and copper is also corroborated by the fact that Cu foils are excellent substrates for chemical vapour deposition of graphene, without the formation of a carbide interlayer [1, 25-28]. Copper provides the appropriate platform for maintaining the structural integrity of graphene.
5.2 Experimental and theoretical methods

**Graphene film preparation:** Transparent and conducting graphene thin films were deposited onto (100) silicon and microscope glass substrates from freshly prepared suspensions of exfoliated nanographite. The preparation of the suspensions was carried out by means of a well-established procedure [32], and the sequence of the procedure is shown in Fig. 5.1. First, a graphene suspension is prepared by mechanical exfoliation of nanographite in Ribonucleic acid (RNA) solution via sonication. Subsequently, the suspension was allowed to sit overnight so that heavier particles sediment. The upper part of the solution (60 – 70%) was decanted and centrifuged (Fisher Scientific; accuSpinTM 400) at 6000 rpm for 1 hr. The supernatant was then used to make graphene films using the vacuum filtration: 15 ml of suspension of graphene flakes was vacuum-filtered on a cellulose membrane, transferred to a p-doped Silicon (p-Si) substrate. This was then baked in an oven at 50°C for 5 hrs.

![Graphene film preparation diagram](image)

**Fig. 5.1:** Graphene thin film preparation by vacuum filtration.
Etching of the sample (to eliminate the filter membrane) was carried out using consecutive acetone and methanol baths. A similar procedure was adopted to deposit graphene on microscope glass from 25 ml of solution. The graphene films were subsequently annealed at 300°C for 1 hour in order to expel oxygen molecules that may set off in-situ oxidation of Cu-NPs. Annealing also helps to get rid of the RNA adsorbent [32].

**Copper nanoparticles deposition:** To decorate graphene with Cu-NPs, we introduced the graphene thin films in an ultra-high vacuum radio frequency (RF) magnetron sputtering chamber. Sputtering of the target was carried out by ionizing argon introduced in a vacuum deposition chamber by using an Omega FMA 5508 (range: 0 – 100 mL/min) flow meter. The deposition chamber was coupled to a glove box (NEXUS II Vacuum Atmospheres Co.) kept under nitrogen environment [33]. The glove box allowed for sample storage, electrical measurements and additional treatments without directly exposing the samples to ambient conditions, thus preventing the particle oxidation and degradation associated with exposure to oxygen [34,35]. Two different sets of graphene thin film samples were sputtered in the system described above. In both cases, we set the 13.56 MHz RF sputtering power at 33W, while the Ar flow was set at 40 SCCM of argon flow and the base vacuum of the chamber prior to Ar introduction was better than 5x10^{-7} Torr. The RF power was coupled to the chamber using a matching network (RF VII Inc.) in auto-tune mode. The first set of nine samples formed a “matrix” in which graphene thin films sputtered for 2, 3 and 5 minutes respectively, were annealed at 300°C, 400°C or 550°C in the glove box. The second set was formed by three samples in which graphene thin films sputtered for 3 minutes where annealed at 300°C for 1hr, 2hrs and 4hrs respectively, which resulted in different area
coverage of the nanoparticles on the graphene surface. In both cases sputtered copper films formed a semicontinuous system of interconnected copper particles [33] and the role of annealing was critical for obtaining well-isolated copper particles.

**Graphene/Cu-NPs characterization:** The work function and topography of the samples were mapped simultaneously using a scanning Kelvin probe force microscope (SKPFM), which is a Witec Alfa 300S atomic force microscope (AFM) integrated with a Kelvin Probe accessory as described in Chapter 3. Additional morphology characterization of our graphene films decorated with Cu-NPs was performed using a LEO (Zeiss) 1530 field emission scanning electron microscope (SEM) operating at 1 kV, also described in Chapter 3. The resistance of the samples deposited on microscope glass substrates was measured from I-V curves taken at ±3 V on a probe station with a two point probe configuration (Signatone S-725) and a Keithley 2400 source meter. Normal incidence transmittance of the samples was determined in the visible-near-IR range (λ = 400–800 nm) using a Varian DMS80 spectrometer.

**Theoretical formulation:** In order to investigate the effect of Cu-NPs on the work function of graphene we used a modified tight binding model to calculate the electronic properties of graphene influenced by the presence of Cu-NPs. The tight binding model was described in detail earlier in Section 2.2. The Hamiltonian describing the π-electron network for our system is given by Eq. (2.50), with the exception that the ionization energy can change over the lattice. The modified tight-binding Hamiltonian is

\[
H = \sum_{i,\alpha} E_i c_{i,\alpha}^{\dagger} c_{i,\alpha} + \sum_{i,j,\alpha} t_{ij} c_{i,\alpha}^{\dagger} c_{j,\alpha}, \tag{5.1}
\]
where $c^+ (c)$ is the creation (annihilation) fermionic excitation operator, $\varepsilon_i$ is the ionization energy, or the local work function, at lattice site $i$, $t_{i,j}$ is the hopping integral between sites $i$ and $j$, and $\sigma$ is the spin projection. Numerically, we formed a Hamiltonian matrix for a graphene flake of 80×80 aromatic rings using the same method that was presented in Chapter 4 for generating the Hamiltonian matrices of graphene nanoribbons (see also Appendix B for more details). Cu-NPs were incorporated in our model by introducing a modified local potential $\Delta U_{mod}$ for sites in contact with the particles. In our model we assume that there is a cross-section area where contact between the Cu-NP and graphene takes place, and within this contact region we have a modified but uniform local potential $\Delta U_{mod}$. This modified potential changes the diagonal $\varepsilon_i$ and off diagonal $t_{i,j}$ matrix elements, as prescribed by Eq. (2.46). The modified diagonal and off-diagonal matrix elements are labelled by $\varepsilon_{mod}$ and $t_{mod}$, whereas the unaffected sites are labelled $\varepsilon_0$ and $t_0$, corresponding to the work function and nearest-neighbour interaction energy of bare graphene. A schematic representation of Cu-NPs in contact with graphene is shown in Fig. 5.2.

![Diagram showing graphene sites covered with Cu-NPs](image)

**Fig. 5.2:** A schematic representation of graphene covered by Cu-NPs showing the contact regions (dashed circles). Sites in contact with nanoparticles are labelled with modified diagonal $\varepsilon_{mod}$, and off-diagonal $t_{mod}$ matrix elements. Lattice site unaffected by Cu-NP contacts are labelled by $\varepsilon_0$ and $t_0$, for the diagonal and off-diagonal elements, respectively.
The eigenvalues of the modified matrix Hamiltonian were then solved using computational resources provided by the SHARCNET computer network. The changes in the work function of graphene as a consequence of changes in the local work function of graphene due to the presence of Cu-NPs were subsequently deduced. This was done by observing the shift in the highest occupied molecular orbital (HOMO) due to the introduction of the modified potential $\Delta U_{mod}$, for sites in contact with Cu-NPs. The HOMO was extracted by populating the $\pi$-electronic levels of graphene according to the Pauli Exclusion Principle with the total number of $\pi$-electrons available in the structure.

5.3 Results and Discussions

5.3.1 Controlling particle size and density on graphene films

Fig. 5.3 (a-c) show the SEM images of graphene films decorated with Cu-NPs obtained after their thermal treatment in the glove box. At a constant RF power and chamber pressure, samples sputtered for 5 minutes exhibit denser nanoparticles than samples sputtered for 3 and 2 minutes, respectively. Hence, more particles are involved in the nucleation phenomena that take place in the proximity of the graphene surface during thermal treatment. Denser particles also require higher annealing temperature to active complete nucleation to obtain copper islands with larger diameter as shown in panel d of Fig. 5.3. On the other hand, by extrapolating the surface area covered by Cu-NPs from AFM micrographs for different surface area coverage it is found that the annealing time decreases the surface coverage area of our graphene films, as shown in Fig. 5.3(e). These adjustable experimental parameters, namely the sputtering time, annealing temperature and annealing time, allow us to control the
average particle diameter and the area of the graphene films covered by Cu-NPs. Using these experimental parameters a set of samples were produced for a comprehensive parametric study of the effect of Cu-NPs on the electronic properties of graphene films.

Fig. 5.3: SEM images of graphene films decorated with Cu-NPs. The particles were nucleated on the graphene via thermal treatment in a nitrogen environment in the glove box. Cu-NPs were first sputtered for different durations of 2, 3 and 5 minutes, respectively, and annealed at (a) 300°C, (b) 400°C and (c) 550°C. (d) Variation of the average diameter of Cu-NPs decorated on the graphene samples shown in the SEM images. (e) Fraction of graphene surface covered by Cu-NPs obtained after annealing for different duration in the glove box.
5.3.2 Influence of Cu-NPs on the work function of graphene

When Cu-NPs are deposited on the graphene surface, only weak bonds based on Van der Waals interactions occur between the two systems, leaving the electronic structure of graphene near the Dirac point substantially intact [29]. Although the band structure of graphene is not significantly affected by the adhesion of Cu-NPs on its surface, the different electron densities in graphene and copper, leading to different work functions in the two materials when they are considered individually, may affect the occupation level of the $\pi$ and $\pi^*$ bands in the proximity of the canonical point in graphene, as well as the Fermi energy in Cu-NPs, when the two systems are interfaced. This may have important implications since it strongly increases the density of carriers and the electrical conductivity of graphene flakes. Therefore, it is critical to assess the relative shifts in the Fermi level of transparent and conducting graphene films decorated with Cu-NPs as a function of the diameter and concentration of the nanoparticles. We tackle this problem both computationally and experimentally, using a tight binding methods and experimental work functions determined using SKPFM. A typical AFM image and SKPFM micrograph of a transparent and conducting graphene film with $f_{Cu} = 15\pm5\%$ area coverage of Cu-NPs (average diameter: 35\pm2 nm) are shown in Figs. 5.4 (a) and (b), respectively. Detailed analysis of the work function for graphene in the presence of Cu-NPs was carried out using a set of SKPFM micrographs of this type. Two physical parameters associated with the Cu-NPs were found to strongly affect the amount of the energy shift of the Fermi level of graphene due to the attachment of Cu-NP: the diameter of the adhering nanoparticles and the surface area coverage.
**Effect of the nanoparticle diameter:** We observe a variation in the work function of Cu-NPs decorated on graphene depending on the diameter of the Cu-NPs. The work function of metal nanoparticles reduces with the diameter of the particles, based on a classical description of the image potential for metals as outlined by Wood [30]. In order to remove an electron from a metal, work needs to be done against the image force which increases inversely with the curvature of the metal surface. This classical description for the size dependence of nanoparticles on their work function has been verified experimentally for spherical metallic nanoparticles (with diameter of several nm) based on photoemission measurements [6]. Fig. 5.4(c) is a plot of the work function of Cu-NPs vs. the particle diameter simultaneously measured by SKPFM and AFM. The vertical height of the Cu-NPs was extracted from the AFM topography micrographs and used as the measure of the particle diameter since there is much greater accuracy associated with the vertical dimension in comparison with the in-plane dimensions of AFM which is limited by the sharpness of the AFM tip. The work function of individual particles was extracted using the colour scale in Fig 5.4(b) and (e) and Eq. 3.1, after calibrating the work function of the tip using a standard p-type silicon substrate with a known work function of ~5.03eV. The trace in Fig. 5.4(c) comes from the theoretical model based on the method of images. An expression for the changes of the work function of a copper surface due do curvature was given in [30]:

$$\varphi = \varphi_\infty + \frac{1.08}{D} eV,$$

where \(\varphi_\infty\) is the work function of a planar particle in the limit of infinite diameter, and \(D\) is the diameter of the metallic nanoparticle in nm [30]. The theoretical model is in excellent agreement with the KP-AFM measurements.
Fig. 5.4: Representative (a) AFM and (b) SKPFM micrographs on a graphene film decorated with Cu-NPs. The diameter and work function extracted from the micrographs are plotted in (c). (d) AFM and (e) SKPFM micrographs for Cu-NPs on indium tin oxide. (f) Plot of work function vs. Cu-NP diameter extracted from the micrographs.

In Fig. 5.4(c) we see that the work function for the absorbed Cu-NPs is below the work function of bare graphene, which produces a down shift of the Fermi level for graphene into the conduction band. This shift increases the electron carrier density, effectively making
graphene $n$-type as doped by the Cu-NPs. The trace in Fig. 5.4(c) may also suggests that very small Cu-NPs with diameter below $\sim 5$ nm could have a work function larger then graphene, effectively shifting the Fermi level into the valence band (where majority carriers become holes), provided these small particle retain their metallic properties.

For comparison, we sputtered Cu-NPs on an indium tin oxide (ITO) substrate. ITO is well known to possess a work function of 4.7eV [31]. The Kelvin probe micrograph and the corresponding AFM topography for Cu-NPs on ITO are shown in Fig. 5.4(d) and (e) respectively. The work function vs. particle diameter extracted from the micrographs is plotted in Fig. 5.4(f) showing a decreasing trend in the work function of absorbed Cu-NPs with decreasing diameter, contrasting with the behaviour for Cu-NP absorbed on graphene. Here the Cu-NPs are doping ITO with hole injection leading to $p$-type doping of ITO. The trace in Fig. 5.4(f) is given by Eq. (5.2) where the plus sign is replaced by a minus sign, since the work function of Cu-NP reduces with increasing curvature.

From our analysis of the work function for individual Cu-NPs absorbed on graphene we can deduce the change in the local work function of graphene for sites in contact with Cu-NPs based on their diameter. We would now like to understand the way in which Cu-NPs dopes graphene globally. Specifically, we would like to know how the electronic band structure of graphene is modified by decorating its surface by an ensemble of Cu-NPs.

To gain insight into the effect on the global band structure as a consequence of local changes in the work function of graphene due to the presence of Cu-NPs we employ a modified tight binding model. Here we model absorbed Cu-NPs on graphene by modifying the diagonal ($\epsilon_{mod}$) and off-diagonal ($t_{mod}$) matrix elements for carbon sites in contact with the Cu-NPs, and we use the experimentally obtained work function and nearest-neighbour
interaction energy for the diagonal ($\varepsilon_0$) and off-diagonal ($t_0$) matrix elements for sites not in contact with Cu-NPs. This model allows us to investigate the influence of Cu-NPs on the work function of graphene taking into account, the distribution of the Cu-NPs on graphene, and the fraction of area covered by Cu-NPs.

From our simulations, we find that the modified off-diagonal matrix elements $t_{mod}$ describing the interaction between $sp^2$ hybridized carbon and copper generate deep states for $t_{mod} > t_0$, as in Fig. 5.5(a), and shallow states for $t_{mod} < t_0$, as in Fig. 5.5(b). These states appear symmetrically in both the valence and conduction bands. The Fermi level is unaffected by the appearance of these states. This is because the electron-hole symmetry of the band structure remains intact. However, the modified diagonal elements $\varepsilon_{mod}$ generate states asymmetrically in the conduction band for $\varepsilon_{mod} > 0$ (see Fig. 5.5(c)) and states in the valence band for $\varepsilon_{mod} < 0$ (see Fig. 5.5(d)), thereby breaking the electron-hole symmetry and shifting the Fermi level into an electronic band. For the case where all sites on the graphene lattice are modified (i.e., a film of Cu covering the entire graphene surface), the value of the diagonal matrix element defines the energy at the canonical point, while maintaining the symmetric structure of the bands. However, as report by Giovannetti [19], for a Cu film absorbed on graphene the Fermi level shifts into the conduction band through charge injection from the Cu film to graphene. This is in sharp contrast with our finding for Cu-NPs, where theory suggests that even without any charge transfer a shift in the Fermi level away from the canonical point can take place due to the breaking of electron-hole symmetry. This results from the fact that the local work function is variable over the graphene lattice between sites covered by Cu-NPs and sites without particles.
Fig. 5.5: Electronic density of state (DOS) calculated for a bare graphene flake of dimensions 80x80 rings (black trace) and graphene covered with 59 Cu-NPs with radius $r = 3a$ distributed randomly (red trace). Panels (a)-(d) illustrate the dependence of the DOS on the modified diagonal and off-diagonal matrix elements. (a) $t_{\text{mod}} = t_0 / 2$, generating shallow states near the Fermi level, (b) $t_{\text{mod}} = 2t_0$, generating deep states symmetrically in the valence and conduction bands. (c) $\epsilon_{\text{mod}} - \epsilon_0 = 0.3$ eV, generating states in the valence band, (d) $\epsilon_{\text{mod}} - \epsilon_0 = -0.3$ eV, generating states in the conduction band, breaking the electron-hole symmetry.

**Influence of particle distribution on the work function and DOS:** In order to investigate the influence of the particle distribution on the work function of graphene we modelled a set of particle distributions by randomly generating the positions of the particles over the graphene lattice. For comparisons between the various distributions we selected cases where the surface area covered by Cu-NPs is the same. From these simulations we note that the distribution of particles influences the electronic density of states (DOS) and consequently the shift in work function ($\Delta \phi$) of graphene. To illustrate this we select two
very distinct distributions of approximately the same surface area coverage (~20%). In one case we place 59 particles of radius \( r = 3a \), where \( a \) is the bond length of carbon atoms in graphene, randomly on the graphene lattice. In the other case we place a single particle of radius \( r = 23a \) at the center of the graphene lattice. The two distributions are schematically shown in Fig. 5.6(a) and (b). A plot of \( \Delta \varphi \) vs. the difference in the local work function of Cu-NP-covered graphene sites and bare graphene sites (given by \( \Delta \varepsilon = \varepsilon_{\text{mod}} - \varepsilon_0 \) in our model) is shown in Fig. 5.6(c). For small \( \Delta \varepsilon \) (\( \Delta \varepsilon < 0.3 \) eV) the shift in the work function of graphene is nearly the same for the two distributions. From our SKPFM measurements of Cu-NPs absorbed on graphene the maximum difference in the work function between the sites covered by Cu-NPs and bare graphene sites is ~2.6 eV, which indicates that distributions of our Cu-NPs has little influence on the work function shift of graphene at \( f_{\text{Cu}} \sim 0.2 \) coverage, and that the determining factor for \( \Delta \varphi \) is \( f_{\text{Cu}} \). However, for large \( \Delta \varepsilon \) (\( \Delta \varepsilon > 0.3\)eV) the difference in \( \Delta \varphi \) for the two distributions become large and therefore particle distribution plays a much greater role in determining the shift in the work function of graphene.

On the other hand, the profile of the density of states (DOS) for graphene is influenced by the particle distribution, even for small \( \Delta \varepsilon \). The DOS profiles for the two distributions at \( \Delta \varepsilon = 0.3 \) eV are shown in Fig. 5.6(d), illustrating the distinction. Although the profiles are distinct, the Fermi energy shift is approximately the same, which can be visualized from the symmetry of the DOS. An important feature of the DOS profiles shown in Fig. 5.6(d) is that the DOS near the canonical point is minimally effected by the Cu-NPs, suggesting that the electron-hole symmetry breaking does not dramatically influence the mobility of the \( \pi \)-electrons in graphene, which is governed by the band structure at the Fermi level near the canonical point. At very large \( \Delta \varepsilon \) (e.g., \( \Delta \varepsilon = 2\)eV) the DOS profiles for the two
distribution becomes much more distinct (i.e., see Figs. 5.6(e) and (f)). For the case where 59 particles are randomly distributed on the graphene lattice, the DOS profile near the canonical point is dramatically altered from pristine graphene. On the other hand the DOS profile near the canonical point for the single particle is preserved even at very large $\Delta\varepsilon$.

Fig. 5.6: (a) Schematic representation of (a) 59 Cu-NPs of radius $r = 3a$ and (b) 1 Cu-NP of radius $r = 23a$ (both with $f_{Cu} \sim 0.2$) distributed randomly on a graphene lattice. (c) Calculated shift in the work function vs. $\Delta\varepsilon = \varepsilon_{\text{mod}} - \varepsilon_0$ for the two distributions. (d) The density of states for the two distribution with $\Delta\varepsilon = 0.3$ eV. (e) and (f) are the DOS for the two distribution at $\Delta\varepsilon = 2$ eV.
5.3.3 Conductivity and transparency of graphene films decorated with Cu-NPs

From an applications point of view, it is of paramount important to understand the effect of an ensemble of nanoparticles on the electronic properties of graphene. An example of such an application is to enhance the conductivity of transparent films for the front contact of solar cells. Doping graphene by decorating its surface with Cu-NPs as opposed to a film of Cu allows for the transmittance of light through the film. Therefore, it would be possible to enhance the conductivity of the graphene thin films by introducing Cu-NPs, while maintaining the transparency of the film. In fact, for our film with $f_{Cu} = 18\%$ the transmittance reduces by only $\sim 9\%$ (see Fig. 5.7(a)), while its conductivity increases by more than 400\% (see Fig. 5.7(b)). In addition to the enhanced conductivity and the preservation of transparency, the presence of Cu-NPs give rise to surface plasmonic bands (see Fig. 5.7(a)), which can be used for wide range of applications, including surface-plasmon sensors and plasmon-enhanced photocells.

Fig. 5.7: (a) UV-visible spectroscopy for a set of films with different coverage, showing a reduction in transmittance. The dips near 550 nm are the typical surface plasmon resonance bands observed for nanoparticles. (b) Sheet resistance vs. fraction of area covered with Cu-NPs.
5.4 Conclusions

Graphene thin films were produced using mechanical exfoliation of nanographite and filtration process. Cu was RF sputtered onto the films and subsequently thermally annealed to produce Cu-NPs on graphene. The sputtering time, annealing temperature and annealing time, allowed us to control the average particle diameter and the area of the graphene films covered by Cu-NPs.

The local work function of graphene films decorated with Cu-NPs was investigated using SKPFM and a modified tight-binding model. It was shown that the work function of individual Cu-NPs absorbed on graphene varied according to the classical description of the image charges for conductors.

A tight-binding model was employed to investigate the influence of particle distribution and area coverage of particles on the band structure and work function of graphene. It was shown that for typical values of the work function difference between Cu-NPs and graphene the distribution of the particles has minimal effect on the shift in work function. Our model also suggests that a large contact is more effective at preserving the band structure of graphene in comparison with an ensemble of many particles randomly distributed on the graphene surface.

From our model we also find that local variations in the work function of graphene due to the presence of Cu-NPs breaks the electron-hole symmetry of graphene shifting the Fermi level away from the canonical point and effectively doping graphene, even in the absence of charge transfer.
References

CHAPTER 6

Electronic Excitation Spectrum of Graphene Nanoribbons Using

Green's Function Techniques

In the previous chapters we used the tight-binding Hamiltonian with NN hopping to write down a matrix Hamiltonian, which was then solved numerically in order to extract the eigenvalues of various graphene structures. In this chapter we will use the tight-binding Hamiltonian (see Eq. (2.48)), together with the Green's function formalism introduced in Section 2.1, to find analytical expression for the \( \pi \)-electron Green's functions correlating any two lattice points on a zigzag (ZZ) graphene nanoribbon (GNR). As we will see, these Green's functions have contributions from both bulk-like and edge modes. The two point Green's function's derived here contain information about the \( \pi \)-electron excitation modes and their spectral weights. The corresponding spectral functions for these Green's functions will be used in the next chapter to find explicit expressions for the Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction between two magnetic impurities in a graphene nanoribbon.

6.1 Introduction

A schematic representation of the ZZ-GNRs is depicted in Fig. 6.1. Graphene has two interpenetrating sublattices, denoted here by A (black dots) and B (white dots). For ZZ-GNRs the rows with odd label \( n \) consist of only A sublattice sites and the even \( n \) rows of only B sites (see Fig. 6.1 for row labels). We would like to find the Green's functions for any two point on the GNR lattice. These two points may, in general, be on either the same or different rows, on the same or different sublattices, on the edge or at interior points. These Green's
functions will allow us to deduce how a signal will propagate (both in terms of the modes supported by the structure and their intensity) between any two points. The propagation of signal (or electronic perturbation in our case) is the starting point for understand many physical phenomena including the RKKY interaction.

Fig. 6.1. Geometry for a graphene nanoribbon with a zigzag edge at row $n = 1$ (coloured red). In this representation the ribbon is infinitely long in the $y$-direction, but finite (with $n = 1, 2, ..., N$) or semi-infinite ($N \to \infty$) in the $x$-direction.

As previously mentioned, the relevant electronic excitations in graphene are related to the $\pi$-electronic bands. As we will see in this chapter, signal propagation can be mediated by both bulk and edge modes in a GNR. Interestingly, there are two distinct types of edge modes in ZZ-GNRs. The first type which we will refer to as the "zero mode" [1] is related to the geometrical structure of ZZ edges, while the second type is related to a difference in the hopping energy between edge sites and between interior sites [2]. For a general discussion of edge modes in GNRs and their properties refer to Section 1.3. In general the hopping parameter along the ZZ edge may be different (see red connecting lines between edge sites)
from the hopping between interior sites, since edges are under coordinated and are typically passivated by functional groups.

In Section 6.2 we will derive the electronic Green's functions for any two point on a ZZ-GNR lattice using the Green's function equation of motion and an analytical tri-diagonal matrix inversion method [3]. Both finite \((N \text{ finite})\) and semi-infinite \((N \to \infty)\) GNR widths will be considered in our tri-diagonal formalism. The Green's functions derived in Section 6.2 will be in terms of the inverse matrix elements. From the poles of the Green's functions the bulk and edge mode dispersion relation for our structure will be deduced. In Section 6.3 the derived bulk and edge modes will be used to write explicit expressions for the Green's functions in terms of contributions from these different modes. Furthermore, the spectral function will be derived from the imaginary part of the Green's functions. In Section 6.4 we will make some concluding remarks, while RKKY applications are developed in Chapter 7.

### 6.2 Derivation of the electronic Green’s functions for GNRs

Graphene nanoribbons are 1-D structures with translational symmetry only along the \(y\)-axis in our representation (see Fig. 6.1). After making a 1-D Fourier transform of the fermionic excitation operators and the hopping parameter the tight-binding Hamiltonian Eq. (2.48) in 2\(^{\text{nd}}\) quantization notation becomes

\[
H = \sum_{m,n} t_{n,m}(q_y) c_{q_y,m}^+ c_{q_y,n},
\]

(6.1)

where \(c_{q_y,m}^+ (c_{q_y,m})\) is the creation (annihilation) operator with row label \(m\), at wavenumber \(q_y\), and \(t_{n,m}(q_y)\) is the hopping parameter linking rows \(n\) and \(m\). Using the above Hamiltonian
and the Green's function equation of motion in the frequency representation (see Eq. (2.36)), as applied to the fermions we obtain the general expression

$$\omega \left\langle \frac{c_{q,j}^+ ; c_{q,j}}{\omega} \right\rangle = \left( \frac{1}{2\pi} \right) \delta_{j,j'} + \sum_{m} t_{j,m}(q_y) \left\langle \frac{c_{q,j,m}^+ ; c_{q,j}}{\omega} \right\rangle,$$

(6.2)

where we have used

$$[c_{q,j}^+, H] = \sum_{m} t_{j,m}(q_y) c_{q,j,m}^+.$$

(6.3)

Eq. (6.3) can easily be derived using the commutation and anti-commutation relations discussed in Subsection 2.1.1. In Eq. (6.2) $\omega$ is the angular frequency of excitation spectrum, and the 1-D transformed hopping parameter $t_{j,m}(q_y)$ for $j$ corresponding to the first two rows in Fig. 6.1 is given by

$$t_{1,m}(q_y) = 2t_e \cos(\frac{\sqrt{3}}{2} q_y a) \delta_{1,m-1},$$

(6.4a)

$$t_{2,m}(q_y) = 2t_e \cos(\frac{\sqrt{3}}{2} q_y a) \delta_{2,m+1} + t \delta_{2,m-1},$$

(6.4b)

where $t_e$ and $t$ are the hopping parameters for the edge and bulk, respectively. For larger $j$ values we have

$$t_{j,m}(q_y) = t[2 \cos(\frac{\sqrt{3}}{2} q_y a) \delta_{j,m+1} + \delta_{j,m+1}].$$

(6.5)

where the upper (lower) signs correspond to $j$ odd (even). Also, since the finite-width ZZ ribbon corresponds to $N$ even, analogous expressions to Eq. (6.4) applied for $j = N-1$ and $N$ at the other edge.

Using Eqs. (6.2)-(6.5) we can generate $N$ finite-difference Green's function equations. We would like to use an analytical matrix formalism to find the general expressions for all Green's functions for the system, as we will see below. In order to obtain a matrix for the set of finite-difference equations that is analytically invertible we eliminate the odd-$j$ terms (sublattice A) so that our set of equation contain only terms with even-$j$ (sublattice B), by
analogy with surface calculations for two-sublattice antiferromagnets [4]. This rearrangement leads to \( \frac{1}{2}N \) coupled equations for the even terms, which can be written in a matrix form for the Green’s functions as \( \mathbf{M} \mathbf{G}_j = \mathbf{b}_j \). Here \( \mathbf{G}_j \) is a \( 1 \times \frac{1}{2}N \) column matrix of the even-\( j \) Green's functions in Eq. (6.2) for any fixed integer value of \( j' \), and \( \mathbf{M} \) is a \( \frac{1}{2}N \times \frac{1}{2}N \) tridiagonal matrix given by

\[
\mathbf{M} = \begin{bmatrix}
  d + \Delta & -1 & \cdots & 0 & 0 \\
  -1 & d & \cdots & 0 & 0 \\
  \vdots & \vdots & \ddots & \vdots & \vdots \\
  0 & 0 & \cdots & d & \Delta'' - 1 \\
  0 & 0 & \cdots & \Delta'' - 1 & d + \Delta'
\end{bmatrix},
\]  

(6.6)

where \( d \) is a parameter related to the electronic excitation frequency \( \omega \) by

\[
d = \frac{\omega^2 / t^2 - 4 \cos^2(\frac{\sqrt{3}}{2} q_s a)}{2 \cos(\frac{\sqrt{3}}{2} q_s a)},
\]  

(6.7)

and \( \Delta \) describes the perturbation due to the ZZ edges:

\[
\Delta = 2 \left( \frac{t^2 - t_z^2}{t_z^2} \right) \cos(\frac{\sqrt{3}}{2} q_s a).
\]  

(6.8)

Similar expressions for \( \Delta' \) and \( \Delta'' \) can also be easily found. Finally, the form of the inhomogeneous term \( \mathbf{b}_j \) in the matrix equation, taking the case where \( j' \) is also an even integer, is a \( 1 \times \frac{1}{2}N \) column matrix with its elements defined by

\[
(b_j)_j = \frac{\omega}{4\pi t^2 \cos(\frac{\sqrt{3}}{2} q_s a)} \delta_{j,j'}.
\]  

(6.9)

The finite tridiagonal matrix \( \mathbf{M} \) in Eq. (6.6) can be inverted analytically, allowing us to solve for the required Green’s functions for any even value of \( N \), by using the method as outlined for magnetic systems in [3]. Denoting \( \mathbf{B} = \mathbf{M}^{-1} \), the Green’s functions are obtained from \( \mathbf{G}_j = \mathbf{B} \mathbf{b}_j \). Briefly, the method consists of splitting \( \mathbf{M} \) into two parts as \( \mathbf{M}_0 + \mathbf{D} \), where
\( M_0 \) is the matrix obtained if \( \Delta \) is replaced by zero in Eq. (6.6). Matrix \( D \), which contains the edge perturbation effects has only two nonzero elements, both on the leading diagonal with

\[ D_{1,1} = D_{N/2,N/2} = \Delta. \]

The above decomposition is helpful because \( M_0 \) can be inverted analytically and \( D \) is a sparse matrix. In fact, we can employ the identity that \( B = (M_0 + D)^{-1} = [I + (M_0)^{-1}D]^{-1}(M_0)^{-1} \), where \( I \) is the \( \frac{1}{2}N \times \frac{1}{2}N \) unit matrix, together with the result adapted from [3] that

\[
[(M_0)^{-1}]_{l,l'} = \frac{x^{l+l'} - x^{l-l'}}{(1-x^{N+2})(x-x^{-1})}.
\]  

(6.10)

Here \( x \) is a complex parameter defined by \( x + x^{-1} = d \), and subject to the auxiliary condition that \( |x| \leq 1 \), and \( l \) and \( l' \) are row and column indices of the inverted matrix. Now, denoting

\[
\beta(q_r) = 2 \cos(\frac{\sqrt{3}}{2}, q_r a),
\]

(6.11)

it is convenient to rearrange Eq. (6.7) as

\[
\omega^2 = \ell^2 [\beta(q_r) + x] [\beta(q_r) + x^{-1}].
\]

(6.12)

We first consider the result for \( B \) in the limit of \( N \to \infty \), before returning to the finite-\( N \) case.

**Case 1: \( N \to \infty \).**

When \( N \to \infty \) the terms in Eq. (6.10) of order \( x^N \) tend to zero (because of the definition of \( x \)), and we are left with the much simpler result that

\[
[(M_0)^{-1}]_{l,l'} = \frac{x^{l+l'} - x^{l-l'}}{(x-x^{-1})}.
\]

(6.13)

We note that the \( l \) and \( l' \) labels appear in the Green's functions in combinations \( |l-l'| \) and \( (l + l') \), which can be associated with the spatial dependence of bulk and edge modes, respectively [4]. The elements of the matrix \( B \) are then easily found to be
\[ B_{ij'} = \frac{1}{x - x^{-1}} \left[ x^{i+j'} \left( \frac{1 + x^{-1} \Delta}{1 + x \Delta} \right) - x^{i+j'} \right] . \] (6.14)

The Green’s functions, which embody information about all the excitation frequencies and their spectral weights, are given by

\[ \left\langle \left\langle c_{q,j}^* ; c_{q,j'} \right\rangle \right\rangle_{\omega} = \frac{\omega}{2\pi \beta \omega} B_{j/2,j'/2}. \] (j and j’ even) (6.15)

Using the finite-difference equations represented by Eq. (6.2), it is straightforward to extend the above Green’s function results to cases where j and j’ may be odd or even. Here we quote the Green functions involving the edge (putting j = 1).

\[ \left\langle \left\langle c_{q,j}^* ; c_{q,1} \right\rangle \right\rangle_{\omega} = \frac{\beta t}{2\pi \omega} B_{1,1} \] (j’ = 1), (6.16a)

\[ \left\langle \left\langle c_{q,j}^* ; c_{q,j'} \right\rangle \right\rangle_{\omega} = \frac{t_t}{2\pi \omega} B_{1,j/2} \] (j’ even > 1), (6.16b)

\[ \left\langle \left\langle c_{q,j}^* ; c_{q,j'} \right\rangle \right\rangle_{\omega} = \frac{t_t}{2\pi \omega} \left( \beta B_{1,j+1/2} + B_{1,j'-1/2} \right) \] (j’ odd > 1). (6.16c)

For completeness we also list all other Green’s functions which can also be obtained using Eqs. (6.2) and (6.15).

\[ \left\langle \left\langle c_{q,j}^* ; c_{q,1} \right\rangle \right\rangle_{\omega} = \frac{1}{2\pi \beta t} \left( B_{j,j+1/2} + \beta B_{j,j'+1/2} \right) \] (j even and j’ odd > 1), (6.17a)

\[ \left\langle \left\langle c_{q,j}^* ; c_{q,j'} \right\rangle \right\rangle_{\omega} = \frac{1}{2\pi \beta t} \left( \beta B_{j,j+1/2} + B_{j+1,j'/2} \right) \] (j odd > 1 and j’ even), (6.17b)

\[ \left\langle \left\langle c_{q,j}^* ; c_{q,j'} \right\rangle \right\rangle_{\omega} = \frac{1}{2\pi \beta \omega} \left( \beta^2 B_{j+1,j+1/2} + \beta B_{j+1,j'+1/2} + \beta B_{j+1,j+1/2} + B_{j+1,j'+1/2} \right) \] (j and j’ odd > 1). (6.17c)
The set of Green functions expressed in Eqs. (6.15)-(6.17) are all the Green's functions correlating any two point on a semi-infinite graphene ribbon.

The spectrum of electronic excitation in the semi-infinite ribbon case may be deduced from the above results, following applications of the tridiagonal matrix method to other systems [3-6]. The bulk (propagating) modes correspond to \(|x| = 1\), and if we set \(x = \exp(i3qxa/2)\) as a phase term in Eq. (6.7) we recover the usual bulk dispersion relation for graphene (see, e.g., [7] and Eq. (1.4)):

\[
\omega_b(q_x, q_y) = \pm t \sqrt{\beta^2(q_y) + 2\beta(q_y)\cos(\frac{1}{3} q_y a) + 1}.
\]  

(6.18)

In addition, we see that there is a pole of the Green’s functions arising due to the factor \(1+x\Delta = 0\) in Eq. (6.14), where \(\Delta\) is the edge parameter defined by Eq. (6.8). This solution \(x = -1/\Delta\) will correspond to a physical mode, a localized edge mode, provided \(|\Delta| > 1\) which ensures that the previous requirement that \(|x| < 1\) is satisfied. Solving for the dispersion relation of this edge mode gives

\[
\omega_t(q_y) = \pm t \sqrt{(t_e/t)^2 \beta^2(q_y) + (t_e^2/t^2)(t_e^2 - t^2)}.
\]  

(6.19)

The localization condition for edge modes gives rise to two regions in the dispersion spectrum. One corresponds to \(\Delta > 1\) and it follows from Eq. (6.8) that it occurs when \(0 < (t_e/t)^2 < 0.5\), while the other case with \(\Delta < -1\) occurs when \((t_e/t)^2 > 1.5\). These modes have a wavenumber cut-off arising from the form of \(\Delta\). For \((t_e/t)^2 \rightarrow 0\), the physical range for these modes is given by \(-\frac{2\pi}{3\sqrt{3}a} < q_y < \frac{2\pi}{3\sqrt{3}a}\), corresponding to the region between the two Dirac points in the 1\(^{st}\) Brillouin zone. The range reduces with increasing \((t_e/t)^2\), and in the limit \((t_e/t)^2 \rightarrow 0.5\) the range shrinks to zero. For the case where \((t_e/t)^2 > 1.5\), the behaviour is slightly different. In the limit \((t_e/t)^2 \rightarrow 1.5\), the wavenumber range again reduces to zero, but
in the limit \((t_e/t)^2 \to \infty\) the range becomes \(-\frac{\pi}{\sqrt{3}a} < q_y < \frac{\pi}{\sqrt{3}a}\), i.e., it corresponds to the entire Brillouin zone. The edge modes with \((t_e/t)^2 < 0.5\) and \((t_e/t)^2 > 1.5\) have frequencies below and above the bulk modes, respectively, and will be referred to as acoustic and optic-type modes, respectively.

At first sight, it might seem that we have described all the modes, and indeed this is the case for the poles of the even-even Green's functions in Eq. (6.15). However, we note from the first and third line of Eq. (6.16) and the last of Eq. (6.17) that the odd-odd Green's function have an additional pole arising from the factor of \(\omega\) in the denominator. From Eq. (6.12) it follows that \(\omega = 0\) implies we must have either \(x = -\beta(q_y)\) or \(-1/\beta(q_y)\). In fact, it is the former condition that corresponds to localization at the ZZ edge, as maybe verified from the form of the odd-odd Green's functions. For example, taking for simplicity the case of \(t_e = t\), it is easily shown using Eq. (6.12) and (6.16) that

\[
\left\langle \left\langle c_{q_y,1}^* c_{q_y,j'} \right\rangle \right\rangle = \frac{x^{(j+1)/2} \beta(q_y) + x^{-1}}{2\pi \omega} = \frac{x^{(j+1)/2}}{2\pi} \sqrt{\frac{\beta(q_y) + x^{-1}}{\beta(q_y) + x}} \quad (j' \text{ odd } > 1).
\]

From Eq. (6.11) we have \(|\beta(q_y)| < 1\), or \(\cos(\frac{\sqrt{3}}{2} q_y a) < 0.5\), for the localized mode and this corresponds to the range \(\frac{2\pi}{3\sqrt{3}a} < q_y < \frac{\pi}{\sqrt{3}a}\) in the positive region of the first Brillouin zone.

These are the edge modes ("zero" modes) discussed in Chapter 1 and predicted by Fujita et al. [1]. They occur only on the odd-\(j\) rows and their spatial decay length is proportional to \(-1/\ln|\beta(q_y)|\), which implies long penetration as the Dirac point (where \(\beta(q_y) = 1\)) is approached, contrasting with strong localization at the ZZ edge as the zone boundary (where \(\beta(q_y) = 0\)) is approached. Examples for the dispersion relations of all bulk and edge modes are given in Fig. 6.2.
Fig. 6.2: Dispersion curves for mode frequencies versus longitudinal wave number for a semi-infinite graphene ribbon \((N \rightarrow \infty)\), showing examples of bulk modes (shaded regions) optic edge modes with \(t_e/t = 1.6\), acoustic edge modes with \(t_e/t = 0.4\), and the zero mode. \(\mathbf{K}\) and \(\mathbf{K}'\) indicate the Dirac points at \((q_x, q_y, z) = \left( \pm \frac{2\pi}{3a}, \pm \frac{2\pi}{3a}, 0 \right)\).

**Case 2: \(N\) finite**

For a finite-width ribbon \((N\) finite) we need to employ the full form of Eq. (6.10), where the additional terms incorporate effects due to the second edge at \(n = N\) and lead to two important differences for the modes and the Green’s functions (by formal analogy with results in [3] for ferromagnetic films). One difference concerns the \(t_e \neq t\) edge modes, where both the frequencies and existence conditions are slightly modified because the modes at the two edges influence one another. We find that the previous condition \(1 + x\Delta = 0\) from Eq. (6.14) with \(|x| < 1\), is generalized to

\[
(1 + x\Delta)^2 - x^{N+2}(1 + x^{-1}\Delta) = 0. \tag{6.21}
\]

For large enough \(N\) (such that \(x^N \rightarrow 0\)) this leads to two decoupled modes, one at each edge,
with properties as before. In practice, we estimate for graphene that the large-$N$ approximation is good for $N$ greater than about 200, which corresponds to ribbons of width ~20nm. For smaller $N$ the two edge modes couple to give even- and odd-symmetry combinations, with the approximate solutions $x^\pm = (-1/\Delta) \pm \alpha$, where 
\[ \alpha = \left| (1 - \Delta^2) \Delta^{N/2} \right| \ll 1, \]
which may typically be the case for $N$ greater than about 20. The two modes corresponding to $x^+$ and $x^-$ have slightly different frequencies, as deduced using Eq. (6.12), and also the previous existence conditions are modified. The Fujita-type edge modes occur as before at $\omega = 0$, but now have decay characteristics with respect to both edges. Since the two edges for a ZZ-GNR are on different sublattices the zero modes for the two edges exist on different sublattices, and the zero mode becomes nested only for finite ribbons where the penetration of the two edges allows for overlap between the edge modes. This is the regime where the coupling of the edges, and hence correlation effects, have been observed.

We note that even though the edge modes at wavenumbers near the Dirac points are deeply penetrating, we might expect large damping for these modes since the zero modes merge into the bulk-modes at the Dirac point.

The other main difference that arises due to finite $N$ is that the bulk modes become quantized, consisting of discrete branches close together, because the $q_x$ wave numbers are required to satisfy boundary conditions at the edges. This can also be seen from numerical simulations of mode frequencies for ZZ-GNRs (see, e.g., [5]).

### 6.3 Bulk and edge mode Green's functions for GNRs
We have formally derived a set of Green's functions (i.e., see Eqs. (6.15)-(6.17)) that correlate any two sites on the semi-infinite graphene lattice, including the edge. These Green's functions are written in terms of the inverse matrix elements defined in Eq. (6.14), and have pole associated with both edge and bulk modes. As an illustrative example, here we will derive explicit expressions for the Green's function relating two sites on the edge (Eq. (6.16a)) using both the edge and bulk modes, where the two modes are treated separately.

First we will derive an expression for the Green's function of Eq. (6.16a) in terms of the two edge mode contributions. Eq. (6.16a) is proportional to the inverse matrix element $B_{1,1}$, which can be expressed in the form

$$B_{1,1} = \frac{x + \Delta}{1 + \Delta(x + x^{-1}) + \Delta^2},$$

using Eq. (6.14), with some algebraic rearrangement. Recall that the term $x + x^{-1} = d$. Using the definitions for $d$ and $\Delta$, given in Eqs. (6.7) and (6.8), respectively, the denominator in Eq. (6.22) can be written as

$$1 + \Delta(x + x^{-1}) + \Delta^2 = \frac{\Delta}{\beta \gamma^2} (\omega^2 - \omega_e^2),$$

where $\omega_e$ is the edge mode frequency defined in Eq. (6.19). Also recall that the pole corresponding to the edge mode gives the condition $x = 1/\Delta$. Substituting Eqs. (6.22), (6.23), and the condition $x = 1/\Delta$ into Eq. (6.16a), we find the edge mode contributions to the Green's function with labels $j = j' = 1$:

$$\langle \langle c_{q_1}^*; c_{q_1} \rangle \rangle_{\omega, e} = \frac{B^2 \gamma^2 \left(1 - \Delta^2\right)}{2 \pi \omega \left(\omega^2 - \omega_e^2\right)}. \tag{6.24}$$

Here the subscript label $e$ in front of the Green's function corresponds to the edge mode contribution.
To find the bulk mode contribution we set \( x = \exp(3q_x a / 2) \) in Eq. (6.22), to satisfy the condition \(|x|=1\), as before, when deriving the bulk mode dispersion relation. This immediately give the bulk mode contribution to the Green's function with label \( j=j'=1 \):

\[
\left\langle c_{q_x,1}^+ ; c_{q_x,1} \right\rangle_{\omega,b} = \frac{t^2 \beta \cos(3q_x a / 2) + i \sin(3q_x a / 2) + \Delta}{2\pi \omega + \Delta \cos(3q_x a / 2) + \Delta^2},
\]

(6.25)

where the subscript \( b \) denotes the bulk mode contribution. In general we might add the contributions from both the edge and bulk modes to get the total contribution to the Green's function. In general we have

\[
\left\langle c_{q_x,1}^+ ; c_{q_x,1} \right\rangle_{\omega} = \left\langle c_{q_x,1}^+ ; c_{q_x,1} \right\rangle_{\omega,e} + \left\langle c_{q_x,1}^+ ; c_{q_x,1} \right\rangle_{\omega,b}.
\]

(6.26)

In a similar fashion all other Green's functions defined in Eqs. (6.15)-(6.17) can be written explicitly in terms of the edge and bulk contributions.

Often we are interested in the spectral functions. As we will see in the next chapter, the general expression for the RKKY interaction is directly related to the spectral functions for our system. We can relate the imaginary part of the Green's functions in the frequency representation to the spectral functions through the fluctuation dissipation theorem derived in Section 2.1 and given by Eq. (2.33). Here we will form the imaginary part of the Green's functions for both the edge and bulk mode contributions given by Eqs. (6.24) and (6.25), respectively. Starting with the edge mode contribution, the angular frequency term \( \omega(\omega^2 - \omega_c^2) \) in the denominator of Eq. (6.24) can rewritten as

\[
\frac{1}{\omega(\omega - \omega_c)(\omega + \omega_c)} = -\frac{1}{2\omega_c^2} \left[ \frac{2}{\omega} - \frac{1}{(\omega - \omega_c)} - \frac{1}{(\omega + \omega_c)} \right].
\]

(6.27)

Using the analytic continuation method [8], where we introduce an infinitesimal term \( i\eta \) (\( \eta \to 0 \)) to the spectral frequency \( \omega \) of the Green's function, Eq. (6.24) becomes
\[
\left\langle \left\langle c_{q,1}^*; c_{q,1} \right\rangle \right\rangle_{\omega + i\eta, e} = -\frac{\beta^2 t_c^2}{4\pi \omega_c^2} \left[ \frac{2}{\omega + i\eta} - \frac{1}{(\omega - \omega_c + i\eta)} - \frac{1}{(\omega + \omega_c + i\eta)} \right]. \tag{6.28}
\]

The imaginary part of Eq. (6.28) can be obtained using the identity Eq. (2.30), which leads to the expression
\[
\text{Im}\left\langle \left\langle c_{q,1}^*; c_{q,1} \right\rangle \right\rangle_{\omega, e} = \frac{\beta^2 t_c^2}{4\omega_c^2} \left[ \delta(\omega) + \delta(\omega - \omega_c) + \delta(\omega + \omega_c) \right]. \tag{6.29}
\]

The term \(\delta(\omega)\) corresponds to the zero mode discussed earlier for ZZ-GNRs, while the terms with \(\delta(\omega - \omega_c)\) and \(\delta(\omega + \omega_c)\) correspond to the edge modes described by Eq. (6.19).

By inspection the imaginary part of Green's function in Eq. (6.25) associated with the bulk contribution is
\[
\text{Im}\left\langle \left\langle c_{q,1}^*; c_{q,1} \right\rangle \right\rangle_{\omega, e} = \frac{t_c^2 \beta}{2\pi \omega} \frac{\sin(3q_x a / 2)}{1 + 2\Delta \cos(3q_x a / 2)} . \tag{6.30}
\]

As mentioned earlier the spectral functions are formally related to the imaginary part of Green’s functions through the fluctuation dissipation theorem (see, e.g., [9, 10] and Eq. (2.33)). In the low temperature limit, where the Fermi distribution function is close to unity, the spectral function is related to the Green's function by
\[
\left\langle \left\langle c_{q,j}^*; c_{q,j} \right\rangle \right\rangle_{\omega} = -2 \text{Im}\left\langle \left\langle c_{q,j}^*; c_{q,j} \right\rangle \right\rangle_{\omega}
\]
in the usual notation [9].

For completeness, here we quote the edge and bulk contributions to the imaginary part of the Green's functions for the more important cases (i.e., when \(j = 1\)). Table 6.1 lists the edge contribution for the set of Green's functions, while Table 6.2 lists the bulk contribution.
### Table 6.1: The edge mode contribution for a set of Green's functions as indicated by their row index.

<table>
<thead>
<tr>
<th>$j, j'$</th>
<th>$\text{Im}\left\langle \left\langle c^+<em>{q,j} ; c</em>{q,j'} \right\rangle \right\rangle_{\omega,e}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$j = 1$, $j' = \text{even}$</td>
<td>$\frac{t_e \beta}{4 \omega_e} (-1)^{j/2} \left( \Delta^{-1} - \Delta^{-j/2} \right) \left[ \delta(\omega + \omega_e) - \delta(\omega - \omega_e) \right]$</td>
</tr>
<tr>
<td>$j = 1$, $j' = \text{odd} &gt; 1$</td>
<td>$\frac{t_e t \beta}{4 \omega_e^2} (-1)^{(j-1)/2} \Delta^{-(j-1)/2} \left( 1 - \beta \Delta^{-1} \right) \left[ \delta(\omega - 0) - \delta(\omega - \omega_e) - \delta(\omega + \omega_e) \right]$</td>
</tr>
</tbody>
</table>

### Table 6.2: The bulk mode contribution for a set of Green's functions as indicated by their row index.

<table>
<thead>
<tr>
<th>$j, j'$</th>
<th>$\text{Im}\left\langle \left\langle c^+<em>{q,j} ; c</em>{q,j'} \right\rangle \right\rangle_{\omega,b}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$j = 1$, $j' = \text{even}$</td>
<td>$\frac{t_e}{2 \pi^2} \sin\left( \frac{\pi}{2} q, a j' \right) \left( 1 + \Delta \cos\left( \frac{\pi}{2} q, a \right) \right) - \Delta \sin\left( \frac{\pi}{2} q, a \right) \cos\left( \frac{\pi}{2} q, a j' \right)$</td>
</tr>
<tr>
<td>$j = 1$, $j' = \text{odd} &gt; 1$</td>
<td>$\frac{t_e}{2 \pi \omega} \left[ \beta \Delta + (\beta + \Delta) \cos\left( \frac{\pi}{2} q, a \right) + 1 \sin\left( \frac{\pi}{2} q, a (j' - 1) \right) \right] + \left( \beta - \Delta \right) \sin\left( \frac{\pi}{2} q, a \right) \cos\left( \frac{\pi}{2} q, a (j' - 1) \right)$</td>
</tr>
</tbody>
</table>

### 6.4 Conclusions

The electronic Green's functions for long graphene nanoribbons with zigzag edges, treated in a tight-binding approximation with hopping, were derived using an analytical tridiagonal matrix inversion method. A set of Green's functions relating any two points on the graphene nanoribbon lattice was deduced. The excitation spectrum (as deduced from the poles of the derived Green’s functions) consists of modified bulk-like modes and localized edge modes of two types. We studied the localization properties and existence conditions for the edge modes that can occur when $t_e$ is sufficiently different from the bulk $t$, and we clarified the role of the “zero” edge modes, which appear as poles only in certain Green’s functions (namely odd-odd Green's functions). Although we focussed mainly on semi-infinite ribbons, a brief analysis of the finite width effect for ribbons was also carried out (in terms of...
the Green’s functions) in order to examine the width limitations. We showed that the coupling of the two edges becomes significant for ribbons with widths below ~10nm. This is in the regime where spin polarization of edges are reported in the literature previously cited.

References

CHAPTER 7

Influence of Zigzag Edges on the RKKY Interaction in Graphene Nanoribbons

In this chapter we derive a general expression for the Ruderman-Kittel-Kasuya-Yosida (RKKY) type interaction between two impurity spins placed on a graphene nanoribbon lattice. The general expression for the RKKY interaction involves a convolution product of the spectral functions derived in Chapter 6. The RKKY interaction is mediated by both edge and modified-bulk modes. We consider two distinct case where the impurity spins are placed on sites involving the zigzag edge in order to illustrate how the edge influences the RKKY interaction.

7.1 Introduction

Although pristine graphene is diamagnetic, defect-induced magnetism in graphene and related structures has been a topic of intensive study, e.g., [1-10]. One of the dominant forms of interaction between magnetic centers in graphene is attributed to a Ruderman-Kittel-Kasuya-Yosida (RKKY) type interaction, and this has received much attention in recent years (see, e.g., [2, 11-27] and references therein) as discussed below. Studies of the RKKY interaction are critical for applications using graphene as a platform for spin-related phenomena. The conventional RKKY interaction between pairs of localized spins is well known in metals and magnetic semiconductors as an effective interaction arising via the itinerant electrons [28]. In graphene the role of the itinerant electrons is played by the $\pi$-electrons. In this study we are motivated to investigate the role of zigzag edges in graphene
nanoribbons by taking into account the full spectrum of $\pi$-electronic excitations, which includes modified bulk modes and localized edge modes, discussed earlier in Chapter 6. The latter consist of modes that are localized due to modifications in the edge hopping, as well as the zero-frequency edge modes introduced by Fujita et al. [29].

It is well known that the RKKY interaction between magnetic impurities on an infinitely extended graphene lattice [2, 11, 16] has a $1/R^3$ fall-off with separation $R$, which is different from the $1/R^2$ fall-off expected for an RKKY interaction mediated by a two-dimensional electron gas [30]. In addition, the RKKY interaction exhibits oscillations with a periodicity that can vary depending on several factors, including the doping state of graphene and the chiral direction of the displacement vector between the impurity spins. In the case of doped graphene the period of oscillation is related to $2k_f$ [2, 13], where $k_f$ is the Fermi momentum. In undoped graphene the period of oscillation becomes spatially anisotropic [12, 13] with a proportionality to $1+\cos[(K-K')\cdot R]$, where $K-K'$ is the displacement between two adjacent Dirac points in $k$-space. Another characteristic of the RKKY interaction in graphene is the ferro(antiferro)-magnetic coupling between impurity spins depending on their placement on the lattice. Two moments placed at sites on the same graphene sublattice in an infinitely-extended sheet couple ferromagnetically, while two moments on different sublattices couple antiferromagnetically [11]. On the other hand, an impurity spin placed at plaquette sites always couples antiferromagnetically in the long distance limit. This coupling scheme is valid for a bipartite lattice at half-filling, with hopping between the two sublattices only, which is the case for undoped graphene with nearest-neighbour hopping. However, in the case of doped graphene where the electron-hole symmetry is lifted this coupling scheme no longer holds [13].
Uchoa et al. [22] pointed out that magnetic impurity adatoms placed at the center of a hexagon on the graphene lattice (plaquette sites) or at single vacancy sites can be effectively screened by a "super-Ohmic" bath. The screening of the magnetic moments for this class of adatoms reduces the range of interaction mediated by itinerant $\pi$-electrons producing a sharper fall-off as $1/R^2$. By contrast, screening does not play a role for impurity spins places on carbon sites on the graphene lattice.

Apart from the RKKY interaction in infinitely-extended graphene, there have been numerous studies of other graphene-related structures, including bi-layer graphene [17], disordered graphene [23], carbon nanotubes [24, 25], graphene nanoflakes [15], and graphene nanoribbons (GNRs) [14, 18, 19, 21, 24]. In particular, GNRs are of great interest since they exhibit special magnetic properties associated with their edge states, and they are expected to play an important role in the future of graphene-based spintronic devices [31]. For a discussion of edge modes in GNRs refer to Section 1.3 and Chapter 6.

Any realistic model of the RKKY interaction in GNRs needs to take into account the contributions arising from edge modes. Bunder et al. [18] have investigated the influence of the "zero modes" at ZZ edges and concluded that the presence of edge modes changes the RKKY coupling scheme deduced by Saremi [11], whereby ferromagnetic coupling occurs between spins on the same sublattice and antiferromagnetic coupling between spins on opposite sublattices. For spins placed at the edges the coupling mediated by the zero modes are not always ferromagnetic on the same edge and antiferromagnetic at different edge sites, but instead oscillates between ferro- and antiferro-magnetic coupling with variation in the spatial separation.

Szalowski [14] also investigated RKKY interactions numerically, focusing on A-GNRs using a matrix tight-binding Hamiltonian with nearest-neighbour hopping only. It was
illustrated that RKKY coupling between impurities in semiconducting A-GNRs exhibits an exponential decay, which is characteristic of structures with electronic band gaps. For metallic A-GNRs the author concluded that the RKKY coupling depends on the location of the impurity spins and in particular that the RKKY fall-off is $1/R$ for impurities placed at an edge on different sublattices, characteristic of one-dimensional metallic systems [30]. For impurity spins placed at an edge on the same sublattice the RKKY coupling was found to be nearly independent of their spatial separation in the long-distance regime.

Motivated by the continuing need for a more comprehensive theory for RKKY interactions, including clarification regarding the role of all types of localized modes at ZZ edges, we develop here an analytic theory, along with some numerical estimates, for a GNR geometry where the ribbons are assumed to be wide with ZZ edges and to be effectively infinitely long. In the width direction they have a large number, $N$, of rows of atoms and in some cases it will be appropriate to consider the semi-infinite limit $N \to \infty$. In this limit electron correlation effects are expected to be minimal and the tight-binding Hamiltonian for the description of the $\pi$-electrons in graphene should be valid. Our analysis takes into account the full spectrum of electronic excitations, which play a role in mediating the RKKY interaction. These excitations consist of two types of localized edge modes, i.e., those analogous to the "zero modes" [29] and those when the edge hopping is different [31]. In addition, the bulk-like (or propagating) modes are shown to have their spectral weighting modified near a ZZ edge.

One of our motivations is to study the effects on the RKKY interactions due to the locations of the impurity spins, both relative to each other and to the edge. This involves an analysis of the excitation spectrum in graphene nanoribbons, as derived in Chapter 6. Although the formalism to be derived for the RKKY interaction is general, we will focus in
particular on two special cases. In one case we consider two magnetic impurities placed on an outer edge of the ribbon, while in the other case we consider just one impurity at an edge with the other located at a perpendicular distance away from the edge. We show that in both cases the RKKY interaction is mediated by the modified bulk $\pi$-electronic modes and by the edge modes. We deduce the distinct spatial dependences for the RKKY exchange interaction for all cases investigated. The formalism for the RKKY interaction and its connection with the electronic excitation spectrum is presented in Section 7.2. Then in Section 7.3 we deduce results for the RKKY interaction, expressed alternatively in terms of a spatial and wave-vector form, for the two special cases mentioned above. The conclusions and possible extensions of this work are given in Section 7.4.

7.2 RKKY interaction formalism for a ribbon structure

Fig. 7.1. Assumed geometry and choice of coordinate axes for a graphene nanoribbon with zigzag edges, showing the rows labelled by integer $n = 1, 2, ..., N$. There are two localized spins (taken here to be at the edge in row $n = 1$) as magnetic impurities.
A schematic representation of the ZZ-GNRs under consideration is depicted in Fig. 7.1. As described in previous chapters, graphene has two interpenetrating sublattices, denoted here by A (black dots) and B (white dots). In the ZZ case the rows with odd label $n$ consist of only A sublattice sites and the even $n$ rows of only B sites. The localized spins may, in general, be on either the same or different rows corresponding to either of the sublattices. They may be located at an edge or at an interior site.

Here we derive a formalism that expresses the RKKY interaction in terms of electronic correlation functions (or Green’s functions) previously found in Chapter 6 for a ZZ GNR. Then the required Green’s functions for the two specific cases outlined above will be used in order to derive explicit expressions for the RKKY interaction mediated by both the edge modes and modified-bulk modes in the two cases.

In the absence of magnetic impurity sites the itinerant $\pi$-electron system will be described by a tight-binding Hamiltonian of the form

$$H_t = -\sum_{n,m,n',m'} t_{n,m,n',m'} \left( c_{n,m,o}^+ c_{n',m',o} + H.c. \right),$$  \hspace{1cm} (7.1)

where $c_{n,m,o}^+$ ($c_{n,m,o}$) are the $\pi$-electron creation (annihilation) fermion operators at row $n$, column $m$ and spin projection $\sigma$. Also $t_{n,m,n',m'}$ denotes the corresponding hopping parameter, assumed to act between nearest neighbours only. In addition to the tight-binding Hamiltonian, a contact Hamiltonian is introduced as a perturbation due to the magnetic impurities and given by

$$H_c = A \left( s_{i,j} \cdot s_{i,j} + s_{i',j'} \cdot s_{i',j'} \right).$$  \hspace{1cm} (7.2)

Here $s_{i,j}$ and $s_{i',j'}$ are the spins of the localized magnetic moments and $\pi$-electrons, respectively, at sites $(i, j)$ and $(i', j')$, and $A$ is the contact potential. The $\pi$-electron spin
operators can be expressed in terms of the fermionic operators by
\[ s_{ij}^+ = c_{ij\uparrow}^* c_{ij\uparrow}, \]
\[ s_{ij}^- = c_{ij\downarrow}^* c_{ij\downarrow}. \]

Since we are dealing with a ribbon geometry (either semi-infinite or finite width), there is no translational symmetry along the x-axis. Therefore we make a one-dimensional (1-D) Fourier transform, in accordance with Bloch's theorem [28], with respect to the y-direction only to re-express the field operators for describing the \( \pi \)-electron system. The term in the contact Hamiltonian \( H_c \) corresponding to the impurity spin at \((i,j)\) becomes
\[
H_c^{i,j} = \frac{1}{2} A \sum_{k_y} \left( S_{i,j,k_y}^- S_{i,j,k_y}^+ + S_{i,j,k_y}^+ S_{i,j,k_y}^- + S_{i,j,k_y}^z S_{i,j,k_y}^z \right), \tag{7.3}
\]
where
\[
S_{k_y}^\pm = e^{i k_y y} \sum_{q_y} c_{q_y,i,j,\alpha}^* c_{q_y,i,j,\alpha}, \tag{7.4}
\]
\[
S_{k_y}^z = e^{i k_y y} \sum_{q_y} \left( c_{q_y,i,j,\alpha}^* c_{q_y,i,j,\alpha} - c_{q_y,i,j,\alpha} c_{q_y,i,j,\alpha}^* \right). \tag{7.5}
\]

Here \( k_y \) and \( q_y \) are wavenumbers along the longitudinal axis of the ribbon, and \( \sigma_+ \) and \( \sigma_- \) denote the spin projections \( \uparrow \) and \( \downarrow \), respectively.

The RKKY interaction can be treated as a scattering phenomenon, where the itinerant electrons scatter from the magnetic impurity sites. The probability of a transition from a state \( |\alpha\rangle \) with energy \( \Omega_\alpha \) to a state \( |\alpha'\rangle \) with energy \( \Omega_{\alpha'} \) is given by
\[
P = \sum_{\alpha} \left( \langle \alpha | H_c^T \rangle \langle \alpha' | H_c^T \rangle \delta(\Omega_\alpha - \Omega_{\alpha'}) \right), \tag{7.6}
\]
where \( H_c^T = H_c^{i,j} + H_c^{i,j'} \). The correction energy due to scattering from the two impurity centers is found to be
\[
E = \frac{1}{2\pi} \int_{-\infty}^{\infty} dt \left( \langle \alpha | H_c^{i,j}(t) H_c^{i,j}(0) | \alpha \rangle \right), \tag{7.7}
\]

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where we have denoted $H_c(t) = e^{i\mathcal{H}t}e^{-i\mathcal{H}t}$, where $\mathcal{H}$ is the full Hamiltonian of the system.

The contribution to the RKKY interaction, related to the coupling of the impurity sites involves only the cross terms in Eq. (7.7) and corresponds to an energy term of the form

$$E^{\text{RKKY}}_{\text{ee}} = -\frac{1}{2}J_{i,j,k,l}^* S_{i,j}^+ S_{k,l}^-,$$

(7.8)

Here the effective RKKY exchange integral is given in real space by

$$J_{i,j,k,l} = \sum_{k_y} J_{j,k}^\ne(k_y) e^{-ik_y(y-y)},$$

(7.9)

which is related to its 1-D transform in $k$-space by

$$J_{j,k}(k_y) = A^2 \sum_{q_y} \sum_{\omega} \left\langle c_{q_y,j}^+ c_{q_y,j} \right\rangle_{\omega} \left\langle c_{k_y,q_y,j}^+ c_{k_y,q_y,j} \right\rangle_{-\omega}.$$

(7.10)

Thus the effective exchange in $k$-space is found to be a convolution product of two spectral functions (i.e., the frequency Fourier transforms of correlation functions between the $\pi$-electron operators at frequency $\omega$) involving the different wavenumbers as indicated above.

This is a generalization of the expression in the case of an infinite graphene sheet [11].

The spectral functions (or their corresponding Green’s functions) involve contributions from all excitations, i.e., both bulk (b) modes and localized edge (e) modes, as derived in Chapter 6. Therefore the contributions to the effective exchange may be of three types, which we may label as bulk-bulk (bb), edge-edge (ee), and edge-bulk (eb). By contrast, in the case of previous calculations for complete graphene sheets, as in [11, 12], only bb terms arise. Even in that case, the bulk modes of a complete graphene sheet differ from those in the ribbon since their spectral weighting is modified (see Chapter 6). The edge modes we will consider here comprise both those introduced by Fujita et al. [29], where the modes are due to the geometrical structure of the honeycomb lattice with ZZ edges, and the
other edge modes arising due to a difference in the interaction (hopping) energy between π-electrons along the ZZ edge and the bulk [32].

7.3 Results for RKKY interaction

We now make estimates for the effective exchange, as given by Eqs. (7.9) and (7.10), for two distinct choices that highlight the influence of zigzag edges on the RKKY interaction. In the first case we place two spins on the edge \(j = j' = 1\) of a semi-infinite ribbon, while in the second case we place one spin at the edge \(j = 1\) and the second at an interior site on an odd row \(j' = n > 1\), where \(n\) is odd.

A. Interaction between two spins on an edge

This first case corresponds to the arrangement in Fig. 7.1, where the magnetic impurities are both in the \(n = 1\) edge of a wide nanoribbon at a longitudinal distance apart. Using Eqs. (6.29) and (6.30), we can find the spectral functions required for the RKKY exchange interaction in the semi-infinite limit (taking \(N \to \infty\)). The spectral function, including both bulk and edge modes in the low temperature limit where

\[
\left\langle c_{q_x,j}^+ c_{q_y,j}\right\rangle_{\omega} = -2 \left\langle c_{q_x,j}^+ c_{q_y,j}\right\rangle_{\omega} \text{ is found to be of the form}
\]

\[
\left\langle c_{q_x,1}^+ c_{q_y,1}\right\rangle_{\omega} = -\frac{t_c^2}{\pi \omega^2} \left[ \begin{array}{c} \sin(3q_x a/2) \\ 1 + 2\Delta(q_y) \cos(3q_x a/2) + \Delta^2(q_y) \end{array} \right] \beta(q_y) + \frac{t_c^2}{2\omega^2} \left[ 1 - \Delta^2(q_y) \right] \beta^2(q_y) \left[ \delta(\omega - \omega_c) + \delta(\omega + \omega_c) \right] + \frac{t_c^2 \beta^2(q_y)}{2\omega^2 \left[ 1 - \beta(q_y) \Delta(q_y) \right]} \delta(\omega),
\]

where \(\Delta(q_y)\) and \(\beta(q_y)\) are defined in Eqs. (6.8) and (6.11), respectively. The first term above is the bulk-mode contribution arising when \(\omega = \omega_b(q_x,q_y)\) as in Eq. (6.18) and the second term
is an additional edge-mode contribution when $\omega = \omega_e(q_y)$ as in Eq. (6.19) and the existence condition for edge modes is satisfied (see discuss in Section 6.2). The final term is a contribution to the spectral function from the zero edge modes when $q_y$ is in the range discussed earlier. With the aid of Eq. (7.10), which involves a convolution of two similar spectral functions, we may deduce the RKKY interaction.

First, we analyze the edge-edge (ee) contribution to the RKKY interaction analytically for this geometry by substituting the second term in Eq. (7.11) into Eq. (7.10) for each of the two spectral functions at the specified wavenumbers ($q_y$ and $k_y+q_y$) and frequencies ($\omega$ and $-\omega$). This gives rise to terms with several delta functions, which must be integrated with respect to both frequency $\omega$ and the longitudinal wavenumber $q_y$.

Transformation of the delta functions lead to an overall factor

$$\delta\left[\omega_e(q_y) - \omega_e(k_y + q_y)\right] = \frac{\delta(q_y + \frac{1}{2}k_y)}{2\sqrt{3t_e^2} \sin\left(\frac{\sqrt{3}}{2}k_y a\right)}$$

(7.12)

after the integration over $\omega$. The integration over $q_y$ can next be carried out, leading to the final approximate form for the ee contribution to the RKKY interaction as

$$J_{ee}^{ee}(k_y) = \frac{A^2}{48t_e(t_e/t)^2} \left[\frac{(t_e/t)^2 - 2}{(t_e/t)^2 - 1}\right]^2 \frac{1}{|k_y|a}$$

(7.13)

in the small wavenumber regime $|k_y|a << 1$. The above ee contribution to the RKKY interaction is inversely proportional to $|k_y|$ in this wavenumber regime and it depends strongly on the ratio $t_e/t$ as shown in Fig. 7.2. This ee contribution is much larger in the low-frequency (acoustic) region, relative to the high-frequency region. An interesting question arises as to whether the $\delta(\omega)$ term in Eq. (7.11) leads to a further edge contribution to the RKKY interaction. This is presently unclear, because the resulting convolution product of two delta functions with the same argument ($\omega = 0$) is ill-defined. Also, if each delta function is
replaced by a Lorentzian whose width is later allowed to tend to zero, serious problems arise with how the limits are taken. In fact, this formal difficulty is related to the discrepancy described by Bunder and Lin [18] regarding an analytic continuation at zero frequency, although conflicting results were reported by Black-Schaffer [27] (see further discussions in [33]). We return briefly to this matter in Section 7.4.

Fig. 7.2. Plot of the $ee$ RKKY interaction vs. the edge to bulk hopping ratio, for any fixed small $k_y$ for Case A. No edge modes of this type can exist in the intermediate (shaded) region.

Next, by substituting the bulk component of the spectral function, as given by the first term of Eq. (7.11), into Eq. (7.10) we can find the bulk-mode ($bb$) contribution to the RKKY interaction for this case. Before presenting numerical calculations of general validity, it is useful to examine some analytical approximations, based on the expectation that the $bb$ contribution to the RKKY interaction will be dominated by the $\pi$-electron states near the Dirac point (where $\omega$ in the dispersion relation is small). This is by analogy with similar arguments used in calculations for the infinite graphene sheet [11]. Expanding the terms in
the RKKY expression about the Dirac point at \( \left( \frac{2\pi}{3a}, \frac{2\pi}{3\sqrt{3}a} \right) \) in \( k \)-space and keeping terms to the lowest order in the expansion parameter, we end up with an integral expression of the form

\[
J_{11}^{\text{bulk}}(k_y) = - A^2 \left( \frac{1}{2\pi} \right)^2 \left( \frac{t}{t_c} \right)^4 \int \int \frac{\delta_x \delta_y'}{\omega^2(q_y)} dq_y d\omega, \tag{7.14}
\]

where \( \omega = t \sqrt{3\delta_x^2 + \delta_y^2} \) is the approximate dispersion relation near the Dirac point. Here \( \delta_x \) and \( \delta_y \) are rescaled dimensionless wavenumbers used when expanding about the Dirac point and given by \( \delta_x = \pi - \frac{t}{t_c} q_x a \) and \( \delta_y = \frac{\pi}{3} - \frac{\sqrt{3}}{3} q_y a \). The quantity \( \delta_x' \) is obtained using the condition \( |\omega(q_x, q_y)| = |\omega(q_x', k_y + q_y)| \), from Eq. (7.10). We find the relation

\[
\delta_x' = \sqrt{\delta_x^2 + 3\sqrt{3}\delta_y k_y a - \frac{9}{4} k_y^2 a^2}.
\]

The integration limits in Eq. (7.14) can be found using the above approximation for the dispersion near the Dirac point and noting that the bottom of the conduction band in the dispersion relation corresponds to the contour \( \delta_x = 0 \). This leads to integration from \( \delta_y = -\omega / \sqrt{3}t \) to \( \delta_y = \omega / \sqrt{3}t \) for a fixed \( \omega \). Then the integration over \( \omega \) is taken from \( \omega_{\text{min}} = \frac{3}{2} k_y a t \) (as inferred from the small finite value of the external wavenumber label \( k_y \) and the hopping parameter \( t \)), to an upper integration limit is given by a chosen cut-off frequency \( \omega_{\text{cut}} \) (in order to limit the integration to within a region near the Dirac point). For small \( k_y \) we can use the condition \( \delta_x^2 \gg 3\sqrt{3}\delta_y k_y a - \frac{9}{4} k_y^2 a^2 \) and carry out the integration in Eq. (7.14) to obtain an analytical expression for the bulk-mode RKKY contribution in \( k_y \)-space as

\[
J_{11}^{bb}(k_y) = \frac{4}{3at} A^2 \left( \frac{1}{2\pi} \right)^2 \left( \frac{t}{t_c} \right)^4 \left[ \frac{\omega_{\text{cut}}^2}{3t^2} - \frac{3}{4} k_y^2 a^2 \left( \frac{3}{2} \ln \left( \frac{\omega_{\text{cut}}}{\frac{3}{2} k_y a t} \right) + 1 \right) \right]. \tag{7.15}
\]
This approximate expression depends on the choice of cut-off frequency $\omega_{\text{cut}}$, which is expected to be of order $t$. The introduction of a cut-off frequency is analogous to [11].

To improve on the above estimate we can use our full RKKY expression and integrate over the entire band numerically. We then obtain a curve for the RKKY exchange vs. the external wavenumber $k_y$, as shown by the dashed line in Fig. 7.3. Special care was taken to ensure proper numerical convergence of the RKKY exchange integral, particularly near the Dirac points. For comparison our analytical expression in Eq. (7.15) for the RKKY exchange at small $k_y$ is also plotted in Fig. 7.3 for three choices of cut-off frequencies. We find excellent agreement for small $k_y$ (specifically $k_y a < 0.2$) when we set $\omega_{\text{cut}} = 2t$.

![Fig. 7.3: Plot of the $bb$ contribution to the RKKY interaction vs. wavenumber $k_y$ for case A. The dashed line corresponds to the full band integration for the RKKY exchange calculated numerically. The full lines correspond to the approximate analytical expression of Eq. (7.15) for various choices of $\omega_{\text{cut}}$.](image)
Fig. 7.4: Plot of the $bb$ RKKY contribution vs. spatial separation. An oscillating behaviour between ferro- and antiferro-magnetic coupling is observed when $J_{bb}$ is plotted continuously. By contrast, for $J_{bb}$ vs. spatial separation on the discrete lattice sites along the edge the behaviour is a decaying function with fall-off $1/R^2$, and the coupling is always ferromagnetic (see (b) and (d) for the analytic and numerical cases, respectively).

Now, using the analytical expression given by Eq. (7.15) and setting $\omega_{cut} = 2t$, we can deduce the spatial dependence of the $bb$ RKKY contribution vs. the longitudinal separation of the two spins along the ZZ edge. It is interesting that, although the functional form of the $bb$ RKKY contribution oscillates between ferro- and antiferro-magnetic coupling (i.e., see Fig. 7.4(a)) as the separation between the two spins increases continuously, nevertheless at the discrete points corresponding to the lattice sites on the ZZ edge the coupling is always
ferromagnetic. This coupling scheme is consistent with estimates by Saremi [11] for infinite graphene sheets, noting that in our case the edge consists of sites on the same sublattice. We conclude that the \( bb \) RKKY contribution for two spins on the edge has predominantly a \( 1/R^2 \) fall-off in contrast to the \( 1/R^3 \) fall-off between spins on an infinitely-extended graphene lattice. This is illustrated in Fig. 7.4(b) where the fits for \( 1/R, 1/R^2, \) and \( 1/R^3 \) are shown along with the calculated RKKY curve. We arrive at similar results, when we carry out the above analysis using the full-band numerical calculations, as shown in Figs. 7.4(c) and (d).

B. Interaction between a spin on the edge and a perpendicular interior spin

In the previous subsection the vector separation between the impurity spins was chosen to be in the longitudinal direction (parallel to the \( y \) axis). To highlight the directional dependence of the RKKY interaction in a stripe, we now briefly discuss the exchange interaction for the case when one spin is on the \( j = 1 \) edge and the second spin is located at an interior site in row \( j' > 1 \), where \( j' \) is odd, as depicted in Fig. 7.5. In this case the spectral function required for the RKKY calculation is found to be (see Table 6.2)

\[
\langle c_{q_x}^{\dagger} c_{q_x} \rangle \propto \frac{t_c}{\pi \cos \left( \frac{\Psi}{1 + 2 \Delta \cos \left( \frac{q_x}{2} a + \Delta \right)} \right)},
\]

where

\[
\Psi = [\beta \Delta + (\beta + \Delta) \cos \left( \frac{3}{4} q_x a \right) + 1] \sin \left[ \frac{3}{4} q_x a (j' - 1) \right] + (\beta - \Delta) \sin \left( \frac{3}{4} q_x a \right) \cos \left[ \frac{3}{4} q_x a (j' - 1) \right],
\]

and the \( q_x \) dependence for \( \Delta \) and \( \beta \) is implicit. In the above expression we have ignored the edge-mode \( (ee) \) contribution, due to attenuation effects in the interior of the ribbon. In fact, the attenuation of the edge mode for this case arises from the factor \( \Delta^{-(j'-1)/2} \) (see Table 6.1).
The corresponding attenuation length of the edge-mode from the edge of the ribbon is shown in Fig. 7.6 where the attenuation length is plotted vs. \((t_e/t)^2\). This makes the RKKY edge contribution much less important in this configuration, except when \((t_e/t)^2\) is just below 0.5 or just above 1.5.

Fig. 7.5: Schematic geometry in Case B with one spin on the edge \((j = 1)\) and the other at a perpendicular distance in the interior on the same sublattice (odd \(j > 1)\).

Fig. 7.6: Dependence of the penetration depth along the x-axis \((L_x)\) of the edge modes into the interior of the graphene nanoribbon plotted versus \((t_e/t)^2\).
Hence the dominant contribution to the RKKY exchange integral will typically come from the bulk modes, but again with modifications to the spectral weight due to the edge. A general expression for the $bb$-contribution to the RKKY interaction is obtained for this case by substituting Eqs. (7.16) and (7.17) into Eq.(7.10), and using the symmetry relation \( \langle c_{q,1}^+ c_{q,1}^\dagger \rangle \omega = \langle c_{q,1}^+ c_{q,1}^\dagger \rangle \omega \). In principle it is again possible to expand the RKKY exchange integral about the Dirac point as in the previous subsection in order to find an analytical expression for this case.

### 7.4 Conclusions

Calculations were presented for the RKKY effective exchange interaction in long graphene nanoribbons with zigzag edges, treated in a tight-binding approximation with hopping. We obtained an analytical expression for the RKKY interaction as a convolution product of spectral functions, which describe the extended-range effective interactions between two impurity spins located at any two points on a graphene nanoribbon.

We have shown that the RKKY interactions depend on the locations of the impurity spins relative to each other and to any edge, while contributions will arise from both the bulk and edge modes. Two specific cases were examined, leading to distinct expressions for the spatial dependence. The edge-mode contributions to the RKKY interaction were found to be more important for the geometry with both impurity spins at the edge (case A), as expected. However, in both cases the bulk mode contributions are modified by the presence of the edge (via modifications to the density-of-states terms compared with an infinite sheet). In case A, which is of greater interest because both impurity spins are located at an edge, we made detailed estimates for the dependences of the RKKY interaction on $k_y$ and on spatial
coordinates. Approximate analytic expressions were deduced, along with results obtained from numerical integration over the Brillouin zone, giving good overall consistency. The zero modes play a role in these calculations in affecting the spectral weights of all modes through an overall $1/\omega$ factor in the relevant (i.e., odd-odd) correlation functions.

In extensions of the current work, it would be interesting to make more extensive studies of the fall-off and oscillatory behaviour when one spin is in the edge and the other is an interior spin, not just as in case B (when the line joining the two impurity spins is at 90 degrees to the edge direction), but for the joining line in different chiral directions away from the edge site. For instance (by comparison with Fig. 7.5), the interior spin could be placed at a distance transverse to the spin on the edge for a spatial separation anywhere along the armchair direction, or it could be placed at an angle of 60 degrees with respect to the edge (along a zigzag direction).

Another interesting topic for future investigations would be to follow up in more detail with studying GNRs of finite ribbon width (finite $N$) and the correlations between the two edges that would arise. As deduced in Section 6.2, the semi-infinite approximation is well justified for $N$ greater than about 200, whereas for $N$ between about 20 and 200 there is a regime of significant edge correlations (with perturbations of the modes, as mentioned in Chapter 6) and for $N < 20$ the effects of edge correlations are strong. In particular, for $N$ of order 20 or less, the modes (bulk or edge) become discrete and hybridized (see, e.g., numerical calculations in [34]). For this regime our Green's function method could help in clarifying the role of the zero edge modes.
References


CHAPTER 8

Applications of Electron Spin Resonance

In this chapter we discuss some applications of electron spin resonance (ESR) and the physical parameters that can be obtained from this technique. We demonstrate the versatility of the ESR technique by investigating two materials. These studies include investigating the paramagnetic characteristic of \( \text{Au}_{25}^+ \) core-shell molecular clusters and the defect formation mechanism of epitaxially grown amorphous Si films. The work presented here is based on a number of publications in collaboration with the department of chemistry at the University of Western Ontario, and the National Research Council of Canada.

8.1 ESR in positively charged \( \text{Au}_{25} \) molecular nanoclusters

This section is based on a publication with Mahdi Hesari and Mark S. Workentin [1]. Some additional discussions on temperature independent Van Vleck paramagnetic nature of \( \text{Au}_{25}^+ \) while also be presented, which has not yet been published. Many of the theoretical concepts presented here were discussed with Michael Cottam. All sample fabrication and characterizations were carried out by Mahdi Hesari under the supervision of Prof. Mark S. Workentin, except for electron spin resonance (ESR) characterization. The theoretical models and simulations for interpreting the ESR spectra was carried out by myself under the supervision of Michael Cottam and Giovanni Fanchini.
8.1.1 Introduction

During the last few decades, extensive research has been conducted on gold nanoparticles, with a focus on their optical [2, 3], structural [3] electronic [4], chemical [5], and physical [6] properties. The continual studies of gold nanoparticles are driven by the feasibility and success of their real life applications in biomedical [7], plasmonics [8], and data storage devices [9]. One of the major drawbacks for the use of nanostructured gold in nanotechnology has been the lack of methods of synthesis that would allow for a more deterministic size distribution of the nanoparticles. This is critical because several properties of metallic nanostructures are strongly dependent on their size [10]. Recently, the synthesis of monodispersed Au$_{25}$ nanoclusters has overcome this problem [11-13]. Au$_{25}$ nanoclusters offer many interesting advantages over larger gold nanoparticles, including a well-defined molecular structure, which leads to deterministic optical [14, 15], electrochemical [16], and catalytic properties [17-19].

The first report of monodispersed Au$_{25}$ nanoclusters by Jin and co-workers[12] has opened an avenue for many additional studies. Murray et al. [20] suggested the possibility of different charge states in Au$_{25}$ and demonstrated the synthesis of Au$_{25}^n$ molecular clusters with tuneable charge states, $n = -1, 0, \text{and } +1$ [20, 21]. Tuning the charge state has the potential to make Au$_{25}^n$ suitable for additional applications in nanoelectronics and spintronics, but the dependence of many physical (including magnetic) properties of Au$_{25}^n$ on the specific charge state is unknown, especially for the Au$_{25}^+$ form.

The structure of Au$_{25}$ is now well-established [22-24] and theoretical models, including density functional theory (DFT) calculations [25], suggest that negatively charged Au$_{25}^-$ is diamagnetic, with 6 electrons occupying a triply degenerate highest occupied
molecular orbital (HOMO). Consequently, the higher oxidation state, \( \text{Au}_{25}^0 \), should be paramagnetic [26]. A paramagnetic centre in \( \text{Au}_{25}^0 \) was demonstrated by Jin and co-workers [26] using electron spin resonance (ESR) after converting the anionic form \( \text{Au}_{25}^- \) into the neutral form, using hydrogen peroxide as an oxidant.

In this work, we perform an ESR investigation of \( \text{Au}_{25}(\text{SC}_2\text{H}_4\text{Ph})_{18} \) molecular clusters identical to those previously observed by Jin et al. [26]. We present the ESR powder spectra of these molecular clusters and we demonstrate for the first time the presence of an EPR-active centre in the positively charged \( \text{Au}_{25}^+ \) species.

**8.1.2 Experiment**

The \( \text{Au}_{25}\text{L}_{18}^- \) [\( \text{L} = \text{S(CH}_2)_2\text{Ph} \)] molecular clusters (here indicated as \( \text{Au}_{25}^- \) for simplicity) were prepared following the procedure reported by Murray and \textit{et al.} [11] and Maran and \textit{et al.} with some modifications [20, 21]. Briefly, \( \text{HAuCl}_4\cdot3\text{H}_2\text{O} \) salt and tetraoctylammonium bromide (TOABr) were co-dissolved in tetrahydrofuran (THF) and placed in an ice bath. Then, phenylethane thiol was added and stirred at room temperature until the mixture turned colourless. The solution was placed again in the ice-bath and ice-cold aqueous solution of \( \text{NaBH}_4 \) was added quickly under vigorous stirring. After the completion of the reaction, the solution was gravity filtered and the solvent volume was reduced under vacuum. Excess \( \text{NaBH}_4 \) and phenylethane thiol was removed by washing the crude sample with water/ethanol mixture and then recrystallized using toluene/ethanol solvent mixture to yield dark-brown needle crystals. The purity and structure of the crystals were checked using different characterization techniques, including: UV-visible spectroscopy [21], \(^1\text{H} \) nuclear magnetic resonance [20], X-ray crystallography [23, 24] and electrospray ionization mass spectrometry. The same procedure was applied to synthesize the \( \text{Au}_{25}^0 \), but
with the exclusion of TOABr. The molecular clusters were converted into \( \text{Au}_{25}^+ \) according to a protocol established [20], via electron transfer between the molecular cluster and the peroxide which leads to the formation of \( \text{Au}_{25}(\text{SC}_2\text{H}_4\text{Ph})_{18}^+\text{C}_6\text{F}_5\text{CO}_2^- \).

To investigate the paramagnetic centres in our samples, we recorded under the same conditions the ESR powder spectra of 30 mg of \( \text{Au}_{25}^+ \) and \( \text{Au}_{25}^0 \) molecular clusters. Such measurements were performed on a Jeol FA 200 ESR spectrometer operating at \( \sim 9.5 \) MHz in X-band. For a description of the ESR spectrometer refer to Chapter 3. Our specimens were placed in Suprasil\textsuperscript{TM} tubes of 5 mm diameter. The microwave power was kept at 64 mW to prevent saturation of the ESR signal. The magnetic field was scanned from 0 to 1700 mT. To investigate effects of temperature on the \( \text{Au}_{25} \) molecular clusters, test tubes with the sample inside were sealed with a Wilmad 552-5 tip-off manifold and evacuated to less than \( \sim 10^{-2} \) mTorr. Low temperature ESR temperature measurements were recorded with the samples placed in a Jeol liquid nitrogen ESR cryostat, automatically controlled by a temperature control unit.

8.1.3 Model

For EPR-active electronic states, the spin Hamiltonian can be decomposed into three terms [27]:

\[
H_{\text{Spin}} = H_Z + H_{\text{HF}} + H_{\text{SHF}}. \tag{8.1}
\]

In Eq. (8.1), the first term represents the electronic and nuclear Zeeman Hamiltonian (see Eq. (2.59)), as discussed in subsection 2.3.1. For the core of an \( \text{Au}_{25} \) molecular cluster, formed by thirteen \( ^{197} \text{Au} \) nuclei, this term is

\[
H_Z = \mu_{\text{B}} \mathbf{B} \cdot \mathbf{g}_s \cdot \mathbf{S} + \sum_{k=1}^{13} \mu_{\text{B}} \mathbf{B} \cdot \mathbf{g}_k^{4u} \cdot \mathbf{I}_k^{4u}. \tag{8.2}
\]
Here, \( \mathbf{B} \) is the external magnetic field, \( \mu_B \) is the Bohr magneton, \( \mu_n \) is the nuclear magneton, \( \mathbf{g} \), and \( \mathbf{S} \) are the gyromagnetic tensor and the effective spin operator for the singly-occupied molecular orbital (SOMO) and \( \mathbf{I}_1^{du} \) and \( \mathbf{g}_1^{du} \) are the nuclear spin operator and gyromagnetic tensor for the \( k \)-th Au nucleus. The second term in Eq. (8.1) is the hyperfine Hamiltonian (see Eq. (2.69)) that expresses the interaction of the unpaired electron spin with the nuclear spin of the nucleus on which the SOMO state is localized and can be written as

\[
H_{HF} = \mathbf{S} \cdot \mathbf{A} \cdot \mathbf{I}_1^{du},
\]

(8.3)

where \( \mathbf{I}_1^{du} \) is the nuclear spin operator associated with the nucleus on which the SOMO state is localized. The hyperfine tensor \( \mathbf{A} \), appearing in Eq. (8.3), can be written as the sum of an isotropic component and a traceless tensor \( \mathbf{A}_{\text{Anis}} \) (see Eq. (2.68)):

\[
\mathbf{A} = A_{Is} \mathbf{I}_3 + \mathbf{A}_{\text{Anis}}.
\]

(8.4)

Here, \( \mathbf{I}_3 \) is the 3x3 identity matrix and \( A_{Is} \) is the isotropic hyperfine coupling constant, written as

\[
A_{Is} = \frac{2}{3} g \mu_0 \mu_n \left| \Psi_{\text{SOMO}}(0) \right|^2,
\]

(8.5)

where \( g = 2.0023 \) is the Landé \( g \)-factor for the free electron and \( \mu_0 \) is the magnetic permittivity of vacuum. Eq. (8.5) is nonzero only if the eigenfunction \( \Psi_{\text{SOMO}}(0) \) associated with the SOMO has an \( s \)-type atomic component, and therefore a non-vanishing distribution at the nucleus \( r = 0 \). The second term in Eq. (8.4) is nonzero only in the case of higher-order atomic components of \( \Psi_{\text{SOMO}}(r) \) (i.e., \( p \)-type, \( d \)-type, or higher). We note that even though the form of the Hamiltonian given in Eq. (8.1) is in terms of the effective spin of the SOMO, admixtures of orbital angular momentum related to the SOMO are included through the anisotropic \( g \) and hyperfine tensors, as discussed in Subsections 2.3.1 and 2.3.2.
The third term in Eq. (8.1), the superhyperfine Hamiltonian, can be written as

\[ H_{\text{SHF}} = \sum_{k=2}^{13} S \cdot T_k \cdot I_k^{4u}, \quad (8.6) \]

where the summation in Eq. (8.6) is carried out over all nuclei in the core, with the exception of the central nucleus on which the SOMO state is localized \((k = 1)\). Eq. (8.6) is analogous to Eq. (8.3), except that it is related to the hyperfine coupling between the SOMO and nearby nuclei, rather than the central nucleus where the SOMO is mostly localized. In order to minimize the number of adjustable parameters, our model assumes that \(T_k\), the superhyperfine coupling tensor, is isotropic. We anticipate that \(H_{\text{SHF}}\) only affects the linewidth of our calculated spectra, while the essential features of the experimental ESR signal are controlled by the Zeeman and hyperfine components of the Hamiltonian, due to the localization of the SOMO in the proximity of the central gold nucleus (see later).

Simulations of our experimental data were performed using the Jeol Anisimu™ software package (version 2.2.0). For powder spectra this routine integrates and averages the crystal spectra calculated for all possible angles with respect to the external field \(B\). Calculations of the Zeeman and superhyperfine components of the spin Hamiltonian were carried out by dividing the core into three sets of equivalent atoms as shown in Fig. 8.1. Specifically: i) \(k = 1\) represents the central gold nucleus where the SOMO was previously reported [26] to be centered, ii) \(k = 2, \ldots, 7\) represent the nearly regular hexagonal ring of six gold nuclei located in the plane around the central gold atom, and iii) \(k = 8, \ldots, 10\) and \(k = 11, \ldots, 13\) represent the six out of plane gold nuclei, three located above and three below the plane determined by nuclei 1, \ldots, 7. In all our simulations an additional broad and featureless Lorentzian line with \(g\sim2.002\) has been added in order to take into account the ESR signal
possibly related to free electrons in our powder system. The intensity, linewidth, and g-value of this signal were kept constant for spectra recorded at different temperatures.

Fig. 8.1: Detail of the core of Au$_{25}^0$, comprising 13 Au atoms. Atoms are labelled with the notation used in Equations (8.2)-(8.6). The approximate structure of the SOMO is also shown, shaded in blue.

8.1.4 Results and discussion

The ESR powder spectra of Au$_{25}^+$ for various measured temperatures are shown in Fig. 8.2 with their corresponding simulated spectra based on the Hamiltonian described by Eq. (8.1). The intensity does not substantially change with the measurement temperature, indicating a temperature independent magnetic susceptibility for our sample. This is consistent with temperature independent Van Vleck paramagnetism, which will be discussed in Subsection 8.1.5. However, variations in the temperature produce a number of slight differences between the room temperature and the low temperature spectra evident in Fig. 8.2, which also compares the ESR powder spectra of Au$_{25}^+$ (panel a) with those of Au$_{25}^0$ (panel b). We performed the simulations in panel b by using the same values of the g-tensor determined by Jin et al. from their simulations of ESR solution spectra [23]. ESR powder spectra are less tolerant than solution spectra to small fluctuations of the simulation
parameters and this explains the slight discrepancy in the positions of the theoretical and experimental lines in Fig. 8.2(b).

Fig. 8.2: (a) Experimental and simulated ESR spectra of positively charged \( \text{Au}_{25}^+ \) molecular clusters at varying temperatures; (b) experimental and simulated ESR spectra of neutral \( \text{Au}_{25}^0 \) molecular clusters in powder (pow.) form (present work) and in toluene solution (sol.) as previously reported by Jin et al. [23].

At all measurement temperatures, it can be observed that the ESR spectra of \( \text{Au}_{25}^+ \) exhibit five local maxima and five local minima. All of these modulations can be simulated, at least qualitatively, by imposing \( H_{\text{SHF}} = 0 \) in Eq. (8.1). This points to the fact that all the components of \( T_k \) in Eq. (8.3) are very small, indicating that the superhyperfine couplings of the SOMO with the nuclear spins of any \(^{197}\text{Au} \) other than the central nucleus play a negligible role in determining the shape of the experimental ESR spectra. Conversely, the inclusion of relatively strong superhyperfine coupling in our simulations would generate a sequence of 15 local maxima and local minima in our simulated EPR spectra, which is not experimentally observed. From the analysis of the superhyperfine interactions, we conclude
that the eigenfunction of the SOMO state is strongly localized in the proximity of the central
gold atom in the icosahedral core, although weak and unresolved superhyperfine coupling
with other $^{197}$Au nuclei may contribute in broadening the linewidth of the measured ESR
spectra. This conclusion is also in very good agreement with density functional theory (DFT)
calculations on $\text{Au}_{25}^+$ molecules [25].

Fig. 8.3 shows the principal values of the gyromagnetic and hyperfine coupling
tensors as a function of temperature, which are a measure of the spin-orbit coupling and the
electron spin coupling with nuclear spins, respectively. These values are extracted from the
least-square computer simulations of the experimental powder spectra of $\text{Au}_{25}^+$ and $\text{Au}_{25}^0$
reported in Fig. 8.2a and b, respectively. $g_s$ is nearly biaxial in $\text{Au}_{25}^0$, with $g_{s,x} \sim g_{s,y} \sim g_s = 2.4 \pm 0.1$ and $g_{s,z} \sim g_s = 1.82 << g_s$. These values are the same reported in [26] from their
solution spectra of $\text{Au}_{25}^0$. In addition, they suggested that, in $\text{Au}_{25}^0$, the SOMO has a nearly
100\% $p$-type wavefunction, which implies $|\Psi_{\text{SOMO}}(0)|^2 = 0$ and, accordingly to Eq. (8.5), a
negligible hyperfine interaction between the electron spin associated with the SOMO and the
nuclear spin of the $^{197}$Au atom localized at the center of the molecule.

Our powder spectra of $\text{Au}_{25}^0$ appear to corroborate, at least qualitatively, the findings
in [26]. Specifically the spectra shown in Fig. 8.2(b), can be simulated by assuming
$A_{\text{Anis}} \approx 0$ and $A_{ls} = 11.7$ mT in Eq. (8.4). This is a much smaller value than the contact
isotropic hyperfine coupling coefficient of $^{197}$Au, $a_0 = (2/3) g^* \mu_B \nu N \cdot |\Phi_s(0)|^2 = 102.6$ mT
[22]. Writing the SOMO wavefunction of $\text{Au}_{25}^0$ in the form of a linear combination of
normalized atomic orbitals of the central atom

$$\Psi_{\text{SOMO}}(\mathbf{r}) \approx \alpha \Phi_s(\mathbf{r}) + \sum_n \gamma_n \Phi_p^{(n)}(\mathbf{r}) + \sum_m \gamma_m \Phi_p^{(m)}(\mathbf{r}),$$

(8.7)
it can be determined that the s-type atomic component of the SOMO is $A_{1s}/a_0 \approx 10\%$, with a nearly 90\% $p$-type wavefunction. Due to the negligible anisotropic interaction with the nearest neighbour $^{197}$Au nuclei of the molecular core, situated in-plane, the $p$-type component of the SOMO can be almost entirely assigned to the out-of-plane wavefunction $\Phi_p^{(2)}$, consistent with the observations in [26].

Fig. 8.3: ESR simulation parameters for $\text{Au}_{25}^n$ molecular clusters shown in Fig. 8.2. (a) The anisotropy of the gyromagnetic tensor in $\text{Au}_{25}^0$ and $\text{Au}_{25}^+$ are compared, with the positively charged species showing a more isotropic g-tensor as a consequence of a smaller spin-orbit coupling and stress; (b) detail of panel (a) showing the variations of the g-tensor components of $\text{Au}_{25}^+$ as a function of temperature; (c) hyperfine tensor components of $\text{Au}_{25}^+$ as a function of temperature and (d) isotropic ($a_{1s}$), uniaxial ($b_{1u}$) and rhombohedral ($b_{Rh}$) hyperfine constants extracted from the $A$-tensor and related to the character (s-type, p-type, or d-type) of the single-occupied molecular orbital.
Conversely, two relevant differences appear when attempting to simulate the ESR powder spectra of Au$_{25}^+$ as summarized in Fig. 8.3(a) and (b). First, the gyromagnetic tensor is much less anisotropic in Au$_{25}^+$ than in Au$_{25}^0$, with $g_{s,x} \approx 2.06$, $g_{s,y} \approx 2.04$ and $g_{s,z} \approx 2.05$. Second, a significant anisotropic component of the hyperfine tensor is present in Eq. (8.4).

While the $g$-tensor values for Au$_{25}^+$ are closer to the free electron value, indicating a much weaker spin-orbit coupling and lower stress in positively charged Au$_{25}^+$ molecules, the anisotropy of the $A$ tensor requires additional discussion.

Specifically, from the three principal components of $A_{\text{AnIs}}$ ($A_x$, $A_y$ and $A_z$) the uniaxiality parameter, $b_{Un}$, and the rhombicity parameter, $c_{Rh}$, can be determined [22]:

$$b_{Un} = [A_x - (A_y + A_z)/2] / (3g\mu_B), \quad (8.8a)$$

$$c_{Rh} = (|A_y| - |A_z|) / (2g\mu_B). \quad (8.8b)$$

From the values of $A_x$, $A_y$ and $A_z$ summarized in Fig. 8.3(c), it can be easily calculated that $A_{Is}$ increases from 9.3 mT at -130$^\circ$C to 10.8 mT at room temperature, which is not dissimilar from $A_{Is} = 11.7$ mT, extracted from our ESR simulations for Au$_{25}^0$. Instead, while $b_{Un} = c_{Rh} = 0$ in Au$_{25}^0$, the $A$ tensor appear to be strongly biaxial in Au$_{25}^+$, with $b_{Un}$ decreasing from 0.60 mT to 0.45 mT and $c_{Rh}$ decreasing from 0.65 mT to 0.25 mT as the measurement temperature increases from -130$^\circ$C to room temperature. These data point to the fact that, while the $s$-type atomic component of the SOMO is comparable in Au$_{25}^0$ and Au$_{25}^+$, it tends to increase with temperature, which suggests a stronger isotropy and localization of the SOMO.

Since the theoretical uniaxial hyperfine parameter for nearest-neighbour $^{197}$Au nuclei is $b_0 = 1.88$ mT [22], the relatively high values of $b_{Un}$ determined in our simulations ($b_{Un} \sim b_0$) are also consistent with a relatively high $p$-type atomic component of the SOMO. The need to include the anisotropic components of the $A$ tensor in our simulations suggests that
the in-plane \( p \)-type atomic components, \( \Phi_p(x)(r) \) and \( \Phi_p(y)(r) \), represent a significant portion of the SOMO wavefunction, in addition to the \( d \)-type atomic components, \( \Phi_d(m)(r) \). The strong hybridization of the SOMO wavefunction suggests that a significant relaxation of the \( \text{Au}_{25}^+ \) molecule occur as a consequence of stress release, consistent with the lower stress indicated by the values of the \( g \)-tensor closer to the free electron value in this molecule. This is in excellent agreement with \textit{ab initio} calculations previously reported [26], which indicate a significant \( p \)-type and \( d \)-type components in the SOMO of \( \text{Au}_{25}^+ \). Previously it was also reported that the icosahedral metallic core experiences contraction with decreasing temperature [28], which would result in variations of \( A \), since the contraction would modify the hybridization of the SOMO, consistent with our findings.

8.1.5 \textit{Van Vleck} paramagnetic nature of \( \text{Au}_{25}^+ \)

The intensity of the ESR spectra for \( \text{Au}_{25}^+ \) (shown in Fig. 8.2(a)) are temperature independent. As discussed in subsection 2.4.3, temperature independent paramagnetism typically originates from two sources, extended electronic states (e.g., conduction electrons in a metal), or \textit{Van Vleck}-type paramagnetism, well documented in atomic and molecular structures with heavy orbital mixing [29]. The first type of temperature independent paramagnetism can be dismissed since extended states are not possible in a molecule with discrete electronic energy levels.

Typically \textit{Van Vleck} type paramagnetism is observable for atomic and molecular systems with a diamagnetic ground state in the lowest order of expansion in perturbation theory (see Fig. 8.4). As discussed in Subsection 2.4.1, we can treat the Zeeman energy
splitting, due to an external field as a perturbative correction to the electronic transition energies.

\[ E_1 - E_0 \gg \frac{k_B}{T} \]

**Ground State**

**1st Excited State**

![Diagram](image)

Fig. 8.4: A schematic representation of the HOMO and LUMO for Au\(_{25}^+\). The occupancy of the levels are illustrated for both the ground state and 1\(^{st}\) excited state by arrows representing electrons with spin projection defined by the direction of the arrows.

Using Eqs. (2.81) and (8.2) we can write down the correction to the ground state energy to 2\(^{nd}\) order as

\[
\Delta E_0 \approx \langle 0|H_Z|0 \rangle + \sum_n \frac{\langle 0|H_Z|n \rangle^2}{E_0 - E_n}. \tag{8.9}
\]

In the above expression, the first term is zero if the ground state of the system has a net zero total angular momentum. It has been suggested that although the HOMO of Au\(_{25}^0\) is nearly triply degenerate, the degeneracy is removed for Au\(_{25}^+\) [30], leading to the double occupancy of all filled orbitals (see Fig. 8.4), giving rise to a net zero spin angular momentum of the ground state. Indeed the temperature independent magnetic susceptibility for our sample suggests a significant lifting of the degeneracy. However, the excited state for the system has singly occupied orbitals leading to a net angular moment. Therefore, from the second term in
Eq. (8.9) we see that $H_Z$ acting on the excited states gives a nonzero contribution to the energy correction provided that there is significant mixing of the ground state and the excited states, as we will see shortly. Furthermore, from the electronic configuration we see that the ESR-active 1st excited state of the Au$_{25}^+$ must be a triplet state, and therefore the model discussed earlier for a $S = 1$ spin system is still valid. Dropping the first term in Eq. (8.9) and substituting the electronic contribution to the Zeeman Hamiltonian of Eq. (8.2), the correction to the ground state energy is

$$\Delta E_0 \approx \sum_n \frac{|\langle 0 | \mu_B \mathbf{B} \cdot \mathbf{g} \cdot \mathbf{s} | n \rangle|^2}{E_0 - E_n}. \tag{8.10}$$

For an external field pointing along the $z$-axis we get the simplified expression

$$\Delta E_0 \approx \sum_n \frac{|\langle 0 | \mu_B g_z S_z | n \rangle|^2 B^2}{E_0 - E_n}. \tag{8.11}$$

The magnetic dipole moment using Eq. (8.11) and the definition in Eq. (2.83), is

$$\mu \approx -\sum_n \frac{2B|\langle 0 | \mu_B g_z S_z | n \rangle|^2}{E_0 - E_n}. \tag{8.12}$$

Here we assume the 1st excited state ($n = 1$) term in Eq. (8.12) will dominate. The operator $S_z$ acting on the excited state gives the eigenvalue $\hbar m_s$. For the ESR-active 1st excited state, $m_s = -1,0,1$, and therefore the allow ESR transition corresponds to $\Delta m_s = 1$. The change in the dipole moment for a single molecule in an ESR measurement is

$$\Delta \mu \approx -\frac{4B\mu_B^2 g_z^2 \hbar^2 |\langle 0 | 1 \rangle|^2}{E_0 - E_1}, \tag{8.13}$$
where $|\langle 0 | 1 \rangle|^2$ is the wavefunction overlap between the ground state and the 1st excited state. A factor of 2 was introduce to account for the two possible transitions -1→0, and 0→1.

The total magnetization of $N \text{ Au}_{25}^+$ molecules is $M = \mu (N_2 - N_1)$, where $N_2 - N_1$ is the population difference between two adjacent Zeeman levels. The magnetization will be temperature independent if $E_0 - E_1 \gg k_B T$, since the molecules cannot be readily thermally excited and the entire population will reside in the ground state. This gives $M = \mu N$, and the magnetic susceptibility $\chi = M / B$ of system will be

$$\chi = -\frac{4 \mu^2 g^2 \hbar^2 |\langle 0 | 1 \rangle|^2}{E_0 - E_1} N. \quad (8.14)$$

From the ESR intensity we can find the magnitude of $\chi$, and knowing $N$ and $g_z$ and the energy difference between the ground state and 1st excited state for our system, we can find the orbital mixing $|\langle 0 | 1 \rangle|^2$ using Eq. (8.14).

There are two major consequence of this type of paramagnetism: first the magnetic susceptibility becomes temperature independent, second the magnitude of the spin density for $\text{Au}_{25}^+$ reduces according to Eq. (8.14), in comparison with a specimen exhibiting a paramagnetic ground state. Antonello et. al. [30] have reported $\text{Au}_{25}^+$ to be diamagnetic. The discrepancy between our results and theirs is likely due to the fact that none of their reported measurements were done in powder form. In fact, our results are reproducible and consistent with other characterizations of the sample reported in the literature.
8.1.6 Conclusions

In conclusion, our study demonstrates that Au$_{25}^+$ is paramagnetic. From our powder measurements, EPR-active states were demonstrated to be localized in the icosahedral core of Au$_{25}^n$ molecules with $n = 0$ and $n = +1$. In both Au$_{25}^+$ and Au$_{25}^0$, the singly-occupied molecular orbitals responsible for the EPR signal always show a relatively small ($< 10\%$) $s$-type atomic character and a more important $p$-type character. Two different types of signal were associated with neutral Au$_{25}^0$ molecules and positively charged Au$_{25}^+$ molecules, respectively. For neutral Au$_{25}$, our simulations of EPR powder spectra suggest that the gyromagnetic tensor ($\mathbf{g}$) is highly anisotropic, which may indicate a high amount of spin-orbit coupling and stress in this molecular cluster, while $\mathbf{g}$ is less anisotropic in its corresponding positively charged counterpart, which indicates a more relaxed structure via a distortion of the core. Analysis of the hyperfine tensor ($\mathbf{A}$) indicates that the in-plane $p$-type components and $d$-type components of the SOMO are stronger in Au$_{25}^+$, which points to a more distorted molecule in such cases, with the molecules tending to become more planar at increasing temperature. A temperature-independent magnetic susceptibility suggest a Van Vleck type paramagnetism for Au$_{25}^+$ in powder form.

8.2 Disorder and defect formation mechanisms in molecular-beam-epitaxy grown silicon epilayers

This section is based on a publication in collaboration with Jean-Marc Baribeau, Xiaohua Wu, and David J. Lockwood at the National Research Council of Canada (NRC). All sample fabrication and characterization were carried out by the group at NRC, except for
electron spin resonance (ESR) characterization. ESR measurements, data analysis, literature survey, and the writing of the manuscript was done by me with the assistance of Giovanni Fanchini.

8.2.1 Introduction

Silicon-based materials are at the forefront of the semiconductor industry. For many silicon device applications, including solar cells, light emitting diodes and thin film transistors, materials of the highest quality are required for minimizing the defect density and for tuning the electronic properties by introducing a controlled amount of impurities. There are a variety of techniques available for the deposition of silicon based thin films of high quality, including sputtering [31], chemical vapour deposition [32] and molecular beam epitaxy (MBE) [33]. MBE offers superior control over growth parameters, including the deposition rate and temperature of the substrate. It can be performed in ultrahigh vacuum and allows for growth precision of a single atomic layer. There is strong interest in growing electronic-grade silicon epilayers at lower temperatures. Low temperature growth of epitaxial films is more cost-effective and increases the interface abruptness and strain stability at the interface, and also prevents diffusion of dopants during growth. However, studies have shown that low-temperature MBE limits the maximum thickness for epitaxial growth [34, 35] and is likely to increase the impurities in the film.

Defect investigation is essential for determining the quality of thin films for electronic and solar cell applications. Point defects and grain boundaries decrease the electronic mobility in solids [36]. Paramagnetic defects, including vacancies and dangling bonds, may lead to electronic states close to the Fermi level and frequently act as traps for photogenerated carriers in light emitting diodes and solar cells. There are a number of
methods for characterizing defects in thin films. Transmission electron microscopy can be used to identify extended defects, but not the defect occupation number. A powerful technique for the detection of paramagnetic defects is electron spin resonance (ESR). ESR can quantify paramagnetic centres and unpaired spins at very low concentrations (which may act as charge traps [37] detrimental for carrier mobility photovoltaic processes [38]). ESR can also provide insight about the nature of such defects.

In this work, we present an ESR study of disordered silicon epilayers grown by MBE at different temperatures, which has been complemented by a suite of other characterization techniques, for gaining insight into the nature of paramagnetic defects and the mechanisms controlling their formation. These include cross-sectional transmission electron microscopy (TEM), grazing incidence X-ray diffraction (GI-XRD) and Raman spectroscopy. Emphasis has been placed on correlations between the range of order within the silicon network of films grown at different temperatures and the nature of paramagnetic defects. The relatively low degree of order at short range (i.e. at scales comparable to the Si\Si bond length) and medium range (i.e. at scales ~0.5–1 nm[39]) has also been investigated.

8.2.2 Experimental details

Silicon epilayers were deposited on SiO\textsubscript{2}/Si by MBE in the temperature range from 98 °C to 572 °C, as previously described [39, 40], and they were characterized by TEM, XRD, and Raman spectroscopy to assess their microstructure. <011> cross-section samples were prepared for TEM following standard procedures. The TEM samples were examined in (110) cross-sectional TEM using a Philips EM430 operated at 250 kV. Structural data were obtained by X-ray analysis carried out using a Bruker D8 Discover high resolution system
equipped with a 2.2 kW sealed Cu X-ray tube. For these measurements, a Goebel mirror in the primary optics produced a parallel beam of Cu Kα_{1,2} radiation collimated by a 0.2 mm divergence slit. For the secondary optics, a radial Soller slit was used in conjunction with a linear multi-point detector (Bruker's Vantec) enabling parallel detection over a scattering angle 2θ range of 10°. The various samples were analysed using the technique of grazing incidence X-ray diffraction. For these measurements, the angle of incidence α was fixed at 1° defining a penetration depth of about 1 µm into the Si matrix. The wafer polar angle in the plane of incidence was chosen away from any major symmetry direction to avoid spurious signal from substrate diffraction at low index planes. The Raman scattering measurements for these samples have been reported in detail earlier [39, 40].

Electron spin resonance (ESR) spectra have been recorded at a 100 kHz modulation frequency using a Jeol FA200 spectrometer equipped with an X-band microwave source (for a description of the ESR spectrometer refer to Chapter 3). A built-in Mn marker was used for estimating the spin density. The marker was calibrated by inserting a solution of (2,2,6,6-Tetramethylpiperidin-1-yl) oxyl (TEMPO) at a known spin concentration in the cavity. For each sample, ESR spectra with the marker at the same position has been recorded, which allowed for precise comparison of the total number of spins in different samples, with accuracies within ±5%. The spin densities have been subsequently determined from the size of the samples and their thicknesses with absolute uncertainties of 20% or less. In all ESR measurements the microwave power was kept well below the saturation limit of the signal. The modulation amplitude was kept below 30% of the signal linewidth, in order to prevent modulation artefacts. The g-values have been estimated using the hyperfine lines of the Mn marker. The ESR measurements have been carried out on e-Si wafers with low defect density. In order to rule out the contribution of the substrate and the native oxide layer to the
spin densities, additional measurements have been performed on bare SiO$_2$/c-Si substrates similar to those used for growing the samples.

8.2.3 Results and Discussion

**Cross sectional TEM and electron diffraction patterns**

Fig. 8.5(a)–(c) shows TEM cross-sectional images of Si films grown on SiO$_2$/c-Si substrates at growth temperatures (T) of 414 °C, 493 °C and 572 °C, respectively. The insets of the figures are the corresponding selected area diffraction (SAD) patterns for the films. Concentric rings in the inset of Fig. 8.5(a) are the signature of an isotropic diffraction pattern associated with the dominant amorphous phase in this film, corroborating the absence of preferentially oriented crystallographic planes shown in the TEM micrograph. This indicates that the films grown at 414 °C (and below) are overwhelmingly dominated by highly disordered or amorphous phases.

![TEM images and diffraction patterns](image)

**Fig. 8.5:** TEM cross-sections of silicon films grown on SiO$_2$/c-Si substrates at temperatures of: (a) 414°C, (b) 493°C and (c) 572°C. The insets show the associated selected area diffraction patterns.
From the SAD pattern in Fig. 8.5(b), (film grown at 493 °C) we observe that this film is polycrystalline. Concentric smeared rings, in combination with speckle-like features, are indicative of regions of the material in which a disordered silicon phase coexists with small crystals embedded in it. Fig. 8.5(b) shows that the cross sections of these samples present a number of dark regions with clearly visible crystallographic planes. Such regions are embedded in a lighter matrix, disordered in nature, which is not dissimilar from the sample shown in Fig. 8.5(a). The SAD speckles for the film grown at 572 °C (Fig. 8.5(c), inset) show electron diffraction spots that are even more pronounced than those in Fig. 8.5(b) for the 493 °C sample. The structure of such speckles indicates the formation of epitaxial crystallites. The corresponding TEM image shows dark columnar structures along the growth direction. A previous study [39] reporting on films grown directly on c-Si after etching away in-situ the 2 nm native SiO$_2$ layer, showed uniform epitaxial growth of a Si film up to ~75 nm in thickness at 335 °C without any columnar structures.

**High resolution TEM (HR-TEM)**

Panels (a)–(c) of Fig. 8.6 are HR-TEM images detailing the structure in the proximity of the substrates of the crystalline samples grown at 493 °C (panel a) and 572 °C (panels b and c). These HR-TEM micrographs indicate the existence of a variety of defects, which look different in the two samples. The interface of the 493 °C sample with its substrate has a similar appearance in most of the regions investigated and Fig. 8.6(a) is indicative of the defective morphologies found in this sample. Specifically, a number of polycrystalline inclusions can be observed in Fig. 8.6(a), with sharp grain boundaries at the interface with the amorphous silicon matrix. Grain boundaries are known to be a source of non-preferentially oriented paramagnetic centres in polycrystalline silicon [41].
Conversely, the morphology of the 572 °C sample is different in different regions at the sample-substrate interface. Two typical morphologies are shown in panels (b) and (c) of Fig. 8.6. Specifically, Fig. 8.6(b) shows the presence of a number of crystallites with different crystallite orientations, with grain boundaries at their interfaces. Fig. 8.6(c) shows a number of stacking faults preferentially oriented parallel to the substrate. Grain boundaries between crystals [42] and stacking faults [43] can both be sources of paramagnetic centres. The differences between defects that can be noticed in panels (b) and (c) of Fig. 8.6 may lead to ESR spectra of a very different nature. Unpaired spins associated with stacking faults preferentially oriented parallel to the substrate (panel c) will generate macroscopically anisotropic crystal-type ESR spectra, with an ESR signal depending on the angle of orientation of the substrate with respect to the external field. In contrast, unpaired spins associated with grain boundaries with random orientation (as in panels a and b) will generate powder-type ESR spectra, with local anisotropy in the fine and hyperfine constants (due to
the planar nature of grain boundaries) but no dependence of the ESR signal on the angle of orientation of the sample with respect to the external magnetic field. Therefore, an investigation of the angular dependence of the ESR signal is vital to understand whether stacking faults or grain boundaries are dominant in producing dangling bonds in the 572 °C sample.

*Grazing incidence X-ray diffraction (GI-XRD) patterns*

Fig. 8.7 shows a set of GI-XRD patterns for the films prepared at the higher growth temperatures on SiO$_2$/c-Si substrates. The red bottom trace in the figure is for a reference c-Si (001) wafer with a native oxide layer. The broad peaks at 50° and 80° are typically observed for oxidized Si (001) [44]. At the lower growth temperatures two such broad peaks are seen, but, in addition, a peak at 28° appears, which indicates that regions with (111) planes start to

![Grazing angle X-ray diffraction patterns for films prepared at higher growth temperatures on SiO$_2$/c-Si substrates.](image)

Fig. 8.7: Grazing angle X-ray diffraction patterns for films prepared at higher growth temperatures on SiO$_2$/c-Si substrates.
form parallel to the substrate [45]. At the highest temperatures, additional peaks appear at 47°, 56°, 69°, 76°, and 88° indicating the formation of polycrystalline Si inclusions. The peak intensity ratios are close to those of powder spectra, indicating no preferential direction of the crystallites. We performed a Williamson–Hall (W–H) analysis [46] of the GI-XRD peaks for the various polycrystalline and epitaxial films in order to infer more specific information about the size of the crystallites (which may offer critical insight on the density of grain boundaries in the samples) and the level of strain affecting the films (which may provide information about the different degrees of bond angle distortions in different samples, governing the formation of dangling bonds). In a W–H analysis, two equations relate the position ($\theta_i$) and the full width at half maximum($\Gamma_i$) of $i$-th XRD peak to the volume-weighted crystallite size ($L_0$) and the average strain ($\varepsilon_{str}$) in a thin film:

$$\frac{\pi}{2} \frac{\Gamma_i}{\Gamma_i} = \varepsilon_{sx} \tan(2\theta_i)$$

$$\frac{\pi}{2} \frac{\Gamma_i L_0}{\Gamma_i} \cos(2\theta_i) = k\lambda,$$

where $\lambda$ is the wavelength of the incident X-rays, and $k$ is the Scherrer constant, usually assumed to be $k \approx 1$ [47]. Combining Eqs. (8.15a) and (8.15b) we obtain

$$\frac{\pi}{2} \frac{\Gamma_i \cos(2\theta_i)}{L_0} = \frac{\lambda}{L_0} + 4\varepsilon_{sx} \sin(2\theta_i).$$

In a W–H analysis, $\Gamma_i \cos(2\theta_i)$ is plotted as a function of $4 \sin(2\theta_i)$. The points are then fitted to a straight line so that the parameters $L_0$ and $\varepsilon_{str}$ can be extracted from the intercept and the slope, respectively. In order to create the W–H plots for our samples, the XRD peaks $y_i$ (28°, 47°, 56°, 69°, 76° and 88°) were fitted using Lorentzian line shapes

$$y_i = \frac{A_i}{2\pi} \frac{\Gamma_i}{(\theta - \theta_i)^2 + \left(\frac{\Gamma_i}{2}\right)^2},$$
which allowed us to extract the peak amplitudes $A_i$ as well as $\theta_i$ and $\Gamma_i$ and the uncertainties in determining these parameters. The quality of our W–H plots for samples grown at 493 °C and 572 °C can be seen in Fig. 8.8(a) and (b), respectively. Although the uncertainties of the calculated parameters are quite high (up to 30%) due to the composite nature of our samples, relative uncertainties are a lot less significant. Negative slopes in the W–H plots signify negative values for $\varepsilon_{\text{str}}$, indicating that the crystallites are under compressive stress, as typical for constrained, tetrahedral silicon lattices [48]. $\varepsilon_{\text{str}}$ and $L_0$ for our films grown on fused silica [49], pre-etched c-Si [39, 40], and non-etched c-Si coated with native oxide (SiO$_2$/c-Si), are reported in Fig. 8.9(a) and (b), respectively. No data are reported for films grown on SiO$_2$/c-Si at temperatures below 493 °C, because a crystallite size could not be defined for these amorphous films.

![Williamson-Hall plots for samples grown at 493 °C and 572 °C. Negative slope of the lines indicate that the films are under compressive stress.](image)

Fig. 8.8: Williamson-Hall plots for samples grown at 493 °C and 572 °C. Negative slope of the lines indicate that the films are under compressive stress.
From Fig. 8.9(a) it is apparent that the crystallite size $L_0$ increases with increasing temperature, as expected. Also, the magnitude for $L_0$ corresponds well with the sizes of crystallites detected by HR-TEM. More importantly, $\varepsilon_{str}$ can give vital information about the nature of defects in our samples. It is well known that the formation of dangling bonds is favoured in the presence of stress and bond angle distortions [50]. It is seen that the internal stress in our films strongly decreases with growth temperature, which is the driving force both for formation of crystallites and for stress release. Interestingly, from Fig. 8.9(b), we also note that the substrate on which the epitaxial films are grown affects to a certain extent both crystallite size and stress. This is evident in Fig. 8.9(a) and (b) where we see some difference in both $\varepsilon_{str}$ and $L_0$ for films grown at the same temperature on different substrates.

In succeeding sections we focus on the relation of stress and crystallite size to the order parameters in the samples that were examined using Raman spectroscopy, and eventually we will correlate the crystallite size, stress and degree of disorder with the ESR data.
Raman spectroscopy

Results obtained by Raman spectroscopy on our samples have been discussed in detail by Tay et al. [39] and Baribeau et al. [40]. Therefore, only the major results are recalled here, in order to better correlate our data with the stress level and the nature and type of defects in our samples. Two specific Raman features are of interest in the films: i) the transverse optical (TO) phonon mode at ~475 cm\(^{-1}\) and ii) the transverse acoustic (TA) phonon mode at ~150 cm\(^{-1}\), which is forbidden by selection rules in a perfect Si crystal. The TO band corresponds to the phonon density of states (P-DOS) associated with stretching vibrations of nearest neighbour (NN) silicon atoms and is Raman active even in the absence of disorder. The P-DOS associated with this mode and the related Raman linewidth \(\Gamma_{TO}\), are expected to be broadened by the lack of short-range order, since the frequency of vibration of this mode reflects the Si-Si bond states within the sample. For a microcrystalline structure, with little bond length and bond angle variation, we expect a relatively sharp TO peak, while a significantly broadened peak is expected from an amorphous network [51]. Conversely, the transverse acoustic (TA) band corresponds to collective vibrations that extend well beyond the NN atoms. Acoustic branches of the P-DOS cannot be Raman-active in tetrahedral symmetry [52]. Thus, the intensity of the TA band reflects the relaxation of selection rules as a consequence of a decrease in the medium-range order. Therefore, the intensity ratio \(I_{TA}/I_{TO}\) of the two peaks is used as the appropriate Raman parameter for quantifying the absence of order at medium range.

\(\Gamma_{TO}\) and the \(I_{TA}/I_{TO}\) ratio [39] as functions of stress are shown in Fig. 8.10. It is well known that internal stress in over-constrained, tetrahedral networks of Si atoms give rise to bond-angle distortions [52]. Thus, a correlation between the internal stress in our samples and the Raman disorder parameters, \(\Gamma_{TO}\), and \(I_{TA}/I_{TO}\), may be expected. From Fig. 8.10(a), it
can be inferred that the internal level of strain in our networks correlates very well with $I_{\text{TA}}/I_{\text{TO}}$, as expected. Additionally, we can observe that such a trend exhibits an asymptotic behaviour for both the smallest and the largest values of $I_{\text{TA}}/I_{\text{TO}}$, which correspond to the highest and lowest growth temperature of our samples, respectively. Therefore the maximum and minimum levels of strain can be extrapolated from this trend. The maximum degree of strain ($-2.3\%$) can be associated with the amorphous phase of the Si network, while the minimum level ($-0.6\%$) is observed in the most crystalline epilayers. Interestingly, by comparing Fig. 8.10(a) and (b), we find that a better correlation exists between $\varepsilon_{\text{str}}$ and the medium-range order parameter $I_{\text{TA}}/I_{\text{TO}}$, rather than with the short-range order parameter $\Gamma_{\text{TO}}$. This may be due to the fact that the stress level within our samples is mitigated by averaging the bond angle distortions at medium range.

![Graph](image)

**Fig. 8.10:** Raman parameters as a function of stress representing (a) medium range disorder ($I_{\text{TA}}/I_{\text{TO}}$) (b) short range disorder ($\Gamma_{\text{TO}}$).

**Electron spin resonance (ESR)**

Typical ESR spectra for films grown at low, intermediate and high temperatures are shown in Fig. 8.11(a) and (b). The spectra recorded for samples with the lowest growth
temperatures exhibit a featureless line typical of amorphous silicon with $g=2.0059\pm0.0002$. The spin density of the various films as a function of growth temperature is shown in Fig. 8.12, where the ESR peak-to-peak linewidths are also shown. It is apparent that, when the films are amorphous in nature, a significantly higher spin density is present. The spin density decreases with increasing growth temperatures where the amount of amorphous phase also diminishes substantially. However, even at the highest growth temperatures, the concentration of spins is still higher than in hydrogenated amorphous silicon (a-Si:H) used for electronic and solar applications, where spin densities can be as low as $10^{15}–10^{16}$ cm$^{-3}$ [53]. Generally, the spin concentration is low in a-Si:H for hydrogen contents of 10–15 at. %, corresponding to the optimal passivation of dangling bonds [54]. Deviation of the H content from this optimal value may give rise to a much higher spin density. For our films the hydrogen content is never higher than 4 at.% [40].

Fig. 8.11: (a) ESR spectra (b) g-anisotropy shown for the 572°C sample. (*) represents signals from a Mn reference marker.
Although, disorder and amorphization seem to represent the most important driving forces for the stabilization of defects in our samples in the form of dangling bonds, other mechanisms of defect formation must be invoked in order to justify the presence of considerable amounts of unpaired spins for the films grown at the highest temperatures. In order to elucidate such mechanisms, we investigated the correlation between the spin density, HR-TEM images and indicators of disorder in our samples, including the Raman TO phonon line width and the $I_{TA}/I_{TO}$ ratio.

Fig. 8.13 gives the correlation between spin density and Raman parameters. Specifically, Fig. 8.13(a) shows that a direct correlation exists between the spin density and the width of the Raman TO mode [39] for most of the samples. This correlation is stronger for samples grown at the highest temperatures, above 335 °C, and may indicate that the main driving force for the formation of paramagnetic centres in polycrystalline and epitaxial phases is the lack of short range order and bond angle distortions in strongly localized regions of the samples, including grain boundaries, stacking faults and interfaces between crystallites. Conversely, in the amorphous phases of silicon that are dominant in our samples...
grown at the lowest temperatures, it is well known that most ESR-active defects are dangling bonds \[55\] associated with three-fold coordinated Si sites. Dangling bonds are the consequence of a number of relatively Si\Si bond distortions that affect the order of the amorphous lattice at medium and long range. These findings are consistent with the fact that, at least in the samples grown at the lowest temperatures, a linear correlation exists between the spin density and the Raman I\textsubscript{TA}/I\textsubscript{TO} ratio, as shown in Fig. 8.13(b), which is a measure of intermediate range order. Interestingly, the I\textsubscript{TA}/I\textsubscript{TO} ratio was also shown to correlate well with stress, as in Fig. 8.10(b). Therefore our findings are consistent with the fact that defects typically form in the bulk of materials to reduce high levels of local stress, confirming earlier work \[56\].

![Graph](image)

Fig. 8.13: Spin density as a function of Raman indicators of: short range order, \(\Gamma\text{TO}\) (b) medium range order, \(I\text{TA}/I\text{TO}\).

In addition, our model of defect formation is corroborated by our HR-TEM images as shown in Fig. 8.6. Since paramagnetic defects in heteroepitaxial and microcrystalline phases can form at grain boundaries between different crystallites, or at the interfaces of crystallite and the amorphous phase, a possible source of paramagnetic centres in these samples may be
at the surfaces of small crystallites where the high degree of curvature may cause the formation of imperfections in the surface or interface reconstruction, and defects. Our HR-TEM images have shown a number of possible defects of this type and, specifically, for intermediate growth temperatures (i.e., 493 °C) where a sizeable amount of crystallites coexist with a still large amount of the amorphous phase. For the sample grown at the highest temperature (572 °C) the defects elucidated by HR-TEM are of a different nature. There are several distinct defect features in this sample, including interfaces between randomly oriented crystallites, as shown in Fig. 8.6(b), and stacking faults arranged normally to the substrate in the epitaxial phase of this film (Fig. 8.6(c)).

In the last case, the paramagnetic defects embedded in these stacking faults exhibit a preferential orientation with respect to the film plane. If a significant fraction of the observed spins are associated with oriented stacking faults, we expect an anisotropic crystal-type ESR spectrum that depends on the film orientation to the external magnetic field B. Conversely, a powder-like spectrum, independent of the orientation of the sample with B, is expected if the ESR signal is mainly due to defects located at the interfaces between randomly oriented crystallites. This is because the random orientation of the interfaces between crystallites will average the features of anisotropic ESR spectra in a polycrystalline phase. In order to identify the major contribution of paramagnetic defects in this sample, we investigated the dependence of the ESR signal on the orientation of the films grown at 493 °C and 572 °C with respect to B. In Fig. 8.11(b), it can be seen that, for the 572 °C sample, the ESR spectrum and the gyro-magnetic ratio (g) depends on the relative orientation θ of a film with respect to the external magnetic field B, with \( g_\parallel = 2.0058 \pm 0.0002 \) for \( \theta = 90^\circ \) and \( g_\perp = 2.0028 \pm 0.0002 \) for \( \theta = 0^\circ \). A similar dependence could not be observed for the 493 °C film where the g-value is isotropic and \( g \approx 2.0059 \). Thus, we assign the paramagnetic centres in the 572 °C film
to defects in preferentially oriented stacking faults consistent with the HR-TEM in Fig. 8.6(c) (and not to randomly oriented grain boundaries as in Fig. 8.6(b)) and the paramagnetic centres in the 493 °C film to defects on randomly oriented grain boundaries and interfaces between crystallites, consistently with the HR-TEM image in Fig. 8.6(a).

Another ESR parameter that can be used to extract additional information about the nature of the interaction between spins is the ESR spectral linewidth. Using a statistical approach, Abragham [57] inferred that, in the case of dipolar broadening in magnetically diluted spin systems, the ESR line would be Lorentzian, with a line width given by

$$\Delta B_{1/2} = \frac{4\pi^2}{3\sqrt{3}} q\mu_B N_S,$$  \hspace{1cm} (8.18)

where $N_S$ is the spin density. From Eq. (8.18) a linear relation between $\Delta B_{1/2}$ and $N_S$ is expected. This behaviour is not observed for our samples, as shown in Fig. 8.12(b). In particular, the line width associated with the samples that are amorphous is independent of the spin density. An increase in $\Delta B_{1/2}$ is only observed for the two samples grown at the highest temperatures, which may be due to dipolar broadening in spin-rich regions in connection with grain boundaries and stacking faults, consistent with Eq. (8.18).

### 8.2.4 Conclusions

In conclusion, we have demonstrated that TEM, XRD, Raman and ESR offer complementary information on the nature of defects in disordered silicon epilayers, as well as on the mechanisms governing the amounts in which such defects are formed. Specifically, we have demonstrated that samples grown at the lowest temperature possess a considerable amount of disordered phase, which leads to significant concentrations of dangling bonds, consistent with what is observed in non-hydrogenated and hydrogenated amorphous silicon.
In addition, using HR-TEM, we were able to identify significant amounts of randomly oriented defects at the grain boundaries in samples grown at intermediate temperatures (493 °C) as well as the presence of stacking faults aligned to the substrate in the sample grown at the highest temperature (572 °C), which lead to preferentially oriented paramagnetic centres. Lack of order at the medium range and stress are driving mechanisms for the formation of defects in the disordered samples grown at the lowest temperatures, while the defect density in the samples grown at the highest temperatures better correlates with Raman parameters indicating a relatively low degree of order at short range.

References

(2002).


CHAPTER 9

Conclusions

In this thesis we studied defect-related electronic and magnetic properties of graphene-based materials using a combination of experimental investigations and theoretical modelling. The class of defects we investigated were suitable for a tight-binding description for our systems. The magnetic nature of graphene structures were examined experimentally using electron spin resonance (ESR). Additional materials were also examined using ESR to illustrate the broad applicability of this technique.

In Chapter 4 we looked at weak paramagnetism related to chemically exfoliated graphene nanoribbon (GNR) thin films. By varying the oxidation temperature during the fabrication process we were able to produce ribbons of various lengths, and relatively constant widths. ESR investigation showed variations of paramagnetism for GNRs depending on their length (or length-to-width aspect ratio). It was deduced from the theoretical analysis that long ribbons exhibit paramagnetic defects that are localized, assigned to vacancies, while shorter ribbons exhibit paramagnetism related to extended states, assigned to zigzag edges. At high oxidation temperatures the ribbon features were absent in our samples and the magnetic character of such samples were Curie-type, assigned to amorphous carbon clusters.

One of the possible extensions for the work presented in Chapter 4 is to investigate paramagnetism related to narrower ribbons (~10 nm or less) to see how electron correlation effects may modify our earlier findings. Electronic band gaps for the narrow ribbon structures may cause paramagnetism associated with extended states to be absent. Narrow
GNRs can be produced by unzipping single-walled carbon nanotubes. It would also be interesting to see if the fabrication technique has any influence on the paramagnetic nature of GNRs. Apart from the oxidation method used for the preparation of our GNRs, there are a host of other methods available for creating GNRs (see discussion in Chapter 4).

In Chapter 5 we investigated the role of copper nanoparticles assembled on the surface of graphene thin films, and their influence on the electron properties of graphene. It was found that the work function of individual Cu nanoparticles (Cu-NPs) absorbed on graphene depends on the diameter of the Cu-NPs, based on a classical description of image charges for conductors. Using a modified tight-binding model we incorporated the influence of Cu-NPs on graphene by altering the tight-binding parameters for sites in contact with Cu-NPs. This model was used to deduce the influence of particle distribution on the electron band and work function of graphene. It was shown that, for the small variation in work function induced by the Cu-NPs on graphene, particle distribution affects the work function minimally. Also, it was shown that particles assembled on graphene break the electron-hole symmetry of the electronic band, due to the variation of local work function caused by the presence of the particle. Typically this is not the case for a uniform thin film of Cu, which would modify the work function of graphene uniformly.

Some possible extension may include making graphene thin films with smaller average graphene flake sizes to see move clearly the influence of edge states. We would expect that the shifts in the work function of graphene to influence population of the edge states since these states are close to Fermi surface. Other possible extensions may include etching the Cu-NPs and making holes in graphene. We have already illustrated that Cu-NPs
can be used to etch graphene. The magnetic properties of these hole may give rise to interesting properties.

In Chapter 6 we obtained the $\pi$-electron two-point Green's functions for a semi-infinite graphene nanoribbon using a analytical tridiagonal matrix inversion method. These Green's functions were then explicitly written to obtain the properties of all excitation modes supported by the structure, which include: modified bulk modes, the zero modes (associated with the geometry of zigzag edges), and the edge modes related to edge hopping perturbations. Some implications of the finite-width effects for GNRs were also investigated in terms of modification arising from the inverse matrix element. An immediate extension of the work presented in Chapter 6 would be to obtain the two-point Green's functions for the finite GNR, including edges modes related to both edges. It would be interesting to investigate the coupling between edge modes (leading to edge correlation effects) in greater detail.

In Chapter 7 we investigated the role of zigzag edges on the RKKY interaction between two magnetic impurities in graphene nanoribbons. We place the two impurities at the edge of a semi-infinite ribbon and calculated the RKKY contribution from the bulk and edge modes related to edge perturbation. We also and gave some qualitative account of the role of zero modes. We noted that RKKY contribution for the zero modes are mathematically undefined in the semi-infinite ribbon case but still contribute by perturbing the spectral weights of the bulk-like modes in the RKKY interaction. Some additional discussions were also given related to the interaction between a spin at an edge and one at an interior site.

An immediate extension of this work would be to investigate the form of the RKKY interaction for other impurity spin locations. The possible arrangements for placing the two
spins on the GNR structure are varied and will likely lead to interesting differences. For instance it would be interesting to see how the two spins with their vector separation along a zigzag line may be different from the two spins placed along an armchair line, near an edge. For an infinite graphene sheet the difference are known to be profound. Another important extension would be to find explicit RKKY contribution for a finite GNR.

In the first section of Chapter 8 we looked at the magnetic character of \( \text{Au}_{25}^{+} \), and compared it to the other charge states of the \( \text{Au}_{25} \) molecular cluster. From simulations based on a spin Hamiltonian we found that \( \text{Au}_{25}^{+} \) has anisotropic \( g \) and hyperfine tensors. The \( g \) anisotropy is less significant for the \( \text{Au}_{25}^{+} \) in comparison with \( \text{Au}_{25}^{0} \). From our simulation we were able to estimate the orbital mixing of the singly occupied molecular orbital. We also noted a temperature-independent magnetic susceptibility attributed to Van Vleck-type paramagnetism. An immediate extension would be to carry out a detailed analysis of the Van Vleck nature of \( \text{Au}_{25}^{+} \), by making accurate measurement of the magnitude for the susceptibility in order to deduce experimentally the orbital mixing between the HOMO and LUMO states.

In the second section of Chapter 8 we examined various defects produces in molecular-beam-epitaxy grown silicon epilayers and the mechanisms responsible for their formation. For films grown at the lowest temperatures the samples were highly amorphous, producing an isotropic ESR lineshape profile which was assigned to randomly oriented dangling bonds in the amorphous phase. At higher growth temperatures crystallite structures formed in the samples. The crystallites were of several types, including polycrystalline inclusions, randomly orientated crystallites, and stacking faults defects preferentially oriented parallel to the substrate. The anisotropy of these paramagnetic defects were related to the
lineshape profiles of the corresponding ESR spectra. The average strain of the films were deduced from XRD spectra and correlated to the medium range disorder in the films extrapolated from Raman spectroscopy. We saw good correlation between the paramagnetic spin density as measured by ESR and the disorder in our samples as measured by Raman. A extension of this work would involve exposing the films to high intensity light to see if the nature and concentration of defects can be modified as in the Staebler-Wronski effect.
Appendix A

Magnetic Interaction and Relaxation Times

In the discussion of paramagnetism in Chapter 2 we focused entirely on non-interacting paramagnetic centers, apart from interactions involving paramagnetic centers and nearby nuclei (i.e., the hyperfine effect). Now we will consider what happens when interactions between paramagnetic centers are taken into account. For paramagnetism we ignore strong magnetic effects leading to magnetic ordering and spontaneous magnetization (i.e., we exclude ferro-, antiferro- and ferri-magnetic effects). The type and nature of magnetic interactions in different media under different circumstances are diverse. However, the consequence of such interactions is typically reflected in the absorption profile in magnetic resonant experiments, and its dependence on measurement conditions, such as temperature and excitation field intensity. Here we give an account of the Bloch model [1, 2]. In this model interactions are taken into account through the introduction of phenomenological macroscopic relaxation rates, while ignoring the origin of these damping effects. Later we discuss different interaction phenomena and their effect on the absorption profile.

Using the torque equation we can relate the time rate of change of the bulk magnetization $\mathbf{M}$ to the external applied field $\mathbf{B}$ by

$$\frac{d\mathbf{M}}{dt} = \gamma \mathbf{M} \times \mathbf{B}, \quad (A.1)$$
where $\gamma_e$ is the electron gyromagnetic ratio. Typically, in magnetic resonance experiments a sample is placed in a variable static field $\vec{B}_s$ in order to produce the Zeeman splitting and a second (oscillating) $\vec{B}_o$ field is introduced transverse to the static field in order to induce transitions between the Zeeman levels. Including both field components and with the static field along the $z$-axis we have

$$\vec{B} = B_x \cos(\omega t) \hat{x} + B_y \sin(\omega t) \hat{y} + B_z \hat{z}, \quad (A.2)$$

where $\omega$ is the oscillation angular frequency of the excitation field. First, suppose we ignore the transverse field. According to Eq. (A.1) the magnetization will precess about the $z$-axis, with the components of $\vec{M}$ given by $M_z = M_0$, $M_x = M_0^0 \cos(\omega_B t)$, and $M_y = M_0^0 \sin(\omega_B t)$, where $\omega_B = -\gamma_e B_s$ is the classical Larmor frequency [1-3], and $M_0^0$ is the component of the magnetization perpendicular to the static field. The time average magnetization along the $x$ and $y$-axes is zero. If the magnetization is not in thermal equilibrium (e.g., the static field is suddenly changed in magnitude and/or orientation) then the magnetization will relax to a new equilibrium value at a rate defined by the relaxation times $\tau_1$ and $\tau_2$ introduced phenomenologically. Here we define two distinct relaxation times for the magnetization parallel to the static field ($\tau_1$) and transverse to the field ($\tau_2$). We note that a change in $M_z$ corresponds to a change in the magnetic potential energy $U = -\vec{M} \cdot \vec{B}_s$, so energy must flow between the spin system and the environment. In this respect the relaxation time $\tau_1$ associated with the magnetization component parallel to the static field is called the spin-lattice relaxation time. On the other hand since the time average of $M_x$ and $M_y$ is zero no energy needs to flow out of the spin system during relaxation for these components [3]. The
relaxation time associated with these transverse components is a measure of the time during which the individual moments that contribute to $M_x$ and $M_y$ remain in phase with each other, thus $\tau_2$ is referred to as the spin-spin relaxation time since it corresponds to the phase coupling between spins.

Using the defined relaxation times we introduce damping terms of the form[1, 2]

$$
\frac{dM_x}{dt} = -\frac{M_x}{\tau_2},
$$
$$
\frac{dM_y}{dt} = -\frac{M_y}{\tau_2},
$$
$$
\frac{dM_z}{dt} = \frac{M_0 - M_z}{\tau_1}.
$$

(A.3)

We now return to the case where the excitation field is also present. Since $\vec{M}$ is continuously precessing about $B_z\hat{z}$ we may transform to a rotating reference frame about the $z$-axis at excitation frequency $\omega$ and in the same sense as $\vec{B}_x$. The components of Eq. (A.1) in the rotating reference frame and with damping terms included as in Eq. (A.3) are [1, 2]

$$
\frac{dM_{x\phi}}{dt} = (\omega - \omega_B)M_{y\phi} - \frac{M_{x\phi}}{\tau_2}
$$
$$
\frac{dM_{y\phi}}{dt} = -(\omega - \omega_B)M_{x\phi} + \gamma B_\phi M_z - \frac{M_{x\phi}}{\tau_2}
$$
$$
\frac{dM_z}{dt} = -\gamma B_\phi M_{y\phi} - \frac{M_z - M_z^0}{\tau_1}.
$$

(A.4)

The solutions to the set of coupled linear differential equations can be shown to give
The effects of the oscillating excitation field are often described in terms of dynamical susceptibilities defined by [W1, C2]

\[
M_{x\phi} = -M_z^0 \frac{\gamma_e B_o (\omega_B - \omega) \tau_2^2}{1 + (\omega_B - \omega)^2 \tau_2^2 + \gamma_e^2 B_o^2 \tau_1 \tau_2}
\]

\[
M_{y\phi} = M_z^0 \frac{\gamma_e B_o \tau_2}{1 + (\omega_B - \omega)^2 \tau_2^2 + \gamma_e^2 B_o^2 \tau_1 \tau_2}
\]

\[
M_{z\phi} = M_z^0 \frac{1 + (\omega_B - \omega) \tau_2^2}{1 + (\omega_B - \omega)^2 \tau_2^2 + \gamma_e^2 B_o^2 \tau_1 \tau_2}.
\] (A.5)

The dynamical susceptibilities \( \chi' \) and \( \chi'' \) have physical meanings, representing dispersion and power absorption of the magnetic resonance transition, respectively. It can be shown that the power absorbed by a magnetic system from a linearly polarized excitation field \( B_o \) is given by [1]

\[
P(\omega) = \frac{\omega \chi'' B_o^2}{\mu_0 V}.
\] (A.8)
\[ \Gamma = \left( 1 + \gamma_e^2 B_o^2 \tau_1 \tau_2 \right)^{1/2} / \tau_2. \]  

(A.9)

Note that the linewidth \( \Gamma \) of the absorption profile depends on the relaxations times \( \tau_1 \) and \( \tau_2 \), and on the amplitude of the excitation field. Therefore, one can extract information about the relaxation times using the absorption profile.

We now discuss the mechanisms responsible for the spin-lattice relaxation rates and some of their properties. For the case where spins are imbedded in an insulating material, energy dissipation can take place via phonon scattering [3]. There are three different processes involving phonons with distinct temperature dependence. In a direct process a spin makes a transition from a higher to a lower spin state by emitting a phonon. In the direct process the inverse of the spin-lattice relaxation time \((1/\tau)\) is proportional to temperature \((T)\). In the Raman process a phonon scatters from a spin center inducing a transition between spin states, where the energy between the spin state is imparted to the incident phonon. The spin-lattice relaxation time associated with the Raman process as dependence \(1/\tau \propto T^7\) or \(T^9\). In the Orbach process a two state spin transition is involved, where a phonon induces a transition from an intermediate state to a higher state and the spin relaxes to a lower state by emitting a phonon. For Orbach processes \(1/\tau \propto \exp\left(-\Delta/k_B T\right)\), where \(\Delta\) is the incident phonon energy. For the case of metals energy can be dissipated through the scattering of free electrons. A measurement of spin-lattice relaxation time at various temperatures can help deduce the form of scattering involved.

Spin-spin interaction can originate from many sources, including, magnetic dipole-dipole interactions [3], exchange interactions [5], and Ruderman-Kittel-Kasuya-Yosida (RKKY) type interactions [5]. The last of these is the subject of Chapter 7. Spin-spin and
spin-lattice interactions, and other dynamical processes can lead to lineshape effects in the absorption profile of magnetic resonance experiments, including dipole broadening [2], hyperfine broadening [1], exchange narrowing [6], motional narrowing [1], and Dysonian lineshape effect [7].

References


APPENDIX B

Tight-binding matrix Hamiltonian for graphene nanoribbons

Here we formulate the matrix Hamiltonians for zigzag graphene nanoribbon (GNR) structures as required for calculations in Section 4.4. Similar matrices can also be obtained for armchair ribbons (not shown here). The matrices formulated here can be applied to GNRs of any dimensions and can also be extend to a square graphene flake. The matrix Hamiltonian of Eq. (2.48) can be writing as

\[
H = \begin{bmatrix}
    c_1^+ & c_2^+ & c_3^+ & \ldots \\
    e_1 & t_{1,2} & t_{1,3} & \ldots \\
    t_{2,1} & e_2 & t_{2,3} & \ldots \\
    \vdots & \vdots & \vdots & \ddots
\end{bmatrix} \begin{bmatrix}
    c_1 \\
    c_2 \\
    c_3 \\
    \vdots
\end{bmatrix},
\]

where we have dropped the spin projection label \( \sigma \), and for generality the diagonal matrix elements \( \epsilon \) are allowed to be different for each lattice site. Maintaining unique labels \( \epsilon \) in Eq. (B.1) allows us to modify the onsite ionization energy (or local work function) of the graphene structure.

Zigzag graphene nanoribbons

In order to specify the matrix Hamiltonian in Eq. (B.1) we must define the dimensionally on the ribbons. The convention we use for defining the length and widths of zigzag GNRs is shown Fig. B.1, along with the numbering scheme for sites. Based on the labels of the carbon atoms we can identify the nearest neighbours for each carbon atom, and this allows us to form a matrix. There are two classes of matrices, one for zigzag GNRs with
Fig. B.1: Structural configuration for zigzag ribbons and the number scheme of carbon sites for a series of ribbon dimensions. \( W \) and \( L \) refer to the number of rings along the width and length, respectively. An odd number of rings along the width \((W = \text{odd})\), one for even number of rings \((W = \text{even})\).

These matrices can be written in terms of submatrices. For a zigzag graphene nanoribbon with dimensions \( W \times L \), the main matrix has dimensions of \((2L+2) \times (2L+2)\), while the submatrices each have dimensions of \((W+1) \times (W+1)\). The main matrices are given by...
\[
\begin{bmatrix}
A_1 & B_1 & 0 & 0 & 0 & \cdots & 0 \\
B_1 & A_2^{W+2} & B_2 & 0 & 0 & \cdots & 0 \\
0 & B_2 & A_3^{2W+3} & B_2 & 0 & \cdots & 0 \\
0 & 0 & B_2 & A_4^{3W+4} & B_2 & \cdots & 0 \\
0 & 0 & 0 & B_2 & A_5^{4W+5} & \cdots & 0 \\
\vdots & \vdots & \vdots & \vdots & \vdots & \ddots & \ddots \\
0 & 0 & 0 & 0 & 0 & 0 & B_3 \\
\end{bmatrix}
\]

\[
A_4^{1+(W+1)(2L+1)}
\]

\[
\begin{bmatrix}
A_5 & B_2 & 0 & 0 & 0 & \cdots & 0 \\
B_2 & A_6^{W+2} & B_2 & 0 & 0 & \cdots & 0 \\
0 & B_2 & A_5^{2W+3} & B_2 & 0 & \cdots & 0 \\
0 & 0 & B_2 & A_6^{3W+4} & B_2 & \cdots & 0 \\
0 & 0 & 0 & B_2 & A_5^{4W+5} & \cdots & 0 \\
\vdots & \vdots & \vdots & \vdots & \vdots & \ddots & \ddots \\
0 & 0 & 0 & 0 & 0 & 0 & B_4 \\
\end{bmatrix}
\]

\[
A_7^{1+(W+1)(2L+1)}
\]

and the submatrices $A_1$, $A_2$, $A_3$, $A_4$, $A_5$, $A_6$, $A_7$, $B_1$, $B_2$, $B_3$ and $B_4$ given by

\[
A_i^p = \begin{bmatrix}
\nu & 0 & 0 & 0 & 0 & \cdots & 0 \\
0 & \epsilon_{p+1} & t & 0 & 0 & \cdots & 0 \\
0 & t & \epsilon_{p+2} & 0 & 0 & \cdots & 0 \\
0 & 0 & 0 & \epsilon_{p+3} & t & \cdots & 0 \\
0 & 0 & 0 & t & \epsilon_{p+4} & \cdots & 0 \\
\vdots & \vdots & \vdots & \vdots & \vdots & \ddots & \ddots \\
0 & 0 & 0 & 0 & 0 & t & \epsilon_{p+n} \\
\end{bmatrix}
\]

\[
A_2^p = \begin{bmatrix}
\epsilon_p & t & 0 & 0 & 0 & \cdots & 0 \\
t & \epsilon_{p+1} & 0 & 0 & 0 & \cdots & 0 \\
0 & 0 & \epsilon_{p+2} & t & 0 & \cdots & 0 \\
0 & 0 & 0 & \epsilon_{p+3} & 0 & \cdots & 0 \\
0 & 0 & 0 & 0 & \epsilon_{p+4} & \cdots & 0 \\
\vdots & \vdots & \vdots & \vdots & \vdots & \ddots & \ddots \\
0 & 0 & 0 & 0 & 0 & \epsilon_{p+n} \\
\end{bmatrix}
\]

\[
A_3^p = \begin{bmatrix}
\epsilon_p & 0 & 0 & 0 & 0 & \cdots & 0 \\
0 & \epsilon_{p+1} & t & 0 & 0 & \cdots & 0 \\
0 & t & \epsilon_{p+2} & 0 & 0 & \cdots & 0 \\
0 & 0 & 0 & \epsilon_{p+3} & t & \cdots & 0 \\
0 & 0 & 0 & t & \epsilon_{p+4} & \cdots & 0 \\
\vdots & \vdots & \vdots & \vdots & \vdots & \ddots & \ddots \\
0 & 0 & 0 & 0 & 0 & t & \epsilon_{p+n} \\
\end{bmatrix}
\]

\[
A_4^p = \begin{bmatrix}
\epsilon_p & t & 0 & 0 & 0 & \cdots & 0 \\
t & \epsilon_{p+1} & 0 & 0 & 0 & \cdots & 0 \\
0 & 0 & \epsilon_{p+2} & t & 0 & \cdots & 0 \\
0 & 0 & 0 & \epsilon_{p+3} & 0 & \cdots & 0 \\
0 & 0 & 0 & 0 & \epsilon_{p+4} & \cdots & 0 \\
\vdots & \vdots & \vdots & \vdots & \vdots & \ddots & \ddots \\
0 & 0 & 0 & 0 & 0 & \epsilon_{p+n} \\
\end{bmatrix}
\]

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The \( v \) in the above matrices are place holders for including missing sites, i.e., numbered sites where no atom is located (see Fig. B1). Often one would set the diagonal elements to zero as the energy reference point, whereas it is important to assign a value to \( v \) that is distinctly different from the diagonal matrix elements (to avoid the generation of fictitious states).
CURRICULUM VITAE

Name: Arash Akbari-Sharraf

Education and Degrees:
- University of Western Ontario
  London, Ontario, Canada
  M. Sc. in Physics, 2008-2010
- York University
  Toronto, Ontario, Canada
  B. Sc. in Physics, 2004-2008

Honors and Awards:
- The Lillian Margaret & Walter David Jackson Scholarship in Physics, 2013
- Queen Elizabeth II Scholarship in Science and Technology
  University of Western Ontario, 2012 & 2013
- The W. J. Megaw Prize in Experimental Physics
  York University, 2006
Related work

experience:  
Teaching Assistant  
The University of Western Ontario, 2008-2014

Publication:  


