Energy Dispersion, Magnetism, and Transport in Three Condensed Matter Systems

Dissertation

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ABSTRACT

We calculate energy dispersion relations, transport properties, and the effects of magnetism in three condensed matter systems. Specifically, we investigate the effects of placing chains of metallic particles in an anisotropic medium and in the presence of an external magnetic field. Specifically, we calculate the effects of these perturbations on the energy dispersion relations of the plasmons that propagate along chains of metallic particles. Next, we investigate the effects of adsorbed atoms on graphene. We find that in low concentrations these additional atoms change the density of states and create a magnetic moment that can be tuned with an appropriate external potential. Finally, we investigate the combined effects of a temperature gradient and external magnetic field on the transport properties of the semiconductor InSb. We find that the transport properties, and specifically the spin-dependent Seebeck coefficient, oscillate as a function of magnetic field as the Fermi energy crosses the Landau band minima. We also suggest that by including spin-orbit interactions in the Hamiltonian we can calculate the magnetic field dependence transverse Seebeck effect in an electron doped semiconductor such as InSb.
"The saddest aspect of life right now is that science gathers knowledge faster than society gathers wisdom."

–Isaac Asimov
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As I write my dissertation thesis I am reminded of all the people who inspired my pursuit of physics. I think of my parents, Mark and Barbara Pike, who continually supported my interest in science and allowed me to explore any idea I found interesting. Without this support in my childhood and even later into my college career, I am not sure where I would be today.

During middle and high school several of my teachers continued to inspire my interest in science. Lynn Putnam, who was my 7th grade science teacher, gave me my first real taste of research by introducing me to a program run by NASA called "Protein Crystals in Space." This introduction furthered my interest in science, particularly in the space program and human space flight, an interest I still have to this day. During my senior year of high school, Cary Stamas taught the first physics class I ever attended. This class drew me into physics as he explained the basic principles on simple terms that my high school mind could understand.

My undergraduate schooling started at Grand Rapids Community College which I enrolled in as both a cost saving and time saving measure. Having completed the introductory coursework, I enrolled at Grand Valley State University and completed my Undergraduate Degree in Physics with the help of many professors and students. During my time at Grand Valley, two professors were particularly helpful, Dr. Ross Reynolds and Dr. Milun Rakovic. Dr. Reynolds was the professor of the first college physics class I attended and I took many other physics classes from him. I found his teaching style particularly direct, clear, and well-organized, therefore, while teaching classes during graduate school, I tried to mimic his lecture style. Dr. Rakovic was my undergraduate thesis advisor and, with his help, I
went through the various stages of my first true research project. For this I am forever indebted, since everything I learned about research prior to graduate school I learned from Dr. Rakovic. Including my ability to use and write in \LaTeX{} and my desire to go through a continuous writing process when working on a research project.

I would be amiss if I forgot about The Ohio State University and the Professors, students, and staff found in the Department of Physics. So much of this work was done within this department and building that I would be ashamed not to thank them. Dr. David Stroud, my research advisor for the past four years is instrumental in the development of my work and a truly great inspiration in my research. I would like to thank Drs. Jayaparakash, Lemberger, and Furnstahl, who serve on my dissertation committee, for taking the time out of their schedules to teach me, guide me through my research, and sit on my committee.

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VITA

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Publications

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<td>4.2</td>
<td>Numerical parameters used in the calculation of the spin-dependent transport coefficients. The estimate $\tau \sim 10^{-12}$ s is inferred from the electron mobility quoted in Ref. [100], the estimate for $m_{cv}$ comes from the mass of the heavy hole electron, and the inter-band scattering potential $c_2$ is extracted from the work of Pidgeon et al [113]. The chosen value of $\epsilon_{xz}$ corresponds to 1% strain since we are assuming only a small displacement of the atoms within the unit cell.</td>
</tr>
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Chapter 1
INTRODUCTION

Control of different physical properties in condensed matter systems is critical to the continued advancement of technology in the modern age. The combination of external fields and novel materials has led many researchers to develop new products and led to countless new uses of these products. For example, recent advances in material engineering allow scientists and engineers to create materials on the nanoscale. Which, under strict growth conditions, can be used to create nanoscale devices to test new theories and potentially lead to new commercial products. The seemingly arbitrary control over the growth of these nanoscale devices allows many theorists to start dreaming of devices once thought impossible.

For example, the ability to grow or fabricate nanoscale metallic particles in prearranged patterns allows one to consider the possibility of non-electronic transmission of information. This means the transmission of a signal along a chain or patterned array of metallic particles without the requirement that the particle edges overlap. This means that such an array would contain no electronic current. One possible method of non-electronic transmission could be oscillating electron densities on the metallic particles. These oscillating electron densities are better known as plasmons which oscillate at a well-defined frequency that only depends on the density of electrons in the host metal and the particle shapes. Our research into chains of metallic nanoparticles has focused on plasmonic oscillations and specifically the coupling between the metallic particles which allows for propagation of a linearly polarized electromagnetic wave along the chain. I have also included the effects of the medium in which the metallic chain is placed, whether that medium is a vacuum or an anisotropic dielectric, and the effects of an external magnetic field on the propagation of
the electromagnetic wave.

Until recently the mass production of single layer graphene was complicated and costly; however, recent advances in crystal growth have made it relatively simple for large quantities of single layer graphene to be grown on a single wafer. Experimentalists are also able to control the growth of these graphene sheets to such precision that they can (reasonably) control the level of defects or deformations found in the graphene sheets. Nanoscale engineering of these sheets allows one to place low concentrations of adsorbed atoms (adatoms) on to the sheets in predictable ways. This advancement in nanoscale growth and engineering allows for possibility of controlled experiments at the nanoscale which have not been observed before. Our research into the effects of adatoms placed onto the surface of graphene shows that the presence of a low concentration of adatoms gives rise to a magnetic moment on graphene and that, due to the unique properties of graphene, this moment can be turned on and off with the application of a gate voltage.

Advances in material growth have also lead to the possibility of growing thin samples to test the effects of external fields on different transport properties of both conductors and semiconductors. To be specific, recent work on the semiconductor indium antimony (InSb) showed that if the sample is n-doped (electron doped), its spin transport properties display oscillations as a function of magnetic field which are orders of magnitude larger than previously observed in semiconductors. My research in this area led to a simple theory as to the origins of these magnetic oscillations and gives qualitative correct predictions for the oscillations found in the spin transport properties of InSb.

The outline of this thesis is as follows: I first discuss my theoretical work on predicting the behavior of plasmon waves along a chain of metallic nanoparticles in the presence of an anisotropic medium, such as a liquid crystal, and discuss what happens when this metallic chain-liquid crystal system is influenced by an external static magnetic field. We will find that the dispersion relations of the plasmon waves that propagate along the chain of the metallic particles is affected by both the anisotropic host and magnetic field. This interplay between the liquid crystal host and the external field provides a way of tuning the dispersion relations over a desired frequency range, and in the case of a static magnetic field, may allow
for the realization of a non-reciprocal waveguide in which only a plasmonic wave is allowed
to propagate only in one direction for certain frequencies. The work described here was
published in two places, an additional work is nearly ready for publication. Our plasmon
work is used as the basis of Chapter 2 and found in Refs. 1, 2 and 3.  

Next, we will discuss the effects of absorbed atoms (adatoms) on the two-dimensional
carbon lattice known as graphene. In particular, we will analytically calculate the effects
of these adatoms on the total and local density of states, the spectral function, and the
electron transfer between the adatom and the graphene sheet. This discussion will take
place using a tight-binding Hamiltonian that considers hopping between the carbon atoms,
between the adatom and the nearest neighbor carbon atoms, and the on-site energy of the
adatom. In addition, the electron-electron correlation energy is included using a mean-field
theory for the Hubbard-U term. We find that the hopping parameters strongly affect the
density of states, spectral function, and magnetic properties of the system. This work was
published in two publications which are used as the basis of Chapter 3 and are found in
Refs. 4 and 5.  

Finally, we consider the effects of a strong magnetic field on the doped semiconductor In-
dium Antimony (InSb) and in particular look at magnetic oscillations of different transport
coefficients such as the thermopower and spin-dependent Seebeck coefficient. Our theory
of these effects uses a simple model which describes the effects of a strong magnetic field
on the electron energy (Landau levels) and Zeeman Hamiltonian to describe the effects of
electron spin in a magnetic field. Boltzmann’s transport equations are then used to describe
the various currents found in the system. We find that these magnetic oscillations occur
whenever the Fermi energy of the system crosses a Landau level. This work is contained in
one published article and one article which is still under development. This work is used as
the basis of Chapter 4 and can be found in Ref. 6 and soon in Ref. 7.
Chapter 2
PLASMONIC WAVES ON CHAINS OF METALLIC NANOPARTICLES

2.1 Overview

Small metal particles exhibit resonant excitations known as particle or surface plasmons [8]. Such excitations, if the particles have dimensions small compared to the wavelength of light, can lead to sharp optical absorption peaks, which are typically in the near-infrared or the visible. These absorption peaks play an important role in the optical response of suspensions of metal particles in a dielectric host [9–12], and have been the subject of a large amount of study, both experimental and theoretical.

Until fairly recently, such suspensions consisted of random distributions of metal particles. But because of recent advances in sample preparation, it has become possible to study ordered arrays of such particles [13–16]. In one-dimensional ordered arrays of such closely-spaced particles, Bloch waves of plasmonic excitations can propagate along the chains provided that the interparticle spacing is small compared to the wavelength of light [17–27]. In this limit, the coupling between the plasmons comes mainly from the electric field produced by the dipole moment of one nanoparticle, which induces dipole moments on the neighboring nanoparticle. The dispersion relations for both transverse (T) and longitudinal (L) plasmonic waves can then be calculated in the so-called quasistatic approximation [18–20], in which the curl of the electric field is neglected. This approximation is reasonable when the particles are separated by a distance small compared to the wavelength of radiation. While this approximation neglects some significant coupling between the plasmonic waves
and free photons [24], it gives satisfactory results over most of the Brillouin zone.

In this chapter, we first define what is meant by *surface plasmon*, then give some of the basic properties of liquid crystals before extending the study of propagating plasmonic waves by calculating how their dispersion relations are modified when the metallic chain is immersed in a liquid crystal host. We consider two types of such hosts: a nematic liquid crystal (NLC) and a cholesteric liquid crystal (CLC). An NLC is characterized by a uniaxially anisotropic dielectric tensor and a unit vector parallel to the symmetry axis of this tensor is known as the director. A CLC can be viewed as a nematic in which the director rotates about an axis perpendicular to the plane (the ”twist axis”) with a characteristic pitch angle.

A number of workers have studied how the optical properties of metallic nanoparticle are affected when the particles are immersed in, or coated by, a liquid crystal host. Both experimental and theoretical investigations of this kind have been carried out (see, for example, Refs. [28–39]), as well as studies of related systems, such as metallic screens penetrated by an array of nanoholes in a liquid crystal host [40, 41]). In general, these works have considered the optical absorption or transmission of these systems, and have also investigated how these properties can be tuned by external perturbations such as an applied electric field. They have not, however, considered the propagation of plasmonic waves along chains or other ordered arrays of metallic nanoparticles, which is the subject of this chapter.

To consider the propagation of a plasmonic wave we first need to discuss what is meant by a surface plasmon. Following this discussion, we introduce the properties of a liquid crystal and then use the anisotropic nature of the liquid crystals to discuss the propagation of plasmonic waves through a linear chain of metallic particles.

### 2.2 Particle Plasmons in a Bulk Material

To determine the dispersion relations for plasmonic waves along a metallic chain of nanoparticles in the presence of an anisotropic host we will first consider what happens to a single
metallic particle in vacuum and then describe the coupling between nanoparticles that are closely spaced. This discussion will lead us naturally to the description of the dispersion relations of surface plasmons on a chain of metallic nanoparticles.

Consider what happens to the surface charge density on a metallic sphere when it is placed in an oscillating external electric field. In general, these surface charges will move around the sphere in such a manner as to minimize the net force on each charge in the distribution. I. e. in the absence of an external electric field the positive ions and negatively charged electrons move to minimize the electrostatic energy between them. In general since the mass of the positive ions, \( m_p \), is much greater then the mass of an electron, \( m_e \), one can consider the electrons as moving and the positive ions as fixed in place (this is the Born-Oppenheimer approximation or rigid ion approximation). In the presence of an oscillating electric field the negatively charged electrons will experience a force which separates them from positively charged ions (which we assume are fixed in position). This separation will create an internal electric field which opposes the external oscillating electric field [8]. This implies that an oscillating electric field will set up an oscillating charge current within the system.

Using Maxwell’s equations we can write down the electric field wave equation for an uncharged metallic particle sitting in isolation. The general form of Maxwell’s equations are given (in SI units) as [8, 42]

\[
\begin{align*}
\nabla \cdot \mathbf{D} &= \rho_{\text{free}} \\
\nabla \cdot \mathbf{H} &= 0 \\
\n\nabla \times \mathbf{E} &= -\frac{\partial \mathbf{B}}{\partial t} \\
\n\nabla \times \mathbf{H} &= \mathbf{J}_f + \frac{\partial \mathbf{D}}{\partial t}
\end{align*}
\]

(2.1)

where the displacement field \( \mathbf{D} = \epsilon_0 \mathbf{E} + \mathbf{P} \) [\( \mathbf{P} \) is the polarization], the magnetic field \( \mathbf{H} = \frac{\mathbf{B}}{\mu_0} + \mathbf{M} \) [\( \mathbf{M} \) is the magnetization], \( \rho \) is the free charge density, \( \mathbf{J} \) is the free current density, \( \epsilon_0 \) is the permittivity of free space, and \( \mu_0 \) is the permeability of free space \(^1\). In defining

\(^1\)By definition we have \( c = \frac{1}{\sqrt{\mu_0 \epsilon_0}} \), where \( c \) is the speed of light in vacuum [42].
the displacement current, \( \mathbf{D} \), and the magnetic field, \( \mathbf{B} \), we assumed that the dielectric constant of the metallic sphere is frequency dependent and that the relative permeability of the metallic sphere has no frequency dependence. I.e. that \( \mu(\omega) = \mu_0 \).

Combining the four equations given in Eq. (2.1), with the requirement that the bulk charge current \( \mathbf{J} \) and the net charge density equal zero everywhere in the metallic spheres, we can write out a wave equation for the electric field of the homogeneous system as [8]

\[
-\nabla^2 \mathbf{E} = \frac{\omega^2}{c^2} \varepsilon(\omega) \mathbf{E} \tag{2.2}
\]

where \( c \) is the speed of light in vacuum and \( \varepsilon(\omega) \) is the complex dielectric constant. We also assume the Drude model for \( \varepsilon(\omega) \) which, at high frequencies, satisfies

\[
\varepsilon(\omega) = 1 - \frac{\omega_p^2}{\omega^2}. \tag{2.3}
\]

The requirement that both the net charge density, \( \rho = 0 \), and the free charge current \( \mathbf{J} = 0 \) is required by the considerations made previously. Since the spheres are isolated and neutral both the charge density and current will equal zero.

In Eq. (2.3) the plasma frequency is defined by

\[
\omega_p^2 = \frac{ne^2}{\epsilon_0 m} \tag{2.4}
\]

where \( n \) is the density of electrons on the metallic sphere, \( e \) (\( e < 0 \)) is the electron charge, and \( m \) is the mass of an electron. For a range of frequencies, we find that \( \varepsilon \) is both real and negative; this happens when \( \omega < \omega_p \), and therefore solutions to Eq. (2.2) decay exponentially at these frequencies. However, when \( \omega > \omega_p \) the solution for \( \varepsilon(\omega) \) becomes positive and real and thus Eq. (2.2) has oscillatory solutions and the metal becomes transparent to external fields [8].

As a consequence of Eq. (2.3) the electron gas on the surface of the metallic sphere can sustain charge density oscillations. This is easily seen when one considers the continuity

\[\nabla \times \nabla \times \mathbf{E} = \nabla (\nabla \cdot \mathbf{E}) - \nabla^2 \mathbf{E} \]

was also used during the derivation of Eq. (2.2) with the assumption that \( \nabla \cdot \mathbf{E} = 0 \).
equation given by
\[ \nabla \cdot \mathbf{j} = -\frac{\partial \rho}{\partial t}. \] (2.5)

If we assume that the charge density oscillates at the same frequency as the applied electric field, then, to first order in the electric field, the charge current, \( \mathbf{J}(\omega) \), is related to the oscillating electric field, \( \mathbf{E}(\omega) \), by
\[ \mathbf{J}(\omega) = \sigma(\omega)\mathbf{E}(\omega) \] (2.6)
where \( \sigma(\omega) \) is known as the electrical conductivity of the material and is a known function of the frequency of the oscillating electric field [8]. Then since the electric field, and therefore the current density, oscillate at a frequency \( \omega \), so does the charge density.

We can also determine the electric field induced in a metallic particle by considering what happens to an isolated metallic sphere in an isotropic dielectric. Since the metallic particle is a sphere, we will use spherical symmetry to determine the potential \( V(r, \theta) \) by using the general solution to Laplace’s equation with appropriate boundary conditions. The general form of this potential is
\[ V(r, \theta) = \sum_{l=0}^{\infty} \left( A_l r^l + \frac{B_l}{r^{l+1}} \right) P_l(\cos(\theta)) \] (2.7)
where \( r \) is the radial distance and \( P_l(\cos(\theta)) \) is a Legendre polynomial [42]. One can write down the general solution for both outside and inside the sphere as
\[ V_{in}(r, \theta) = \sum_{l=0}^{\infty} A_l r^l P_l(\cos(\theta)) \] (2.8)
and
\[ V_{out}(r, \theta) = -E_0 r \cos(\theta) + \sum_{l=0}^{\infty} \frac{B_l}{r^{l+1}} P_l(\cos(\theta)) \] (2.9)
where we have required that \( V_{out} = -E_0 r \cos(\theta) \) as \( r \to \infty \). Using the boundary conditions for the electric field at the surface of the sphere we can write down the electric field inside the sphere as
\[ E_{in} = \frac{3}{\epsilon_r + 2} E_0 \] (2.10)
where we assume the sphere has a dielectric constant of \( \epsilon(\omega) \) and the isotropic dielectric
has a constant of \( \epsilon_0 \) making the relative dielectric constant \( \epsilon_r = \frac{\epsilon(\omega)}{\epsilon_0} \).

In Eq. (2.10) even if the external field is zero \( (E_0 \to 0) \) an electric field can still exist inside the metallic particle if \( \epsilon_r + 2 = 0 \). If we assume that the dielectric constant of the metallic particle is of the Drude form, then the frequency with which the internal electric field is oscillating is

\[
\omega = \frac{\omega_p}{\sqrt{\epsilon_0 + 2}}
\]

(2.11)

where \( \omega_p \) is the plasmon frequency defined previously. At this particular frequency the charge density oscillations are confined to the surface of the material then these charge density oscillations are formally known as *surface plasmons*.

A surface plasmon is a solution to Maxwell’s equations if the electric field is confined to the surface of a conducting material. For example, if the electric field is given by

\[
E_x = Ae^{iqx}e^{-Kz}
E_z = Be^{iqx}e^{-Kz}
\]

(2.12)

for \( z > 0 \) (the metal) and

\[
E_x = Ae^{iqx}e^{K'z}
E_z = Be^{iqx}e^{K'z}
\]

(2.13)

for \( z < 0 \) (the vacuum) in which we assumed that the values of the wave numbers \( q, K \) and \( K' \) are real and \( K \) and \( K' \) take only positive values. We find, using continuous boundary conditions at the interface and the Drude form of \( \epsilon(\omega) \), that when \( qc >> \omega \) the electric field decays very quickly to \( z = 0 \) and that the wave is circularly polarized at the interface between the metal and vacuum. Therefore, a wave of this form only exists at or very near the surface and is thus known as a surface plasmon.

With the definition of the plasma frequency given in Eq. (2.4) and the knowledge that charge oscillations lead to propagating waves (for a limited frequency range) we can now determine what happens when metallic particles are placed in ordered arrays. Consider the following: We place many metallic particles in a linear array as depicted in Fig. 2.1 and
create an oscillation in the left most particle. One can easily imagine that the oscillating charge density on the left-most sphere will affect the sphere directly next to it and to a lesser extent all the following spheres. Since the second sphere will see an oscillating electric field it will create an oscillating charge density (i. e. a surface plasmon oscillation) which will affect the next sphere which in turn affects all the remaining spheres in the chain. Of course, the influence of a single sphere falls off as the electric field \(1/r^3\) where \(r\) is the distance from the sphere) [42] but the affect of the linear chain oscillations could occur over much larger distances due to the coupling between the spheres. This last statement is especially true when we neglect damping, as we did in the example above. In the rest of the chapter, after discussing the properties of liquid crystals, we will calculate the dispersion relations for both the damped and undamped case by modifying the dielectric constant of the metallic spheres.

2.3 Physical Properties of Liquid Crystals

In grade school we are taught that all matter exists in one of three phases: solid, liquid, and gas [43]. Each of these phases of matter has unique physical properties that allow us to categorize them. However, experience tells us that this classification is too simple. In fact,
it is known that some materials fail to fall into any particular category and instead show properties of two (or more) of these simple phases. In this section, we will consider one such material, namely a liquid crystal, which displays both solid and liquid properties. To be specific, certain types of organic molecules display physical and mechanical properties in the bulk that place these materials between the solid and liquid phase [44] in what is called a mesomorphic phase [45]. A material in a mesomorphic phase has the mobility of a liquid and some of the symmetry properties of a solid [46].

While the mesomorphic phase exhibits a large variety of symmetries, we consider here only the Nematic and Cholesteric phases. Namely, if the liquid crystal is stratified with the molecules being arranged in layers with their long axes aligned approximately normal to the plane layers then it is called a smectic (soap-like) liquid crystal [46], whereas, if the molecules are preferentially aligned along one direction giving it orientational ordering, then the liquid crystal is known as a nematic (thread) liquid crystal (NLC). In either case, the organic molecules must be elongated and therefore are generally long chain molecules. The degree of ordering of both nematic and smectic liquid crystals is strongly dependent on the temperature of the system as well as other parameters [45].

The molecules in a NLC have no long-range order and therefore have no Bragg peak in a X-ray diffraction pattern [44]. There is, however a general orientational order along a single common axis. This common axis is known as the director axis, \( \hat{n} \), which allows a NLC to be uniaxial medium aligned along \( \hat{n} \). A schematic of an NLC is given in Fig. 2.2(a) which shows the general orientation of the liquid crystal along the director axis \( \hat{n} \).

The bulk alignment of the liquid crystal in the direction parallel to the director does not occur in all liquid crystals. These liquid crystals that do no display bulk alignment are categorized into different types. One such type is known as a cholesteric liquid crystal if the organic molecules rotate by a fixed amount relative to a central axis. This effect gives cholesteric liquid crystals a helical structure. A schematic of a cholesteric liquid crystal (CLC) is shown in Fig. 2.2(b) in which we sketch the organic molecules rotating by a fixed

\(^{3}\)The word smectic comes from the Greek word "σµητικον" meaning grease or slime as coined by G. Friedel [44, 47].
\(^{4}\)The word nematic comes from the Greek word "νημα" = thread as coined by G. Friedel [44, 47].
angle $\alpha_d$ at a fixed separation. Experimentally one finds that the rotation angle is also temperature dependent [44].

In the case of both NLC and CLC the orientation and alignment of the individual organic molecules is controlled both by temperature and external fields [43, 45]. In general the organic molecules that make up the structure of the liquid crystal have small dipole moments. These dipole moments tend to align to an applied electric field of sufficient magnitude [44]. Therefore, one could control the orientation of the director axis, with respect to an external fixed direction, by applying a static electric field along the direction of choice [43]. One also notes that since the individual molecules of a liquid crystals align in a single direction one would expect the optical properties of the liquid crystal to differ for light polarized parallel and perpendicular to the director axis. Hence, a uniaxial liquid crystal acts like an anisotropic optical medium, because waves polarized in different directions will
experience different mediums in which they travel. This effect is described by an anisotropic dielectric tensor through which a wave would propagate [44].

For the purposes of this thesis we assumed that the anisotropic dielectric tensor used here will have values for its three diagonal components $\epsilon_\parallel$, $\epsilon_\perp$, and $\epsilon_\perp$ which are determined in an experiment by Müller et al. [28] for the liquid crystal known as E7 (Merck, Germany). This particular liquid crystal is a mixture of four different liquid crystals which gives E7 its unique physical properties [45]. In particular, Müller et al. found that the principal dielectric constants for E7 are $\epsilon_\parallel = 3.0625$ and $\epsilon_\perp = 2.3104$ [28] and are found to be independent of temperature and frequency.

In our present work, we first consider a chain of metallic nanoparticles immersed in a liquid crystal and we will assume that the alignment of the liquid crystal is unaffected by the presence of the metallic spheres. While this assumption is an approximation, it will be good as long as the spacing between particles is larger then the average length of the molecules composing the liquid crystal. With the approximation that the alignment is unaffected by the metallic particles, we will find that the anisotropic dielectric tensor modifies the three solutions for the dispersion relations when compared to the isotropic case, and, later, on the orientation of an applied magnetic field to the chain and the symmetry axis of the liquid crystal. This theoretical model is first outlined for the case of a nematic liquid crystal and cholesteric liquid crystal in the absence of a magnetic field. Next we address the effects of a magnetic field and how it modifies the dispersion relations of the surface plasmons.

### 2.4 Dispersion Relations of a Metallic Chain in an Anisotropic Host: Formalism

#### 2.4.1 Quasistatic approximation

The fact that the influence of a single sphere on the chain decays as a function of distance allows us to make some simplifying approximations about the electric field created by the surface plasmon oscillations and about the spacing of the spheres. First, we will assume that the spheres are sufficiently far apart so that we can neglect all moments higher then
the dipole moment [42]. This dipole approximation is approximately valid if the spacing between the spheres, \( d \), is greater than 3\( a \) where \( a \) is the radius (see Fig. 2.1). Second, we will assume that the electric field is curl-free; this assumption is approximately valid when both the radius of the particle and the distance between particles are small compared to the wavelength of light [18–20]. Formally, the second approximation represents what is known as the quasistatic approximation.

To treat the propagation of plasmonic waves along a chain of metallic particles in the presence of an anisotropic host medium, we must consider the anisotropy of the metallic chain when we write down the dielectric tensor and when we consider the coupling between the particles. We must also allow for the anisotropy of the medium to couple the various propagation directions (which we find occurs in several different geometries) while allowing for damping and magnetic field effects.

Using the quasistatic approximation, we show that, for the nematic liquid crystal host, both the Longitudinal (\( L \)) and Transverse (\( T \)) waves have modified dispersion relations when the director is parallel to the chain axis. If the director is perpendicular to the chain axis, we show that the previously degenerate \( T \) branches are split into two non-degenerate, linearly polarized branches. For a cholesteric liquid crystal host with twist axis parallel to the chain, we again show that there are two non-degenerate \( T \) branches whose dispersion relations depend on the cholesteric pitch angle, there is also one \( L \) branch. However, the two \( T \) branches are no longer linearly polarized.

### 2.4.2 Derivation of the General Equation for the Coupled Dipole Moments in a Chain of Metallic Nanoparticles

For this chapter we will consider a chain of identical metal nanoparticle, each a sphere of radius \( a \), arranged in a one-dimensional periodic lattice along the \( z \) axis (see Fig. 2.1). The \( n^{th} \) particle is assumed centered at \((0, 0, nd)\) \((-\infty < n < +\infty)\). The propagation of plasmonic waves along such a chain of nanoparticle has already been considered extensively for the case of isotropic metal particles embedded in a homogeneous, isotropic medium [18]. The extension of quasistatic studies to include radiative corrections, i.e., to the case when
the electric fields cannot be approximated as curl-free, has also been carried out; these corrections can be very important even in some long-wavelength regimes [24].

We first consider how the plasmon dispersion relations are modified when the particle chain is immersed in a uniaxially anisotropic dielectric, such as an NLC. Thus we assume that the host medium is a uniaxial dielectric tensor \( \hat{\epsilon}_h \), with principal dielectric constants \( \epsilon_\perp, \epsilon_\perp, \) and \( \epsilon_\parallel \). The medium inside the metallic particles is assumed to have a dielectric tensor \( \hat{\epsilon} = \epsilon(\omega) \hat{1} \) where \( \hat{1} \) is the \( 3 \times 3 \) unit tensor. For simplicity, we take \( \epsilon(\omega) \) to have the Drude form which we presented earlier for the limit of high frequencies. Here we give the full version, which includes the effects of damping, as

\[
\epsilon(\omega) = 1 - \frac{\omega_p^2}{\omega(\omega + i/\tau)} \rightarrow 1 - \frac{\omega_p^2}{\omega^2},
\]

(2.14)

where \( \omega_p \) is the plasma frequency, \( \tau \) is a relaxation time, and the last form on the right-hand side applies when \( \tau \rightarrow \infty \) [See Eq. (2.3) and surrounding text]. The following calculations and results are easily extended to other forms of \( \epsilon(\omega) \) as would be required in order to apply this work to nanoparticle composed of metals such as Au or Ag.

### 2.4.3 General Derivation for the Electric field, \( E(x) \) due to a Dipole at \( x' \)

To first determine the equation for the dispersion relation which couples the individual particles in the metallic chain we begin by writing down the electric field at a point \( x \) due to a sphere with a polarization \( P(x') \). This is done in practice by first considering an isolated metallic particle with an inhomogeneous dielectric tensor embedded in a uniform dielectric background and static (external) electric field [48]. Far from the metallic particle we expect the electric field to be uniform and to approach a constant field given by \( E_0 \) and thus the current density given by Eq. (2.6) can be written as \( J = \hat{\sigma}E_0 \) (We describe these equations for a conductor, however, the same equations can be written down for finite \( \omega \) using \( \epsilon(\omega, x) \)). With the aid of Maxwell’s equations we require that the electrostatic potential \( \Phi(x) \) satisfy

\[
\mathbf{\nabla} \cdot \hat{\sigma}(x) \mathbf{\nabla} \Phi(x) = 0,
\]

(2.15)
with the condition that $\Phi(x) \to -E_0 \cdot x$ as $x \to \infty$. The conductivity tensor, $\sigma(x)$, does depend on position as it will differ inside and outside the metallic sphere. This dependence is formally introduced by requiring that $\sigma(x) = \sigma'$ if $x$ is inside the metallic sphere and $\sigma$ otherwise.

By using a Green’s function approach to solve Eq. (2.15) we can write out a integral equation to find the electrostatic potential as

$$
\Phi(x) = -E_0 \cdot x + \int G(x - x') \nabla' \cdot [\delta\sigma(x') \nabla' \Phi(x')] d^3x'
$$

(2.16)

where $\delta\sigma(x') = \sigma(x') - \sigma$ and we require that $G(x - x') \to 0$ as $|x - x'| \to \infty$. Since the bracketed quantity in Eq. (2.16) only depends on $x'$ we can use both integration by parts and the divergence theorem to rewrite Eq. (2.16) as

$$
\Phi(x) = -E_0 \cdot x + \oint_S G(x - x') \delta\sigma(x') E_{in} \cdot \hat{n} d^2x'
$$

(2.17)

where $\hat{n}$ is an outward normal vector and $S$ denotes the surface of the conducting sphere.

Taking the negative gradient of each side of Eq. (2.17) and using the symmetry of the Green’s function we find that the electric field produced by the metallic particle can be written in component form (see, e.g., Ref. [49]). Note that while the simple derivation above involves the difference in conductivity of the materials we could have written an analogous equation involving the difference in dielectric constants. Therefore, in Eq. (2.18) below, we have substituted the dielectric tensors for the metallic particle and the liquid crystal for the conductivity tensors used in the derivation above. This substitution allows us to write the the electric field produced by the $i^{th}$ particle as

$$
E_i(x) = -\int \mathcal{G}_{ij}(x - x') P_j(x') d^3x',
$$

(2.18)

where repeated indices are summed over. In Eq. (2.18), $P(x') = (\hat{\epsilon} - \hat{\epsilon}_h) \cdot E(x')$ is the polarization of the metallic particle, $\hat{\epsilon}$ is the dielectric function of the metal particle, $\hat{\epsilon}_h$ is the dielectric constant of the host material, and $\mathcal{G}$ denotes a $3 \times 3$ matrix of the second partial derivatives of the Greens function as given below.

5To be specific, Eq. (2.18) is obtained from Eq. (2.9) of Ref. [49] by setting the applied field $E_0 = 0$
2.4.4 Green’s Function for an Anisotropic Dielectric Host

The relevant partial derivatives of the Green’s function are given by

\[ G_{ij}(x - x') = \partial_i' \partial_j G(x - x'), \quad (2.19) \]

where \( G(x - x') \) is a Green’s function which satisfies the differential equation

\[ \nabla \cdot (\hat{\epsilon}_h \cdot \nabla G(x - x')) = -\delta(x - x'), \quad (2.20) \]

with boundary conditions \( G(x - x') \rightarrow 0 \) as \(|x - x'| \rightarrow \infty\). Physically, \( -G_{ij}(x - x') \) represents the \( i^{th} \) component of electric field at \( x \) due to a unit point dipole oriented in the \( j^{th} \) direction at \( x' \), in the presence of the anisotropic host. It is easily shown that \( G_{ji} = G_{ij} \).

We assume that the host dielectric tensor is diagonal and uniaxial with diagonal components \( \epsilon_\perp, \epsilon_\perp \) and \( \epsilon_\parallel \) parallel to the \( x, y, \) and \( z \) axes respectively. The solution to Eq. (2.20) for this case has been obtained in many places (See for example Refs. [49] and [50]). For completeness, we write the solution out here:

\[ G(x - x') = \frac{1}{4\pi \epsilon_\perp \epsilon_\parallel^{1/2}} \left[ \frac{(x - x')^2 + (y - y')^2}{\epsilon_\perp} + \frac{(z - z')^2}{\epsilon_\parallel} \right]^{-1/2}. \quad (2.21) \]

2.4.5 General Equation for the Coupled Dipole Moments

Having determined the electric field produced by the \( i^{th} \) particle in Eq. (2.18) we can now formally write down a self-consistent equation for plasmonic waves along a chain immersed in an anisotropic host. To do this, we consider the polarization of the \( n^{th} \) particle, which we write as \( \mathbf{P}_n(x) = \hat{\delta}\epsilon \cdot \mathbf{E}_{in,n}(x) \), where \( \mathbf{E}_{in,n}(x) \) is the electric field within the \( n^{th} \) particle. This field, in turn, is related to the external field acting on the \( n^{th} \) particle and arising from the dipole moments of all the other particles. We approximate this external field as uniform over the volume of the particle, and denote it \( \mathbf{E}_{ext,n} \). This approximation should be reasonable if the particle radius is not too large compared to the separation between in that equation, and carrying out the integral over a sphere of radius \( a \), Also, Eq. (2.9) is applied to the formally analogous case of an inhomogeneous dielectric rather than an inhomogeneous conductor. Thus, the factor \( \delta\sigma(x') \) in that equation is replaced by \( \hat{\delta}\epsilon \) in Eq. (2.20), \( \sigma_0 \) is replaced by \( \hat{\epsilon}_h \), where \( \hat{\epsilon}_h = \epsilon_h \hat{1} \).

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particles (in practice, an adequate condition is probably \( a/d \leq 1/3 \), where \( a \) is the particle radius and \( d \) the nearest neighbor separation). Then \( \mathbf{E}_{in,n} \) and \( \mathbf{E}_{ext,n} \) are related by \(^{[48]}\)

\[
\mathbf{E}_{in,n} = (\hat{1} - \hat{\Gamma} \cdot \hat{\delta \epsilon})^{-1} \cdot \mathbf{E}_{ext,n},
\]

(2.22)

where \( \hat{\Gamma} \) is a "depolarization matrix" defined, for example, in Ref. \(^{[49]}\).

The primary components of \( \hat{\Gamma} \) are \( \Gamma_{\parallel} \) and \( \Gamma_{\perp} \) are well known for a uniaxial anisotropic host (see, e. g., Ref. \(^{[49]}\), where they are denoted \( \Gamma_{xx} \) and \( \Gamma_{zz} \)). We rewrite them here for convenience:

\[
\Gamma_{\parallel} = -\frac{1}{\epsilon_{\parallel}} \left[ 1 - \sqrt{1 - \lambda} \frac{\sin^{-1} \sqrt{\lambda}}{\sqrt{\lambda}} \right],
\]

\[
\Gamma_{\perp} = -\frac{1}{2} \left[ \Gamma_{\parallel} + \frac{1}{\sqrt{\epsilon_{\perp} \epsilon_{\parallel}}} \sin^{-1} \sqrt{\lambda} \right],
\]

(2.23)

where \( \lambda = 1 - \epsilon_{\perp}/\epsilon_{\parallel} \).

The external electric field, \( \mathbf{E}_{ext,n} \), is the field acting on the \( n^{th} \) particle due to the dipoles produced by all the other particles, as given by Eq. (2.18). Hence, the dipole moment of the \( n^{th} \) particle may be written

\[
\mathbf{p}_n = \frac{4\pi}{3} a^3 \mathbf{P}_{in,n} = \frac{4\pi}{3} a^3 \hat{t} \cdot \mathbf{E}_{ext,n},
\]

(2.24)

where

\[
\hat{t} = \hat{\delta \epsilon} \left( \hat{1} - \hat{\Gamma} \cdot \hat{\delta \epsilon} \right)^{-1}
\]

(2.25)

is a "t-matrix" describing the scattering properties of the metallic sphere embedded in the surrounding material. In Eq. (2.25), \( \hat{1} \) is the \( 3 \times 3 \) identity matrix and \( \hat{\delta \epsilon} = \hat{\epsilon} - \hat{\epsilon}_h \).

Finally, we make the assumption that the portion of \( \mathbf{E}_{ext,n} \) which comes from particle \( n' \) is obtained from Eq. (2.18) as if the spherical particle \( n' \) were a point particle located at the center of the sphere (this approximation should again be reasonable if \( a/d \leq 1/3 \)). With this approximation, and combining Eqs. (2.18), (2.24), and (2.25), we obtain the following self-consistent equation for the coupled dipole moments:

\[
\mathbf{p}_n = -\frac{4\pi a^3}{3} \hat{t} \sum_{n' \neq n} \hat{G}(\mathbf{x}_n - \mathbf{x}_{n'}) \cdot \mathbf{p}_{n'}.
\]

(2.26)
Eq. (2.26) serves as the central equation for the remainder of the chapter. It connects the dipole moment of the \( n^{th} \) particle with the remainder of the particles in the chain while taking into account the anisotropic background in which the chain lies. We now provide various examples of different possible orientations for these chains and also provide numerical calculations of the dispersion relations for linearly polarized incident light along these chains.

### 2.4.6 Nematic Liquid Crystal

Let us first assume that the principal axis of the anisotropic host coincides with the chain direction, which we take as the \( z \) axis. In this case, the \( L \) and \( T \) waves decouple and can be treated independently, because one of the principal axes of the \( \hat{\Gamma} \) tensor coincides with the chain axis. First, we consider the \( L \) waves. To find their dispersion relation, we need to calculate \( G_{zz}(x_n - x_{n'}) \). From the definition of this quantity [Eqs. (2.19) and (2.21)] and from the fact that \( x_n = nd\hat{z} \equiv z_n\hat{z} \), we can readily show that

\[
G_{zz}(x_n - x_{n'}) = -\frac{1}{2\pi\epsilon_\perp} \frac{1}{|z_n - z_{n'}|^3}.
\]

Hence, we obtain the following equations for the \( p_{nz} \)'s:

\[
p_{nz} = \frac{2}{3\epsilon_\perp} a^3 \frac{\delta\epsilon_\parallel}{1 - \Gamma_\parallel\delta\epsilon_\parallel} \sum_{n'\neq n} \frac{p_{n'z}}{|z_n - z_{n'}|^3}.
\]

(2.27)

For transverse modes, the relevant Green’s function takes the form \( G_{xx}(x_n - x_{n'}) = \frac{\epsilon_\parallel}{4\pi\epsilon_\perp} \frac{1}{|z_n - z_{n'}|^3} \). The resulting equation for the dipole moments takes the form

\[
p_{nx} = -\frac{1}{3} \frac{\epsilon_\perp}{\epsilon_\perp} a^3 \frac{\delta\epsilon_\perp}{1 - \Gamma_\perp\delta\epsilon_\perp} \sum_{n'\neq n} \frac{p_{n'x}}{|z_n - z_{n'}|^3},
\]

(2.28)

with an analogous equation for \( p_{ny} \).

To obtain the dispersion relations for the \( L \) modes, we write \( p_{nz} = p_{z0} e^{inkd - i\omega t} \), where \( p_{z0} \) is the wave amplitude. We then find that Eq. (2.27) has a nontrivial solution only if

\[
1 = \frac{2}{3\epsilon_\perp} a^3 \frac{\delta\epsilon_\parallel}{d^3} \sum_{n' \neq 0} \frac{e^{ikn'd}}{|n'|^3},
\]

(2.29)

where the sum runs over all nonzero positive and negative integers. If the frequency-dependence of \( \epsilon(\omega) \) is known, Eq. (2.29) represents an implicit relation between \( k \) and \( \omega \),
corresponding to the dispersion relation. Similarly, for the $T$ modes, the analogous equation is

$$1 = -\frac{1}{3} \frac{\epsilon_\parallel a^3}{\epsilon_\perp d^3} \frac{\delta \epsilon_\perp}{1 - \Gamma_\perp \delta \epsilon_\perp} \sum_{n \neq 0} \frac{e^{ikn'd}}{|n'|^3}.$$  

(2.30)

For the special case of an anisotropic host and only nearest neighbor interactions, the dispersion relation for the $L$ waves is implicitly given by

$$1 = \frac{4}{3} \frac{a^3}{d^3} \frac{\delta \epsilon_\parallel}{1 - \Gamma_\parallel \delta \epsilon_\parallel} \frac{1}{\epsilon_\perp} \cos kd,$$

(2.31)

and for the $T$ waves by

$$1 = -\frac{2}{3} \frac{a^3}{d^3} \frac{\delta \epsilon_\perp}{1 - \Gamma_\perp \delta \epsilon_\perp} \frac{\epsilon_\parallel}{\epsilon_\perp} \cos kd.$$

(2.32)

As a check, we can consider the isotropic limit with a vacuum host, where $\epsilon_\parallel = \epsilon_\perp = 1$, and $\Gamma_{xx} = \Gamma_{yy} = \Gamma_{zz} = -1/3$. In this case, the equations for both the parallel and perpendicular cases, for both nearest-neighbor and further neighbor interactions, reduce to the results obtained in Ref. [18] for both $L$ and $T$ modes, as expected.

Eqs. (2.31) and (2.32) neglect damping of the waves due to dissipation within the metallic particles. To include the effect of damping, one can simply solve Eq. (2.31) or (2.32) for $k(\omega)$, using the Drude function with a finite $\tau$. The resulting $k(\omega)$ will be complex in both cases; $[Imk(\omega)]^{-1}$ gives the exponential decay length of the $L$ or $T$ wave along the chain.\(^6\)

Now, let us repeat this calculation but with the principal axis of the liquid crystalline host parallel to the $x$ axis, while the chain itself again lies along the $z$ axis. The self-consistent equation for the dipole moments again takes the form (2.26), but the diagonal elements of $\hat{G}$ are given by $G_{ii}(x - x') = \partial_i' \partial_i G(x - x')$, where $G(x - x')$ is suitably modified for a host where $\hat{x}$ is the symmetry axis.

\(^6\)Im$k(\omega)$ means we take the imaginary part of the complex quantity $k(\omega)$. 
For the case of interest, where $x = nd\hat{z} \equiv z_n\hat{z}$, $x' = n'd\hat{z} \equiv z_{n'}\hat{z}$, one finds that

$$G_{xx}(x - x') = \frac{1}{4\pi} \frac{\epsilon_{\perp}^{1/2}}{\epsilon_{\parallel}} \frac{1}{|z_n - z_{n'}|^3},$$

$$G_{yy}(x - x') = \frac{1}{4\pi} \frac{\epsilon_{\perp}^{1/2}}{\epsilon_{\parallel}^{1/2}} \frac{1}{|z_n - z_{n'}|^3},$$

$$G_{zz}(x - x') = -\frac{1}{2\pi} \frac{1}{\epsilon_{\perp}^{1/2}} \frac{1}{\epsilon_{\parallel}^{1/2}} |z_n - z_{n'}|^3,$$

with other (off-diagonal) elements of $\hat{G}$ vanishing. The self-consistency condition determining the relation between $\omega$ and $k$ can be written out, for all three polarizations. We write out the result only the case of nearest neighbor dipole-dipole interactions. The resulting dispersion relations can be written in the form $1 = -\frac{8\pi a^3 d^3}{3} \frac{\delta\epsilon_{ii}}{d^3} G_{ii}(d) \cos kd$ for modes polarized in the $i$th direction. Substituting in the values of $G_{ii}$ for the three cases, we obtain

$$1 = -\frac{2a^3}{3d^3} \frac{\delta\epsilon_{xx}}{1 - \Gamma_{xx} \delta\epsilon_{xx} \epsilon_{\parallel}^{3/2}} \cos kd,$$

$$1 = -\frac{2a^3}{3d^3} \frac{\delta\epsilon_{yy}}{1 - \Gamma_{yy} \delta\epsilon_{yy} \epsilon_{\parallel}^{1/2}} \sqrt{\epsilon_{\perp}} \cos kd,$$

$$1 = \frac{4a^3}{3d^3} \frac{\delta\epsilon_{zz}}{1 - \Gamma_{zz} \delta\epsilon_{zz} \epsilon_{\perp}^{1/2}} \epsilon_{\parallel} \cos kd,$$

(2.34)

where $\Gamma_{xx} = \Gamma_{\parallel}$, $\Gamma_{yy} = \Gamma_{zz} = \Gamma_{\perp}$. In this case, $\delta\epsilon_{xx} = \epsilon(\omega) - \epsilon_{\parallel}$, while $\delta\epsilon_{yy} = \delta\epsilon_{zz} = \epsilon(\omega) - \epsilon_{\perp}$. These equations can again be solved for $k(\omega)$ in the three cases, with or without a finite $\tau$, leading to dispersion relations with or without single-particle damping.

### 2.4.7 Cholesteric Liquid Crystalline Host

Next, we consider the case where the host is a cholesteric liquid crystal, also known as a chiral nematic liquid crystal. In such a material, the director, instead of pointing everywhere in the same direction, rotates in space about an axis perpendicular to the director. To be definite, we assume that the director $\mathbf{n}(x)$ has the following dependence on position:

$$\mathbf{n}(x) = \hat{x} \cos(\alpha z) + \hat{y} \sin(\alpha z).$$

(2.35)
That is, the director rotates around the $z$ axis with pitch angle $\alpha$. We still assume that the chain of nanoparticles lies along the $z$ axis. Thus, the director is always perpendicular to that chain as shown in Fig. 2.2b.

As a simple model, we assume that the dielectric tensor of the cholesteric liquid crystal is locally the same as that of an NLC, except that the symmetry axis of the tensor spirals around the $z$ axis with pitch angle $\alpha$. The tensor can then be written

$$\hat{\epsilon}(z) = \hat{R}^{-1}(z)\hat{\epsilon}\hat{R}(z),$$

(2.36)

where $\hat{\epsilon}$ is the dielectric tensor of a nematic liquid crystal with nonzero components $\epsilon_{xx} = \epsilon_{\parallel}$, $\epsilon_{yy} = \epsilon_{zz} = \epsilon_{\perp}$, and $\hat{R}(z)$ is a matrix corresponding to a rotation about the $z$ axis by angle $\alpha z$, with non-zero components

$$R_{xx}(z) = R_{yy}(z) = \cos(\alpha z),$$

$$R_{xy}(z) = -R_{yx}(z) = \sin(\alpha z),$$

$$R_{zz}(z) = 1.$$  

(2.37)

This model is, in fact, a special case of a more general model given for a cholesteric liquid crystal in Ref. [51]. It is less general than the latter because, unlike the case considered in [51], the model used here has, besides the pitch angle, only two independent components of the dielectric tensor ($\epsilon_{\perp}$ and $\epsilon_{\parallel}$) rather than three. However, the model used here should be sufficient to suggest the kinds of qualitative effects of immersing the metal particle chain in a CLC host.

Next, we calculate the dispersion relations for plasmonic waves propagating along the chain of metallic nanoparticles in the presence of this host, using a simple approximation. We again start with Eq. (2.26). For simplicity, we include only nearest-neighbor interactions. Then, for the case of a CLC host, Eq. (2.26) becomes

$$p_n = -\frac{4\pi a^3}{3} \left( \hat{t}_{n+1}\hat{\mathcal{G}}_{n,n+1} \cdot \mathbf{p}_{n+1} + \hat{t}_{n-1}\hat{\mathcal{G}}_{n,n-1} \cdot \mathbf{p}_{n-1} \right).$$

(2.38)

Here $\hat{t}_{n} \hat{\mathcal{G}}_{n,n'} \mathbf{p}_{n'}$ represents the dipolar field at the position of $\mathbf{p}_n$ induced by the dipole $\mathbf{p}_{n'}$.  

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To a good approximation, this field will be the same as that found in the case of an NLC host with director perpendicular to the chain, except that both the induced dipole \( p_{n'} \), and the corresponding dipolar field, are rotated by an amount which increases linearly with position along the \( z \) axis. (This way of expressing the dipolar field is only approximately valid, because the sphere is embedded in a dielectric which is not only anisotropic but also inhomogeneous, varying with position along the \( z \) axis.) With this assumption, the product \( \hat{t}_{n'} \hat{G}_{n,n'} \) can be written

\[
\hat{t}_{n'} \hat{G}_{n,n'} = \hat{R}^{-1}(z_{n'}) (i \hat{G}(z_{n} - z_{n'})) \hat{R}(z_{n'}),
\]

(2.39)

where the components of \( \hat{R}(z) \) are given in Eq. (2.37).

From these equations, we can see that the \( L \) and \( T \) waves are still decoupled, as in the case of an NLC host with director perpendicular to the chain. The \( L \) modes are unchanged from the NLC case, but the \( T \) modes are altered. To see how the \( T \) modes are changed, first note that the elements of \( \hat{G}(z_{n} - z_{n}') \) depend only on \( |z_{n} - z_{n}'| \) and hence are the same for both positive and negative arguments. If we then make the transformation \( p_{n'} = \hat{R}^{-1}(z_{n'}) \cdot \tilde{p}_{n'} \), we find

\[
\hat{R}^{-1}(z_{n}) \cdot \tilde{p}_{n} = -\frac{4\pi a^3}{3} \hat{R}^{-1}(z_{n+1}) [i \hat{G}_{n,n+1} \cdot \tilde{p}_{n+1} + \hat{R}^{-1}(z_{n-1}) i \hat{G}_{n,n-1} \cdot \tilde{p}_{n-1}].
\]

(2.40)

Next, noting that

\[
\hat{R}^{-1}(z_{n \pm 1}) = \hat{R}^{-1}(z_{n}) \hat{R}^{-1}(\pm z_{1}),
\]

(2.41)

we can rewrite Eq. (2.38) as

\[
\tilde{p}_{n} = -\frac{4\pi a^3}{3} [\hat{R}^{-1}(z_{1}) i \hat{G}_{n,n+1} \cdot \tilde{p}_{n+1} + \hat{R}(z_{1}) i \hat{G}_{n,n-1} \cdot \tilde{p}_{n-1}],
\]

(2.42)

where we use \( \hat{R}(z_{1}) = \hat{R}^{-1}(-z_{1}) \).

We now write out Eq. (2.42) explicitly and obtain dispersion relations for the two transverse branches. We consider only the \( x \) and \( y \) components of Eq. (2.42), since the \( L \) branch is unchanged from the purely NLC case and does not couple to the \( T \) branches. Then we can consider only the 2 \( \times \) 2 \( (xy) \) block of the \( \hat{t} \) matrix, which is diagonal with nonzero
components $\delta \epsilon_{\parallel} (1 - \Gamma_{\parallel} \delta \epsilon_{\parallel})^{-1}$ and $\delta \epsilon_{\perp} (1 - \Gamma_{\perp} \delta \epsilon_{\perp})^{-1}$. We also need $\hat{G}_{n,n+1}$ whose components are given by $G_{xx} = [1/(4\pi d^3)](\epsilon_{\perp}^{1/2}/\epsilon_{\parallel}^{3/2})$, $G_{yy} = [1/(4\pi d^3)][1/(\epsilon_{\parallel}^{1/2}\epsilon_{\perp}^{1/2})]$, where $d$ is the lattice constant of the nanoparticle chain. We denote the non-zero diagonal elements of the product matrix $\hat{t}\hat{G}_{n,n+1}$ by $\tau_{xx} = t_{xx} G_{xx}$ and $\tau_{yy} = t_{yy} G_{yy}$.

Finally, we seek a traveling wave solution to Eq. (2.42) of the form $\tilde{\rho}_{n,x} = \tilde{\rho}_{x0} \exp(iknd)$; $\tilde{\rho}_{n,y} = \tilde{\rho}_{y0} \exp(iknd)$. Then, after a little algebra, and using the $2 \times 2$ block of Eq. (2.37) for $\hat{R}(z_n)$, we obtain the following equation determining the two-component column matrix $\tilde{\rho}_0$ whose components are $\tilde{\rho}_{x0}$, $\tilde{\rho}_{y0}$:

$$\tilde{\rho}_0 = -\frac{8\pi a^3}{3} {\hat{M}}(k, \omega) \cdot \tilde{\rho}_0 \tag{2.43}$$

where $\hat{M}$ is found to have components

$$M_{xx} = \tau_x \cos(\alpha d) \cos(kd),$$
$$M_{xy} = -i \tau_y \sin(\alpha d) \sin(kd),$$
$$M_{yx} = i \tau_x \sin(\alpha d) \sin(kd),$$
$$M_{yy} = \tau_y \cos(\alpha d) \cos(kd). \tag{2.44}$$

Eq. (2.43) has nontrivial solutions if

$$\det \left[ 1 + \frac{8\pi a^3}{3} {\hat{M}}(k, \omega) \right] = 0. \tag{2.45}$$

Upon writing out the determinant of Eq. (2.45) we find that it is quadratic in $\cos(kd)$ and therefore we can find two solutions for $\cos(kd)$ (and hence $kd$) as functions of $\omega$, and thus two transverse branches to the dispersion relation.

After simplification of the determinant of Eq. (2.45) we find solutions for $\cos(kd)$ by solving

$$(1 - \Gamma_{\perp} \delta \epsilon_{\perp})(1 - \Gamma_{\parallel} \delta \epsilon_{\parallel}) + L \cos(\alpha d) \cos(kd) + M[\cos^2(kd) - \sin^2(\alpha d)] = 0, \tag{2.46}$$

where

$$L = \frac{2}{3} a^3 \left[ \epsilon_{\perp}^{1/2} \delta \epsilon_{\parallel}(1 - \Gamma_{\parallel} \delta \epsilon_{\parallel}) + \frac{1}{\epsilon_{\parallel}^{1/2} \epsilon_{\perp}^{1/2}} \delta \epsilon_{\perp}(1 - \Gamma_{\parallel} \delta \epsilon_{\parallel}) \right]. \tag{2.47}$$
and

\[ M = 4 a^6 \frac{1}{9} \frac{1}{\omega^2} \delta \epsilon \delta \epsilon . \]  

(2.48)

The left-hand side of Eq. (2.46) is quadratic in \( \epsilon \) and thus has two solutions for \( \epsilon \) as a function of \( \cos(kd) \). If \( \epsilon(\omega) = 1 - \omega_p^2/\omega^2 \), these lead to two solutions for \( \omega \) as a function of \( \cos(kd) \), or equivalently, of \( k \) (since \( \cos(kd) \) is monotonic in \( k \) in the range \( 0 < k < \pi/d \)). We use the convention that \( \omega > 0 \). If we use the Drude form for \( \epsilon(\omega) \) with a finite \( \tau \) to include single-grain dissipation, we write \( \cos(kd) = \frac{\exp(ikd) + \exp(-ikd)}{2} \). Then there are four solutions for \( \exp(ikd) \) and hence for \( k \), of which two have \( \text{Im}(kd) > 0 \) which allows these solutions to decay as \( d \to \infty \). Thus, this procedure again gives two \( T \) branches which include single-particle damping if \( \epsilon(\omega) \) has the Drude form with a finite lifetime.

2.5 Dispersion Relations of Metallic Chains in an anisotropic host: Numerical Examples

As a first numerical example, we calculate the plasmon dispersion relations for a chain of spherical Drude metal particles immersed in an NLC and \( a/d = 1/3 \). We consider two cases: liquid crystal director parallel and perpendicular to the chain axis, which we take as the \( z \) axis. For \( \epsilon|| \) and \( \epsilon\perp \), we take the values found in experiments described in Ref. [28], which were carried out on the NLC known as E7. For comparison, we also show the corresponding dispersion relations for an isotropic host of dielectric constant which is arbitrarily taken as \( \frac{1}{3} \epsilon || + \frac{2}{3} \epsilon \perp = 2.5611 \). The results of these calculations are shown in Figs. 2.3 and 2.4 in the absence of damping (\( \tau \to \infty \) in the Drude expression). As can be seen, both the \( L \) and \( T \) dispersion relations are significantly altered when the host is a nematic liquid crystal rather than an isotropic dielectric; in particular, the widths of the \( L \) and \( T \) bands are changed. When the director is perpendicular to the chain axis, the two \( T \) branches are split when the host is an NLC, whereas they are degenerate for an isotropic host, or an NLC host with director parallel to the chain.

Next, we turn to the case of a chain of metal particles immersed in a cholesteric liquid crystal. We assume that the nematic axis lies in the \( xy \) plane, the chain runs parallel to the
Figure 2.3: Calculated dispersion relations $\omega(k)$ for plasmon waves along a chain of metallic nanoparticles, in the presence of an NLC host. We plot $\omega/\omega_p$, where $\omega_p$ is the plasma frequency, as a function of $kd$, where $d$ is the distance between sphere centers. Green and blue (x’s and +’s): $L$ and $T$ modes for a chain embedded in an NLC with director parallel to the chain. The NLC is assumed to have principal dielectric tensor elements $\epsilon_\parallel = 3.0625$ and $\epsilon_\perp = 2.3104$ parallel and perpendicular to the director, corresponding to the material known as E7. In this and subsequent plots $a/d = 1/3$, where $a$ is the metallic sphere radius. Also shown are the corresponding $L$ and $T$ dispersion relations (black and red solid lines, respectively) when the host is isotropic with dielectric constant $\epsilon_h = 2.5611 = \frac{1}{3}\epsilon_\parallel + \frac{2}{3}\epsilon_\perp$.

$z$ axis, and the nematic axis rotates about the $z$ axis with a pitch angle $\alpha$. The calculated dispersion relations for the two $T$ branches are shown in Fig. 2.5 for two different choices of pitch angle $\alpha$, as well as for $\alpha = 0$, corresponding to the purely nematic case. For comparison, we also show the dispersion relation for the doubly degenerate $T$ branch when the host is an isotropic dielectric with dielectric constant $\epsilon = \frac{1}{3}\epsilon_\parallel + \frac{2}{3}\epsilon_\perp = 2.5611$. We again assume that there is no dissipation. As is evident, the dispersion relations do depend slightly on $\alpha$. But while in the case of an NLC host the two $T$ branches are linearly polarized with polarization along the $x$ and $y$ axes, respectively, the two $T$ branches in the cholesteric case are no longer linearly polarized. Instead, each of these two branches has a polarization
Figure 2.4: Same as Fig. 2.3 except that the director of the NLC is perpendicular to the chain of metal nanoparticles. The frequencies of the \( L \) modes (asterisks, in green) and \( T \) modes (+’s and x’s, shown in dark and light blue), divided by the plasma frequency \( \omega_p \), are plotted versus \( kd \). The NLC has the same dielectric tensor elements as in Fig. 2.3. Also shown are the corresponding \( L \) (solid black) and \( T \) (solid red) branches for an isotropic host with \( \epsilon_h = 2.5611 \). Note that the \( T \) branches which were degenerate in Fig. 2.3 are split into two branches in this NLC geometry.

vector which rotates as a function of \( z \).

2.6 Effects of Magnetic Fields on these Dispersion Relations

In the absence of a magnetic field, the medium inside the metallic particles is assumed to have a scalar dielectric function \( \epsilon(\omega) \) as discussed in the previous sections. If there is a magnetic field along the \( z \) axis, the dielectric function of the particles, \( \hat{\epsilon} \), becomes a tensor, whose components may be written

\[
\begin{align*}
\epsilon_{xx}(\omega) &= \epsilon_{yy}(\omega) = \epsilon_{zz}(\omega) = \epsilon(\omega) \\
\epsilon_{xy}(\omega) &= -\epsilon_{yx}(\omega) = iA(\omega),
\end{align*}
\]  

(2.49)
Figure 2.5: Calculated dispersion relations $\omega(k)$ for plasmon waves along a chain of metallic nanoparticles in the presence of a cholesteric liquid crystal host. We assume that the director rotates about an axis parallel to the chain of metal nanoparticles with a pitch angle $\alpha$. The red (open square and filled square) plots and blue (crosses and triangles) represent the two $T$ branches for $\alpha d = \pi/6$ and $\pi/3$ respectively, while the black (full circles and asterisks) correspond to $\alpha d = 0$ (nematic liquid crystal). In all cases we assume $\epsilon_\parallel = 3.06525$ and $\epsilon_\perp = 2.5611$. The green points (full circles) represent an isotropic host with $\epsilon = \frac{1}{4}\epsilon_\parallel + \frac{2}{3}\epsilon_\perp = 2.5611$.

with all other components vanishing [52]. In the following calculations, we assume that the nanoparticle are adequately described by a Drude dielectric function. (We will exclude the effects of any induced magnetic dipole moment within the liquid crystal). In this case, the components of the dielectric tensor take the form [52]

$$\epsilon(\omega) = 1 - \frac{\omega_p^2}{\omega(\omega + i/\tau)} = 1 - \frac{\omega_p^2}{\omega^2},$$  \hspace{1cm} (2.50)$$

and

$$A(\omega) = -\frac{\omega_p^2\tau}{\omega} \frac{\omega_c\tau}{(1 - i\omega\tau)^2} = \frac{\omega_p^2\omega_c}{\omega^3},$$  \hspace{1cm} (2.51)$$

where $\omega_p$ is the plasma frequency, $\tau$ is a relaxation time, and $\omega_c = eB/(mc)$ is the cyclotron frequency, where $B = B\hat{z}$ is the magnetic field, $m$ is the electron mass, $e$ is its charge and
the second equality is the limit when $\omega \tau \to \infty$.

The dielectric tensor of the liquid crystal, $\hat{\epsilon}_h$, is assumed to have principal dielectric constants equal to

$$
\begin{align*}
\epsilon_{h,xx} &= \epsilon_{h,yy} = \epsilon_\perp, \\
\epsilon_{h,zz} &= \epsilon_\parallel
\end{align*}
$$

(2.52)

when the director axis of the NLC lies parallel to the metallic chain, and

$$
\begin{align*}
\epsilon_{h,xx} &= \epsilon_\parallel, \\
\epsilon_{h,yy} &= \epsilon_{h,zz} = \epsilon_\perp
\end{align*}
$$

(2.53)

when it is perpendicular to the metallic chain.

### 2.6.1 Nematic Liquid Crystal with a Static Magnetic Field Either Parallel or Perpendicular to Director Axis

We now consider the effects of placing a chain of metallic particles into a NLC host with a static magnetic field oriented parallel to the liquid crystal director and parallel to the metallic chain. In this orientation we find that the components of the matrix $\hat{t}$ given in Eq. (2.25) can be written, to first order in the quantity $A(\omega)$ (which is assumed to be small) as

$$
\begin{align*}
t_{xx} &= \frac{\delta \epsilon_{xx}}{1 - \Gamma_{xx}\delta \epsilon_{xx}} \\
t_{yy} &= \frac{\delta \epsilon_{yy}}{1 - \Gamma_{yy}\delta \epsilon_{yy}} \\
t_{zz} &= \frac{\delta \epsilon_{zz}}{1 - \Gamma_{zz}\delta \epsilon_{zz}} \\
t_{xy} = -t_{yx} &= \frac{iA(\omega)}{(1 - \Gamma_{xx}\delta \epsilon_{xx})(1 - \Gamma_{yy}\delta \epsilon_{yy})}.
\end{align*}
$$

(2.54)

From Eq. (2.54) we see that the $\hat{z}$ component of the dipole wave does not couple to the $\hat{x}$ and $\hat{y}$ components. Therefore, we can separate the matrix $\hat{t}$ to a $2 \times 2$ matrix and a $1 \times 1$ matrix. The $2 \times 2$ matrix, after a bit of algebra and the assumption that the dipole
moments can be written as plane waves of the form \( p_n = p_0 n \exp(in k d - i \omega t) \), give a matrix equation for the dipole moment \( p_0 n \) equal to

\[
p_0 n = -\frac{8 \pi a^3}{3} \left[ \begin{pmatrix} G_{xx} t_{xx} & G_{xx} t_{xy} \\ -G_{yy} t_{xy} & G_{yy} t_{yy} \end{pmatrix} \cos(k d) p_0 n \right]
\]

(2.55)

where the relevant greens functions \( G_{xx} = G_{yy} = \frac{\epsilon_\|}{4 \pi \epsilon_\perp} \frac{1}{d^3} \). The remaining \( 1 \times 1 \) matrix is treated in a manner similar to the NLC case with no magnetic field considered previously.

By setting \( p_\pm = p_{nx} \pm ip_{ny} \), \( t_\pm = t_{xx} \pm it_{xy} \) in Eq. (2.55), and noting that \( G_{xx} = G_{yy} \), we can write down the dispersion relation for a chain of metallic nanoparticle in a nematic liquid crystal host with a static magnetic field parallel to the liquid crystal director as

\[
1 = -\frac{2 a^3 \epsilon_\| \epsilon_\perp}{3 d^3} \left( \frac{\epsilon(\omega) - 1}{\epsilon(\omega) + 2} \pm \frac{3 A(\omega)}{(\epsilon(\omega) + 2)^2} \right) \cos(k_\pm d)
\]

(2.56)

where the \( \pm \) corresponds to the left- and right-circularly polarized \( T \) waves. Since the frequency-dependences of both \( \epsilon(\omega) \) and \( A(\omega) \) is assumed known, these equations represent implicit relations between \( \omega \) and \( k_\pm \) for these transverse waves.

For a magnetic field perpendicular to the chain and perpendicular to the NLC director axis (let us say, along the \( x \) axis), the non-vanishing elements of the matrix \( t \) become, to first order in \( A(\omega) \),

\[
\begin{align*}
t_{xx} &= \delta \epsilon_{xx} \\
t_{yy} &= \delta \epsilon_{yy} \\
t_{zz} &= \delta \epsilon_{zz} \\
t_{yz} &= -t_{zy} = \frac{iA(\omega)}{(1 - \Gamma_{yy} \delta \epsilon_{yy})(1 - \Gamma_{zz} \delta \epsilon_{zz})}
\end{align*}
\]

(2.57)

with other elements equal to zero. From Eq. (2.57) it is clear that waves polarized along the \( \hat{x} \) direction are unaffected by the magnetic field. Thus, the \( \hat{y} \) and \( \hat{z} \) components of the polarized waves are coupled. Also, in this geometry, the Green’s functions given by \( G_{yy} = \frac{\epsilon_\|}{4 \pi \epsilon_\perp} \frac{1}{d^3} \) and \( G_{zz} = -\frac{1}{2 \pi \epsilon_\perp} \frac{1}{d^3} \) [2]. Again we assume that the dipole moments are plane
waves and find that the self-consistent equations become:

\[
\begin{align*}
p_{0y} &= \frac{-2a^3}{3d^3} \left[ \frac{\epsilon_{\parallel}}{\epsilon_{\perp}} t_{yy} p_{0y} - \frac{2}{\epsilon_{\perp}} t_{yz} p_{0z} \right] \cos(kd) \\
p_{0z} &= \frac{-2a^3}{3d^3} \left[ -\frac{\epsilon_{\parallel}}{\epsilon_{\perp}} t_{yz} p_{0y} - \frac{2}{\epsilon_{\perp}} t_{zz} p_{0z} \right] \cos(kd). 
\end{align*}
\]

(2.58)

If we solve the pair of equations for \(p_{0y}\) and \(p_{0z}\) for a given value of \(k_{\pm}\), we obtain a nonzero solution only if the determinant of the matrix of coefficients vanishes. For a given real frequency \(\omega\), there will, in general, be two solutions for \(k(\omega)\) which decay in the \(+z\) direction. These correspond to two branches of propagating plasmon (or plasmon polariton) waves, with dispersion relations which we may write as \(k_{\pm}(\omega)\). The frequency dependence appears in \(t_{yz}\), \(t_{yy}\), and \(t_{zz}\) which depend on \(\omega\) [through \(\epsilon(\omega)\) and \(A(\omega)\)]. However, unlike the case where the magnetic field is parallel to the \(z\) axis, the waves are not circularly polarized but are elliptically polarized, and the two solutions are non-degenerate. Because \(A(\omega)\) is usually small, the ellipse has a high eccentricity, and the change in propagation characteristics due to the magnetic field will usually be small for this magnetic field direction.

### 2.6.2 Cholesteric Liquid Crystal with an Applied Magnetic Field Along the Director Axis

We now consider placing the chain of metallic nanoparticle into a CLC host as shown in Fig. 2.2, in the presence of a static magnetic field which couples two of the three polarization modes. For a CLC the matrix \(\hat{t}\) found in Eq. (2.26) and the polarization vector \(p_n\) become rotated as shown previously. As a result of this rotation along the \(\hat{z}\) direction, the coupled dipole equation in Eq. (2.26) changes to

\[
\tilde{p}_n = -\frac{4\pi a^3}{3} \left[ \hat{R}^{-1}(z_1) \hat{t} \hat{G} \cdot \tilde{p}_{n+1} + \hat{R}(z_1) \hat{t} \hat{G} \cdot \tilde{p}_{n-1} \right],
\]

(2.59)

where Eq. 2.37 is used for the rotation matrix \(\hat{R}\) and we define \(\tilde{p}_n\) by \(p_n = \hat{R}^{-1}(z_n) \cdot \tilde{p}_n\).

In the presence of a static magnetic field parallel to both the chain axis and the twist axis of the CLC, the \(L\) branch decouples from the two \(T\) branches as it did in the NLC case discussed previously. The two remaining \(T\) branches are coupled together in Eq. (2.59) and
require the $2 \times 2$ matrix forms of the matrices $\hat{t}$ and $\hat{G}$. Because the off-diagonal elements of the dielectric tensor satisfy $\epsilon_{ji} = -\epsilon_{ij}$, in a magnetic field, it can be shown that $\hat{G}$ is diagonal and unchanged from its zero-field form. We may write the diagonal elements of $\hat{G}$ as $G_{xx} = \frac{1}{4\pi d^3} \frac{\epsilon_{\|}^{1/2}}{\sqrt{\epsilon_{\|} \epsilon_{\perp}}} \epsilon_{1/2}^{\perp} \epsilon_{3/2}^{\|}$ and $G_{yy} = \frac{1}{4\pi d^3} \frac{1}{\sqrt{\epsilon_{\|} \epsilon_{\perp}}}$. The elements of the matrix $\hat{t}$ are unchanged from their form in Eq. (2.57).

Following the methods of the previous sections, we can write down the $2 \times 2$ matrix for the coupled dipole equations in the rotated $\hat{x}$ and $\hat{y}$ directions. This equation is

$$\tilde{p}_0 = -\frac{2a^3}{3d^3} M(k,\omega) \cdot \tilde{p}_0,$$  \hspace{1cm} (2.60)

where $\tilde{p}_0$ is the rotated two-component column vector whose components are $\tilde{p}_{x0}$ and $\tilde{p}_{y0}$. The matrix $M(k,\omega)$ includes the contribution from the scattering matrix $\hat{t}$ and the elements of the $2 \times 2$ rotation matrix defined in Eq. (2.37). The components of the matrix $M(k,\omega)$ are

$$M_{xx} = \frac{\epsilon_{\perp}^{1/2}}{\epsilon_{\|}^{1/2}} \left[ t_{xx} \cos(kd) \cos(\alpha d) + it_{xy} \sin(kd) \sin(\alpha d) \right],$$

$$M_{yy} = \frac{1}{\sqrt{\epsilon_{\perp} \epsilon_{\|}}} \left[ t_{yy} \cos(kd) \cos(\alpha d) + it_{xy} \sin(kd) \sin(\alpha d) \right],$$

$$M_{xy} = \frac{1}{\sqrt{\epsilon_{\perp} \epsilon_{\|}}} \left[ t_{xy} \cos(kd) \cos(\alpha d) - it_{yy} \sin(kd) \sin(\alpha d) \right],$$

$$M_{yx} = \frac{\epsilon_{\perp}^{1/2}}{\epsilon_{\|}^{1/2}} \left[ it_{xx} \sin(kd) \sin(\alpha d) - t_{xy} \cos(kd) \cos(\alpha d) \right].$$  \hspace{1cm} (2.61)

With the external magnetic field parallel to the rotation axis of the CLC, one can determine the dispersion relation for the two $T$ waves as non-trivial solutions to the determinate of Eq. (2.60).

The most interesting result of the dispersion relations corresponding to Eqs. (2.60) and (2.61) is that the presence of a magnetic field will lead to dispersion relations which are non-reciprocal, i.e., $\omega(k) \neq \omega(-k)$ in general. The magnetic field appears only in the off-diagonal elements $t_{xy}$ and $t_{yx}$, which are linear in the field except for very large fields. The terms involving $t_{xy}$ and $t_{yx}$ in Eq. (2.61) are multiplied by $\sin(kd)$ and thus change sign when $k$ changes sign. Thus, the secular equation determining $\omega(k)$ is not even in $k,$
implying that the dispersion relations are non-reciprocal. This non-reciprocity becomes zero when the host is an NLC because, in an NLC, the rotation angle $\alpha = 0$ and all the terms involving $\sin(kd)$ vanish. In the presence or absence of a magnetic field, the difference in wave number of a right-moving or left-moving wave is given by

$$\Delta k(\omega) = |\text{Re}[k_{i,L}]| - |\text{Re}[k_{i,R}]|, \quad (2.62)$$

where $i = \pm$ for the two elliptical polarizations and $L, R$ for either the left-moving or right-moving branch. If, for example, $\Delta k(\omega) \neq 0$ then the left- and right-moving waves have different wave numbers for a given frequency and are non-reciprocal.

### 2.6.3 Faraday Rotation and Ellipticity

By solving Eqs. (2.55) or (2.58) for $k(\omega)$ one finds that the two waves propagating along the nanoparticle chain have different wave vectors $k_+$ and $k_-$ for the same frequency $\omega$. Since any linearly polarized wave is composed of right- and left-circularly polarized waves, this behavior corresponds to a rotation of the plane of polarization of a linearly polarized wave, as it propagates down the chain, and is analogous to the usual Faraday effect in a bulk dielectric. The angle of rotation per unit chain length may be written as

$$\theta(\omega) = \frac{1}{2} [k_+(\omega) - k_-(\omega)]. \quad (2.63)$$

In the absence of damping, $\theta$ is real. If $\tau$ is finite, the electrons in each metal particle will experience damping within each particle, leading to an exponential decay of the plasmon waves propagating along the chain. This damping is automatically included in the above formalism, and can be seen most easily if only nearest neighbor coupling is included. The quantity

$$\theta(\omega) = \theta_1(\omega) + i\theta_2(\omega) \quad (2.64)$$

is then the complex angle of rotation per unit length of a linearly polarized wave propagating along the chain of metal particles. By analogy with the interpretation of a complex $\theta$ in a homogeneous bulk material, $\text{Re}[\theta(\omega)]$ represents the angle of rotation of a linearly polarized
wave (per unit length of chain), and $\text{Im} \theta(\omega)$ as the corresponding Faraday ellipticity i.e., the degree to which the initially linearly polarized wave becomes elliptically polarized as it propagates along the chain.

### 2.7 Dispersion Relations in the Presence of a Static Magnetic Field: Numerical Results

We first consider the case of a NLC in a magnetic field parallel to the liquid crystal director and metallic chain axis. As noted earlier, the $L$ waves are unaffected by a magnetic field, but the $T$ waves are split into left- and right-circularly polarized waves. To illustrate the predictions of our simple expressions, we again take $a/d = 1/3$, and we assume a magnetic field such that the ratio $\omega_c/\omega_p = 3.5 \times 10^{-5}$. For a typical metallic plasma frequency of $\sim 10^{16}$ sec$^{-1}$, this ratio would correspond to a magnetic induction $B \sim 2$ T. We consider both the undamped and damped case where we set $\omega_p \tau = 100$. For propagating waves we also require that $\text{Im} \left[ k_{\pm} \right] > 0$ as these waves decay, as expected, when $z \to \infty$. Using these parameters and the requirement that $\text{Im} \left[ k_{\pm} \right] > 0$, we show in Fig. 2.6 the dispersion relations for the two circular polarizations for plasmonic waves propagating along a metallic chain in a NLC with the magnetic field parallel to the metallic chain axis, with and without single-particle damping. The splitting between the two circularly polarized $T$ waves is not visible on the scale of the figure.

We also plot the corresponding rotation angles $\theta d$ for a distance equal to one interparticle spacing in Fig. 2.7. When there is no damping we find that both the real and imaginary parts of $\theta d$ are approximately zero and they become non-zero only when damping is included by setting $\omega_p \tau = 100$. In this case, both $\text{Re} \left[ \theta(\omega) d \right]$ and $\text{Im} \left[ \theta(\omega) d \right]$ never exceed about $1 \times 10^{-6}$ degrees, showing that a linear incident wave acquires little ellipticity over such distances. Since theory and experiment suggests that the wave intensity typically has an exponential decay length of no more than around 20 interparticle spacings [53], the likely Faraday rotation of such a wave in practice will probably not exceed a millidegree or two, at most, even for a field as large as $2T$. Thus, while the rotation found here is likely to be
measurable, it may not be large, at least for this simple chain geometry with one particle per unit cell. The present expressions also indicate that $\theta d$ is very nearly linear in $B$, so a larger rotation could be attained by increasing $B$.

For the case of the metallic chain in a NLC where $\mathbf{B} \perp \hat{z}$, we find, using the same parameters and requirements as the previous case, that two non-degenerate dispersion relations (one an $L$ and the other a $T$ wave) become mixed even when $B \rightarrow 0$. The dispersion relations, again with and without damping, are plotted in Fig. 2.8 and the corresponding rotation angles are plotted in Fig. 2.9 using Eq (2.63). When compared to Fig. 2.4, one can see that the dispersion relations in Fig. 2.8 are modified due to the finite damping and presence of the magnetic field. The rotation angle in Fig. 2.9 for both the $Re[\theta(\omega)d]$ and
Im[θ(ω)d] are on the order of 2° per interparticle spacing. Therefore, the rotation achieved with $B \perp \hat{z}$ can be large for experimentally available lengths.

Finally, we discuss the results of the metallic chain immersed in a CLC in which the rotation axis of the crystal lies in the $\hat{z}$ direction and in the presence of a magnetic field along $\hat{z}$. Using the same host dielectric constants given above and using a rotation angle of $\alpha_d = \pi/6$, we show in Fig. 2.10 the dispersion relations, plotted against $|kd|$, for the two rotated dipole moments and the corresponding difference in wavenumber between the left- and right-moving waves as $\Delta k(\omega)$. Since we found that $\Delta k(\omega)$ is non-zero in a limited frequency range this suggests that one-way wave-guiding is possible. That is, within this frequency range, if we launched a linearly polarized plane wave with a set frequency $\omega_1$ and wave vector $k_1$ then any reflected or backscattered wave traveling at $\omega_1$ could only travel with the same frequency if it had a wave vector $-k_2$ different in magnitude and direction.
Figure 2.10: a) Black symbols: the dispersion relations for right-moving plasmon waves propagating along a chain of metallic nanoparticle immersed in a CLC host plotted as a function of $|kd|$. Blue Symbols: the dispersion relations for the left-moving plasmon waves propagating along a chain of metallic nanoparticle immersed in a CLC host plotted as a function of $|kd|$. We assume that $\omega_c/\omega_p = 3.5 \times 10^{-5}$, where $\omega_c = eB/mc$ is the cyclotron frequency, $\omega_p \tau = 100$, and $\alpha d = \pi/6$. For $\omega_p = 1.0 \times 10^{16}$ sec$^{-1}$, the chosen $\omega_c/\omega_p$ corresponds to about 2 T. b) The difference in wave number for a given frequency, $\Delta k(\omega) = |Re[k_{i,L}]| - |Re[k_{i,R}]|$ where $i = \pm$ for the two elliptical polarizations and $L, R$ for either the left-moving or right-moving branch. Note that a non-zero value of $\Delta k(\omega)$ implies that for a given frequency the left and right traveling waves have a different wavenumber.

such that $|k_1| \neq |k_2|$.

2.8 Conclusions

The present calculations and formalism leave out several effects which may be at least quantitatively important. First, in our numerical calculations, but not in the formalism, we have omitted all dipolar couplings beyond the nearest neighbors. Inclusion of further neighbors will quantitatively alter the dispersion relations in all cases considered, but these effects should not be very large, as is already suggested by the early calculations in Ref. [18] for an isotropic host. Another possible effect will appear when $a/d$ is significantly greater
than 1/3, namely, the emergence of quadrupolar and higher quasistatic bands \[20\]. These will mix with the dipolar band and alter its shape. For the separations we consider, this multipolar effect should be small. Also, even if \(a > d/3\), the plasmon dispersion relations will still be altered by an NLC host in the manner described here.

The present treatment also omits radiative damping. In the absence of a magnetic field, such damping is known to be small but non-zero in the long-wavelength limit, but it becomes more significant when the particle radius is a substantial fraction of a wavelength. Even at long wavelengths, radiative damping can be very important at certain characteristic values of the wave vector \[24\]. We have not, as yet, extended the present approach to include such radiative effects. We expect that, just as for an isotropic host in the absence of a magnetic field, radiative effects will further damp the propagating plasmons in the geometries we consider, but will not qualitatively change the effects we have described.

Another simplification in our approach should be mentioned. For an NLC host, the present work assumes that the director field is \textit{uniform}, i. e., position-independent. In reality, the director is almost certain to be modified close to the metal nanoparticle surface, i. e., to become nonuniform, as has been pointed out by many authors \[54–58\]. The effects of such complications on the optical properties of a single metallic particle immersed in an NLC have been treated, for example, in Ref. \[31\], and similar approaches might also be possible for the present problem. For a periodic metallic chain, the effects of such particle-liquid crystal interactions might be particularly interesting, possibly leading to periodic alterations in the liquid crystal configuration and also changing the dispersion relations for plasmonic waves along the chain. It would certainly be of interest to include such interactions in calculating the dispersion relations.

From the point of view of applications, the use of a liquid-crystalline host is appealing because liquid crystals are significantly affected by an applied electric field and magnetic fields. For example, the director of an NLC tends to align with the applied field. Thus, the dispersion relations of the propagating plasmonic waves could be, in principle, controlled by such an applied electric field \[45\] as we have indicated here. This control could be quite useful, for example, in developing filters for propagating plasmonic waves. An external
magnetic field will also align the director axis of the liquid crystal, especially at large values of the magnetic field, since a magnetic dipole moment can often be induced within each molecule of the liquid crystal [43]. The effects of a magnetic field on liquid crystal reorientation will be considered in future research.

2.8.1 Summary of Surface Plasmon Dispersion Relation Research

To summarize, we have shown that the dispersion relations for plasmonic waves propagating along a chain of closely spaced nanoparticles of Drude metal are strongly affected by external perturbations. If the host is a uniaxially anisotropic dielectric (such as an NLC), the dispersion relations of both $L$ and $T$ modes are significantly modified, compared to those of an isotropic host, and if the director axis of the NLC is perpendicular to the chain, the two degenerate transverse branches are split. If the host is a CLC, with rotation axis parallel to the chain, we find that the $T$ modes are again split into non-degenerate bands, whose dispersion relations now depend on the pitch angle $\alpha$. However, in contrast to the NLC case, the two $T$ branches are no longer linearly polarized. These effects suggest that the propagation of such plasmonic waves can be tuned, by subjecting the liquid crystal to a suitable electric field, so as to change the frequency band where wave propagation can occur, or to change the polarization of these waves. This control may be valuable in developing devices using plasmonic waves in future optical circuit design.

We also show that the dispersion relations for plasmonic waves propagating along a chain of closely spaced nanoparticle of Drude metal are affected by static magnetic fields. Our calculated dispersion relations and rotation angles show that as a linearly polarized wave propagates down the metallic chain its polarization axis will be Faraday rotated as a function of the number of particles in the chain and, for the case of a perpendicular magnetic field, will be undergo a strong Faraday ellipticity as it propagates along the chain. For the case of a CLC host, we have shown that the dispersion relations for left- and right-traveling waves are different leading to a one-way wave guide. All these effects show that the propagation of such plasmonic waves can be tuned, by either a liquid crystalline host or a magnetic field, so as to change the frequency band where wave propagation can occur, or
the polarization of these waves. This control may be valuable in developing devices using plasmonic waves in future optical circuit design.

2.8.2 Extension of this Work to Other Metallic Systems

While the current work has focused on chains of non-magnetic metallic particles I believe it would be interesting to extend these calculations to include magnetic particles as well. One possible way of calculating the dispersion relations of magnetic particles is by allowing the magnetic permeability $\mu$ to become frequency dependent. The fact that magnetic particles have a frequency dependence is well known in a variety of condensed matter systems. For example, a magnetic sample, in the presence of a static magnetic field and perpendicular time varying magnetic field will undergo a resonance at a set frequency of the time varying field and magnitude of the static magnetic field strength. In particular, one would write out the permeability tensor as [59]

$$
\chi_{11} = \chi_{22} = \frac{\gamma^2 M_s (H + \frac{4\pi}{3} M_s)}{\omega_r^2 - \omega^2},
$$

$$
\chi_{12} = -\chi_{21} = \frac{i\omega \gamma M_s}{\omega_r^2 - \omega^2},
$$

where $H$ is the strength of the magnetic field, $\gamma$ is the gyro-magnetic ratio, $\omega_r = \gamma H$ is the resonance frequency, and $M_s$ is the saturation magnetization.

While I have as of yet not done these calculations, I speculate that the energy dispersion relations will once again be non-reciprocal as the off-diagonal terms of the permeability tensor are non-zero for finite magnetic field strengths.
Chapter 3

ADATOMS ON GRAPHENE: ANALYTIC EQUATIONS
AND MAGNETIC MOMENT FORMATION

3.1 Overview

Graphene is a well known allotrope of carbon in which the carbon atoms bond in a planar $sp^2$ configuration [60, 61]. As a result, the single graphene sheet is effectively two-dimensional [62, 63]. Of the four $n = 2$ electrons which occupy the outer shell of a carbon atom, three are in $sp^2$ orbitals and form in-plane $\pi$ bonds between the nearest-neighbor carbon atoms, while the fourth occupies a $2p_z$ orbital. These $2p_z$ orbitals form a band of states which is responsible for many of the characteristic electronic properties of graphene [62]. Among these properties are a zero band gap at the so-called Dirac point, an electronic dispersion relation that, near the Dirac point, is equivalent to that of massless Dirac fermions, and spin-orbit coupling which is believed to be small because of the low atomic number of carbon [62, 63]. Graphene has a vast number of potential applications, including photovoltaic cells [64], ultracapacitors [65, 66], and spin-transport electronics [67–69].

Recently, a number of researchers carried out experimental and theoretical investigations into the effects of adatoms and impurities on both the band structure and localized magnetic moments in graphene. Among these are theoretical studies of carbon vacancies in graphene [70–72], hydrogen atoms on the surface of graphene [73], and several other types of disorder in graphene [74–76]. In several of these cases and in other work [75–78], impurity effects have been treated using a tight-binding model for the electronic structure of graphene and impurities, vacancies, or adatoms. These calculations have, however, either
been carried out numerically, or in the limit of energies close to the Dirac point, where the graphene density of states can be approximated as linear [79].

Density-functional calculations for adatoms on graphene have also been carried out. They have shown that the introduction of an adatom bonded to the surface of graphene can lead to a quasi-localized state with an energy near the Fermi energy and that the wave function of this quasi-localized state includes contributions from the orbitals of neighboring carbon atoms [72, 73]. In some cases it has been found that, even if the introduced defect or adatom is non-magnetic, a localized magnetic moment can form at the defect site [72].

In this chapter, we extend the previous work on graphene with adatoms in three ways. First, we show that the tight-binding model for adatoms on graphene can, in the limit of low concentrations, be solved analytically in the absence of electron-electron interactions. Specifically, we obtain analytical expressions for the local density of states (LDOS) on the adatom, the total density of states (TDOS) of the adatom-graphene system, and the spectral function $A(k, E)$ for an electron with Bloch vector $k$ and energy $E$ in graphene in the presence of the adatom [80]. All these results are expressed as a function of the graphene density of states, which itself is known analytically for a nearest-neighbor tight-binding model [77, 81].

Secondly, we calculate the magnetic properties of the system using the Hubbard model for the electron-electron interaction, which we treat using a standard mean-field approximation. This treatment leads to a transition between a non-magnetic and magnetic state above a critical value of $U$ which depends on the parameters of the tight-binding model. In the presence of a finite $U$ our model is basically a special case of the well-known Anderson model [82], but with a linear rather than a constant density of states near the Fermi energy. Our results include not only the magnetic moment on the adatom, but also that on the graphene sheet and the charge transfer from the adatom to the sheet, all as functions of the model parameters.

Finally, we show how one could experimentally control the magnetic properties of the graphene-adatom system by introducing a gate voltage to the graphene-adatom system. The application of a gate voltage allows us to tune the Fermi energy of the system by adding or
removing charge carriers which directly effects the location of the Fermi energy. Since the graphene-adatom density of states depends on the Fermi energy in a complex manner, a small change in the Fermi energy will have drastic consequences in the magnetic properties of the system. We show that by changing the gate voltage one could experimentally switch between a magnetic "on" and "off" state.

The remainder of the chapter is organized as follows: We will first summarize the basic physical properties of graphene. This allows us to introduce notation used throughout the chapter and gives us the opportunity to describe the characteristics of graphene that make it such an interesting material. Next, we will discuss the effects of adding additional atoms to the surface of graphene by presenting calculations of the density of states and spectral function. Following this discussion of the density of states, we will discuss the magnetic properties of graphene, including the formation of a magnetic moment, as a function of the tight-binding parameters. We will also discuss switching of the magnetic moment as a function of the chemical potential.

3.2 The Primitive Cell of the Hexagonal Crystal Structure

The structure of graphene is directly responsible for many of its unique physical properties. For instance, the hexagonal structure of the graphene sheet leads directly to a Dirac-like dispersion relation in which the conduction and valence bands of graphene touch at two distinct points in the first Brillouin zone. In the case of a two-dimensional hexagonal crystal, the primitive cell contains two atoms which we denote as \( \alpha \) and \( \beta \). These can be translated by any vector of the form \( n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2 \), where \( n_1 \) and \( n_2 \) are integers and \( \mathbf{a}_1 \) and \( \mathbf{a}_2 \) are basis vectors, to recreate the entire crystal structure. A sketch of the primitive cell and the overall hexagonal lattice is shown in Fig. 3.1, in which the primitive basis vectors \( \mathbf{a}_1 \) and \( \mathbf{a}_2 \) are also shown.

The first Brillouin zone is thus the \( k \)-space representation of this unit cell and is shown in the left sketch of Fig. 3.2. In the right sketch of Fig. 3.2 we have once again shown a cartoon image of graphene but this time we have labeled and color coded the atoms in the
unit cells. This labeling will be used later in our discussion of the tight-binding model.

The unique physical properties of graphene are directly related to its hexagonal crystal structure. In the following sections we summarize how one calculates some of graphene’s unique physical properties. based on this crystal structure, and introduce the tight-binding model on a hexagonal crystal structure.

3.3 Introduction to the Tight-binding Model of Graphene

One of the simplest methods for describing the movement of electrons in a crystal structure is the tight-binding model, which describes the movement, or hopping, of electrons between lattice positions, or atoms, in the crystal structure. For graphene, this hexagonal lattice can be thought of as two inter-penetrating triangular lattices, which we will label $\alpha$ and $\beta$, and thus each unit cell contains two carbon atoms. A simple pictorial illustration of this is given in Fig. 3.2, in which we have also labeled points of high symmetry in the Brillouin zone. These points are used below to describe the calculation of the band structure and
density of states.

3.3.1 Bloch waves and Bloch Electrons

Since we assume that the lattice points are fixed, and therefore the positions of the atomic nuclei are fixed, one can imagine that an electron moving through this lattice would interact with a periodic potential created by the fixed positions of the atomic cores. An electron in a periodic potential is known as a Bloch electron. The consequences of this periodic potential will be discussed briefly before we introduce the tight-binding model.

The most general Hamiltonian one can consider for a Bloch electron traveling in a periodic potential is given as [8]

$$ H = \frac{\hbar^2}{2m} \nabla^2 + U(r) $$

where $m$ is the mass of the electron and $U(r)$ is the periodic potential which we require.
satisfies $U(r + \mathbf{R}) = U(r)$ for all $\mathbf{R}$ in the bravais lattice. One can show (see Ashcroft and Mermin [8]) that the wave function, $\phi_n(r)$, that solves $H\phi_n(r) = E\phi_n(r)$ (where $H$ is given by Eq. (3.1)) can be chosen to have the form of a plane wave times a function with the periodicity of the lattice. Namely,

$$\phi_{n,k}(r) = e^{i\mathbf{k}\cdot\mathbf{r}}u_{n,k}(r)$$

(3.2)

where $u_{n,k}(r + \mathbf{R}) = u_{n,k}(r)$ for all $\mathbf{R}$, where $\mathbf{R}$ is a Bravais lattice vector [8].

While the use of Bloch electrons and Bloch waves can be done using many approximations, the discussion here will focus on using Bloch waves to describe the movement of electrons in the system via the tight-binding approximation. That is, we want to write down a Hamiltonian, $H$, which describes the movement of a Bloch electron through the crystal lattice by considering only sites corresponding to a single atomic orbital. The usefulness of single orbital per site models to discuss electronic properties near the Fermi energy is well documented in the literature. Below we provide a brief outline of how one can describe Bloch electrons using the tight-binding model, and describe how one writes the Hamiltonian in terms of creation and annihilation operators.

Consider a solid which we define as a rigid lattice consisting of both atomic ions and electrons. In general, these ions are much heavier than the electrons ($m_I >> m_e$) and we can safely approximate the positions of the ions as static (Born-Oppenheimer Approximation). With this approximation we can write down a Hamiltonian describing this system as a two-particle Hamiltonian given by

$$H = \sum_i \frac{p_i^2}{2m} + V(x_i) + \sum_{i,j} U(x_i, x_j)$$

(3.3)

where $V(x)$ and $U(x_i, x_j)$ are the effective one- and two-body potentials and $m$ is the mass (or effective mass) of the electron. In general, we seek a solution to Eq. (3.3) as $H\Psi = E\Psi$, which minimize the contribution of the two-body potential [84]. This is done in practice by finding eigenstates of the single particle Hamiltonian, $h_1$, given as

$$h_1 = \frac{p^2}{2m} + V(x)$$

(3.4)
such that the matrix elements of the two-body potential become small.

Since the single particle Hamiltonian given in Eq. (3.4) is periodic the eigenstates of \( h_1 \) are Bloch functions of the form given in Eq. (3.2), where \( u(x) \) has the periodicity of the lattice. Since the Bloch functions are eigenstates of the Hamiltonian, \( h_1 \) we have \[84\]

\[
h_1 \phi_{n,k}(x) = \epsilon_{n,k} \phi_{n,k}(x). \tag{3.5}
\]

To formally introduce the ladder operator notation we now introduce the creation operator for an electron of spin \( \sigma \) in the Bloch state given by \( \phi_{n,k}(x) \) and its Fourier transform given as

\[
c_{i,n}^\dagger = \frac{1}{\sqrt{L}} \sum_k e^{-ikR_i} c_{k,\sigma}^\dagger \tag{3.6}
\]

where \( L \) denotes the number of ions. Using Eq. (3.6) we can now define a field operator, \( \Phi_\sigma(x) \) which creates an electron of spin \( \sigma \) at position \( x \) as \[84\]

\[
\Phi_\sigma(x) = \sum_{n,k} \phi_{n,k}^*(x) c_{n,k,\sigma}^\dagger \tag{3.7}
\]

where the asterisk denotes complex conjugation and the dagger denotes hermitian conjugation. Using the field operator in Eq. (3.7) we can write the Hamiltonian \( H \) in Eq. (3.3) in second quantized form as \[84\]

\[
H = \sum_\sigma \int dx^3 \Phi_\sigma^*(x) h_1 \Phi_\sigma(x) + \frac{1}{2} \sum_{\sigma,\sigma'} \int dx^3 dx'^3 \Phi_\sigma^*(x) U(x, x') \Phi_{\sigma'}(x') \Phi_\sigma(x) \tag{3.8}
\]

where the Hamiltonian \( h_1 \) is given in Eq. (3.4).

Rearranging Eq. (3.8) we find that the Hamiltonian can be written in terms of ladder operators as \[84\]

\[
H = \sum_{\sigma,i,\sigma',j} t_{ij}^n c_{n,i,\sigma}^\dagger c_{n,j,\sigma} + \frac{1}{2} \sum_{a,b,c,d,i,j,k,l} U_{ijkl} a_{a,i,\sigma}^\dagger c_{b,j,\sigma'}^\dagger c_{c,k,\sigma} c_{d,l,\sigma}, \tag{3.9}
\]

where the sum over \( a, b, c, d \) runs over bands and the sum over \( i, j, k, l \) runs over sites, the coefficient \( t_{ij}^n \) gives the hopping energy of the \( n^{th} \) band between the \( i^{th} \) and \( j^{th} \) sites and \( U_{ijkl} \) is the interaction parameter and is expressed in terms of "overlap integrals".
For a single band, the hopping energy \( t_{i,j}^{\alpha} \) reduced to \( t_{i,j} \) and is given by [84]

\[
t_{i,j} = \frac{1}{L} \sum_{k} e^{i \mathbf{k} \cdot (\mathbf{R}_j - \mathbf{R}_i)} \epsilon_k
\]  

(3.10)

and the overlap integral is given by

\[
U_{i,j,k,l} = \int dx dx' \phi^*(x - \mathbf{R}_i) \phi^*(x - \mathbf{R}_j) U(x, x') \phi(x - \mathbf{R}_k) \phi(x - \mathbf{R}_l).
\]  

(3.11)

If we write the Hamiltonian in Eq. (3.9) for the case of \( U = 0 \) we are writing down the tight-binding Hamiltonian. The tight-binding Hamiltonian only includes hopping terms (give by \( t_{i,j} \)) and therefore consists of de-localized electrons. Whereas, if we assume that both \( t \) and \( U \) are non-zero, then we have written down the Hubbard Hamiltonian. Electrons in the Hubbard Hamiltonian are generally localized to a region smaller than the dimensions of the sample and in the extreme limit (when \( U \to \infty \)) are located on a single site.

For this work, we focused on the tight-binding Hamiltonian and only included the interaction term within mean-field theory when including the effects of spin on the magnetic properties of graphene. In the sections to follow, we will use the tight-binding model to work out the density of states of both pure graphene and later graphene with adatoms and show that when you include the interaction term the density of states for spin-up and spin-down electrons would differ. This difference leads to a finite magnetic field which, as shown below, is a function of the various hopping parameters and gate voltage applied to the system.

### 3.3.2 Tight-binding Model of Pure Graphene

Consider a hexagonal lattice of which the lattice in Fig. 3.2(a) is a small portion. We can consider the motion of an electron from the center blue atom (blue atoms sit on the \( \beta \) triangular lattice) to one of the three nearest neighbor red atoms (red atoms sit on the \( \alpha \) triangular lattice) as shown in Fig. 3.2(a) and describe the displacement of an electron moving between any of the three nearest neighbors as \( \mathbf{d}_1, \mathbf{d}_2 \) and \( \mathbf{d}_3 \) which are written in terms of the Bravais lattice vectors \( \mathbf{a}_1 \) and \( \mathbf{a}_2 \) of the primitive cell.

The most general tight-binding Hamiltonian, which allows for hopping between any pair
of atoms, is given by

\[ H_0 = -\sum_{n,\delta,\sigma} (t_{\alpha\beta,\delta} a_{n,\sigma}^\dagger b_{n+\delta,\sigma} + \text{h. c.)} - \sum_{n,\delta \neq 0,\sigma} t_{\alpha\alpha,\delta} (a_{n,\sigma}^\dagger a_{n+\delta,\sigma} + b_{n,\sigma}^\dagger b_{n+\delta,\sigma}). \]  

(3.12)

where the Hamiltonian can be written in terms of the creation and annihilation operators for electrons of spin \( \sigma \) on a site in the \( n^{th} \) primitive cell of the \( \alpha \) and \( \beta \) sub-lattices. We denote the creation (annihilation) operators for the \( \alpha \) and \( \beta \) sub-lattices by \( a_{n,\sigma}^\dagger \) \( (a_{n,\sigma}) \) and \( b_{n,\sigma}^\dagger \) \( (b_{n,\sigma}) \).

In Eq. (3.12), \( t_{\alpha\beta,\delta} \) and \( t_{\alpha\alpha,\delta} \) \( (t_{\alpha\beta}, t_{\alpha\alpha} > 0) \) are hopping integrals which take an electron of spin \( \sigma \) \( (\sigma = \pm 1/2) \) from a lattice site to a neighboring lattice site, and \( \delta \) denotes a Bravais lattice vector of the triangular lattice. In particular, \( t_{\alpha\beta,\delta} \) is the hopping integral between a Bloch electron at an \( \alpha \) site and a Bloch electron at a \( \beta \) site and \( t_{\alpha\alpha,\delta} \) is the hopping integral between an Bloch electron at an \( \alpha \) site and another electron at an \( \alpha \) site. Here we have assumed that \( t_{\alpha\alpha} = t_{\beta\beta} \) and that the first sum represents hopping between sublattices and therefore all possible Bravais lattice vectors are summed over, whereas the second sum only includes hopping between sites on the same sub-lattice and thus, \( \delta = 0 \) is not allowed.

Since we wish to determine the energy of the system as a function of momentum, \( k \), we take the Fourier transform of Eq. (3.12) and find that \( H_0 \) can be written as

\[ H_0 = \sum_{k,\sigma} H_{0,k,\sigma} \]  

(3.13)

where

\[ H_{0,k,\sigma} = -t_{\alpha\beta}(k) a_{k,\sigma}^\dagger b_{k,\sigma} - t_{\alpha\beta}^*(k) a_{k,\sigma} b_{k,\sigma}^\dagger - t_{\alpha\alpha}(k) [a_{k,\sigma}^\dagger a_{k,\sigma} + b_{k,\sigma}^\dagger b_{k,\sigma}], \]  

(3.14)

where the operator \( a_{k,\sigma}^\dagger = \frac{1}{\sqrt{N}} \sum_n a_{n,\sigma} \exp(ik \cdot \delta_n) \), where \( N \) is the number of primitive cells in the graphene lattice and \( \delta_n \) is the \( n^{th} \) Bravais lattice vector of the triangular lattice; an analogous definition holds for \( b_{k,\sigma}^\dagger \). In Eq. (3.14) \( t_{\alpha\beta}(k) = \sum_\delta e^{ik \cdot \delta} t_{\alpha\beta,\delta} \) and \( t_{\alpha\alpha}(k) = \sum_{\delta \neq 0} e^{ik \cdot \delta} t_{\alpha\alpha,\delta} \).

While Eqs. (3.13) and (3.14) are exact, we wish to only consider the effects of nearest neighbor interactions. Therefore, \( t_{\alpha\alpha,\delta} = 0 \), and \( t_{\alpha\beta,\delta} = 0 \) except for the three nearest
neighbors and we rewrite $t_{\alpha\beta}(k)$ as $t(k) = t \sum_{i=1,2,3} e^{ik \cdot d_i}$. The three nearest neighbor vectors are shown in Fig. 3.2(a), where they are denoted by $d_1$, $d_2$, and $d_3$. This allows us to rewrite $H_{0,k,\sigma}$ as

$$H_{0,k,\sigma} = -t(k) a_{k,\sigma}^\dagger b_{k,\sigma} - t^*(k) a_{k,\sigma} b_{k,\sigma}^\dagger.$$  \hspace{1cm} (3.15)$$

The sum over $k$ is confined to the first Brillouin zone and

$$t(k) = t \left[ 1 + 2 \exp \left( \frac{3i k_x a_0}{2} \right) \cos \left( \frac{\sqrt{3} k_y a_0}{2} \right) \right].$$  \hspace{1cm} (3.16)

In Eq. (3.16), $t$ is the hopping energy between nearest neighbor carbon atoms ($t = 2.8 \text{ eV}$ for graphene [78]), and $a_0 = 1.42 \text{ Å}$ is the nearest-neighbor bond length [72]. When one finds the eigenvalues of Eq. (3.13) for the case of nearest-neighbor hopping we find that that the energies of the system are given as $E(k) = \pm |t(k)|$. These energies are plotted in Fig. 3.3 and show the corresponding Dirac like dispersion relations at the symmetry points $\pm K$.

While the nearest-neighbor tight-binding model is interesting in its own right, we wish to investigate the effects of adding additional atoms to the surface of graphene. Therefore, we next expand this simple tight-binding model to include the effects of additional atoms and thus additional electrons to our system.

### 3.3.3 Tight-binding Model of Graphene with Adatoms

In this chapter, we are interested in a system consisting of a perfect lattice of graphene plus a single adatom, which we will assume has one atomic orbital. We also assume that the adatom lies at the so-called $T$ (top) site, above one of the carbon atoms. It has been found, using \textit{ab initio} electronic structure calculations, that several species of adatoms, including H, F, and Au, do occupy a location above one of the carbon atoms [85–87].

We wish to investigate what happens to the density of states when an isolated adatom is adsorbed onto the host graphene at a $T$ site (this location corresponds to hydrogen absorption on graphene) [85, 86]. The extra piece of the tight-binding Hamiltonian, $H_I$,
Figure 3.3: The energy eigenvalues of Eq. (3.13) plotted as $E(k)/t$ vs. $k_x a_0$ and $k_y a_0$. Note the six Dirac points which touch at the symmetry points K and K' and the nearly linear dispersion relation at each point as $E(k) \to 0$.

due to the adatom may be written in real space as

$$H_I = \epsilon_0 \sum_{\sigma} h_{0,\sigma}^\dagger h_{0,\sigma} - t' \sum_{\sigma} \left( h_{0,\sigma}^\dagger a_{0,\sigma} + h_{0,\sigma} a_{0,\sigma}^\dagger \right). \tag{3.17}$$

Here $h_{0,\sigma}^\dagger$ and $h_{0,\sigma}$ are creation and annihilation operators for an electron of spin $\sigma$ ($\sigma = \pm 1/2$) at the site of the adatom, which we assume is located at the site 0 of the $\alpha$ sub-lattice, $\epsilon_0$ is the on-site energy of an electron on that site (relative to the Dirac point of the pure graphene band structure), and $t'$, ($t' > 0$), is the energy for an electron to hop between the adatom and the carbon atom at the site 0 of the $\alpha$ sub-lattice.

$H_I$ can readily be expressed in terms of Bloch eigenstates of $H_0$. These eigenstates may
be written as two-component column vectors with components $\psi_1(k)$ and $\psi_2(k)$ satisfying the eigenvalue equation (hereafter we suppress the spin subscript until needed)

$$
\begin{pmatrix}
\epsilon_k + t_{\alpha\alpha}(k) & t_{\alpha\beta}(k) \\
t_{\alpha\beta}^*(k) & \epsilon_k + t_{\alpha\alpha}(k)
\end{pmatrix}
\begin{pmatrix}
\psi_{1,k} \\
\psi_{2,k}
\end{pmatrix} = 0.
$$

(3.18)

The solution to this eigenvalue problem gives the tight-binding band structure of pure graphene [78], and the corresponding eigenvectors satisfy $\psi_{1,k} = \pm e^{-i\phi_k} \psi_{2,k}$, where the phase factor $e^{-i\phi_k}$ is given by $e^{-i\phi_k} = \frac{t_{\alpha\beta}(k)}{|t_{\alpha\beta}(k)|}$. We can then write the destruction operator for a Bloch electron in the upper and lower bands as $\gamma_{k,1,2} = \frac{1}{\sqrt{2}} (e^{i\phi_k} a_k \pm b_k)$ where we have defined $\gamma_{k,1}$ and $\gamma_{k,2}$ to be properly normalized, so that, for example, the anticommutator $\{\gamma_{k,1}, \gamma_{k,1}^\dagger\} = 1$.

It is readily shown that $H_I$ can be rewritten as

$$
H_I = \epsilon_0 h_0^\dagger h_0 - \frac{t'}{\sqrt{2N}} \left[ h_0^\dagger \sum_k e^{-i\phi_k} (\gamma_{k,1} + \gamma_{k,2}) + h.c. \right].
$$

(3.19)

Thus, in $H_I$, the creation and annihilation operators of the adatom are connected to every eigenstate of the graphene band structure by matrix elements of equal magnitude (though different phase). For a hydrogen adatom, we take $\epsilon_0 = 0.4 \ eV$ and $t' = 5.8 \ eV$, as found in Ref. [78]. The one-electron Hamiltonian, $H_0 + H_I$, is a special case of the Anderson impurity model [82], where the impurity state is coupled to all the band electron states by matrix elements of equal magnitude.

We also include in our calculation the effects of an on-site electron-electron interaction of the Hubbard form,

$$
H_U = U n_{0\uparrow} n_{0\downarrow},
$$

(3.20)

where $n_{0,\sigma} = h_{0,\sigma}^\dagger h_{0,\sigma}$ is the number of electrons with spin $\sigma$ on the $T$ site. For a hydrogen adatom we take $U$ to be the difference between the ionization potential and the electron affinity providing us with a numerical value of $U \sim 12.85eV = 4.59t$ [88, 89].

The Hubbard term given in Eq. (3.20) is quartic in the creation and annihilation operators. Therefore, in order to calculate the properties of the Hamiltonian including this term,
we use a standard mean field theory to rewrite this term (see, e. g., Ref. [90]) in the form

\[ H_U \sim U \left[ h_{0\uparrow}^\dagger h_{0\uparrow} \langle n_{0\downarrow} \rangle + h_{0\downarrow}^\dagger h_{0\downarrow} \langle n_{0\uparrow} \rangle - \langle n_{0\uparrow} \rangle \langle n_{0\downarrow} \rangle \right]. \tag{3.21} \]

With this approximation, the total Hamiltonian, consisting of the sum of Eqs. (3.15), (3.19), and (3.21), becomes quadratic in electron creation and annihilation operators, and can be diagonalized. The Fermi energy, total energy, and magnetic properties of the system can then be obtained by an iterative process as described below. The electronic density of states corresponding to the one-electron Hamiltonian, \( H_0 + H_I \), can be obtained analytically, as we describe below, which makes the calculation of the total energy and the magnetic properties quite simple.

### 3.4 Parameter Dependence of Density of States and Spectral Function

#### 3.4.1 Green’s Function

We use the single particle Green’s function approach to calculate the local and total density of states of the graphene-adatom system, initially omitting the Hubbard-U term. We continue to suppress the spin degree of freedom since, in the absence of the Hubbard term, spin just gives an extra factor of 2. To that end, we first introduce the resolvent operator \( G(z) = \frac{1}{z-H} \), where \( z = E + i\eta, \ (\eta \to 0^+) \), and \( H = H_0 + H_I \). If there are 2\( N \) carbon atoms and 1 adatom, \( G(z) \) can be expressed as an \((2N+1) \times (2N+1)\)-dimensional matrix.

It is convenient to use the 2\( N \) Bloch states (corresponding to \( Nk \) values) created by the operators \( \gamma_{k,1}^\dagger \) and \( \gamma_{k,2}^\dagger \) as the basis for this matrix, plus the adatom orbital corresponding to \( h_{0\uparrow}^\dagger \). If we let the adatom orbital correspond to the first of the \((2N+1)\) states, then one can easily write out the matrix \( z-H \) of which \( G(z) \) is the inverse. The matrix \( z-H \) takes
the following form:

\[
\begin{pmatrix}
  z - \epsilon_0 & \frac{t'}{\sqrt{2N}} e^{-i\phi_{k_1}} & \frac{t'}{\sqrt{2N}} e^{-i\phi_{k_1}} & \ldots & \frac{t'}{\sqrt{2N}} e^{-i\phi_{k_1}} & \frac{t'}{\sqrt{2N}} e^{-i\phi_{k_N}} \\
  \frac{t'}{\sqrt{2N}} e^{i\phi_{k_1}} & z - \epsilon_{k,1} & 0 & 0 & \ldots & 0 \\
  \frac{t'}{\sqrt{2N}} e^{i\phi_{k_1}} & 0 & z - \epsilon_{k,2} & 0 & \ldots & 0 \\
  \ldots & \ldots & \ldots & \ldots & \ldots & \ldots \\
  \frac{t'}{\sqrt{2N}} e^{i\phi_{k_N}} & \ldots & \ldots & \ldots & z - \epsilon_{k,N,1} & 0 \\
  \frac{t'}{\sqrt{2N}} e^{i\phi_{k_N}} & 0 & \ldots & \ldots & 0 & z - \epsilon_{k,N,2}
\end{pmatrix}
\]  

(3.22)

The operator \( G(z) \) is thus the inverse of this matrix.

### 3.4.2 Density of States

We denote the local electronic density of states per spin on the adatom site by \( \rho_{00}(E) \). \( \rho_{00}(E) \) is related to \( G(z) \) by

\[
\rho_{00}(E) = -\frac{1}{\pi} \text{Im} G_{00}(z) = -\frac{1}{\pi} \text{Im} \langle 0 | \frac{1}{z - H} | 0 \rangle. \tag{3.23}
\]

Here \( z = E + i\eta, (\eta \to 0^+) \), and \( \langle 0 | 1/(z - H) | 0 \rangle \) denotes the matrix element of \( 1/(z - H) \) evaluated at the location of the adatom, which we take to be above the atom 0 on the \( \alpha \) sub-lattice. We can then evaluate \( \rho_{00}(E) \) as

\[
\rho_{00}(E) = -\frac{1}{\pi} \text{Im} \left( \frac{1}{z - \epsilon_0 - \frac{t'^2}{2N} G_0(z)} \right), \tag{3.24}
\]

where

\[
G_0(z) = \sum_{k,\lambda=1}^2 \left( \frac{1}{z - \epsilon_{k,\lambda}} \right) \equiv \text{Tr} \left( \frac{1}{z - H_0} \right) \tag{3.25}
\]

and \( \epsilon_{k,2} = -\epsilon_{k,1} \) are the eigenvalues of Eq. (3.18).

The real and imaginary parts of \( G_0(z) \) are related to the (unperturbed) graphene density of states per graphene unit cell (per spin), which we denote \( \rho_0(E) \), by \( -\frac{1}{\pi} \text{Im} G_0(E + i\eta) = N\rho_0(E) \), and \( \text{Re} G_0(E) = N \text{P} \left( \int_{-3t}^{3t} \frac{\rho_0(E')}{E - E'} dE' \right) \), with \( \eta \to 0^+ \) and where the integral runs over the range where \( \rho_0(E') \neq 0 \) [75, 82]. For the form of \( H_0 \) which includes only nearest-neighbor hopping, which includes only nearest-neighbor hopping, \( \rho_0(E) \) has been given by
Figure 3.4: The density of states of pure graphene is given analytically by Eq. (3.26) for parameters described within the text. Note that near $E = 0$ the density of states is linear but for $E \approx t$ the density of states is peaked sharply.

Hobson and Nierenberg [81] and later by Yuan et al [77] as

$$\rho_0(E) = \begin{cases} 
\frac{2E}{t^2 \pi^2} \frac{1}{\sqrt{f(x)}} K\left(\frac{4x}{f(x)}\right) & 0 < x < 1 \\
\frac{2E}{t^2 \pi^2} \frac{1}{\sqrt{4x}} K\left(\frac{f(x)}{4x}\right) & 1 < x < 3,
\end{cases} \quad (3.26)$$

where $x = E/t$, $f(x) = (1 + x)^2 - \frac{(x^2 - 1)^2}{4}$ and $K(m)$ is the elliptic integral of the first kind.

We plot Eq. (3.26) in Fig. (3.4) normalized such that $\int_{-3t}^{0} \rho_0(E)dE = 1$.

The density of states on the carbon sites (per spin) in the presence of an adatom may be written as

$$\rho_g(E) = -\frac{1}{\pi} Im \sum_{k,\lambda} \langle k, \lambda | \frac{1}{z - \Pi} | k, \lambda \rangle,$$

where $z = E + i\eta$, ($\eta \to 0^+$), and can readily be computed. The total density of states per spin is the sum of $\rho_0$ [Eq. (3.24)] and $\rho_g(E)$, and can readily be rearranged to equal

$$\rho_{tot}(E) = N \rho_0(E) - \frac{1}{\pi} Im \left( \frac{d}{dz} \ln[z - \epsilon_0 - \frac{t'^2}{2N} G_0(z)] \right). \quad (3.27)$$
3.4.3 Spectral Function

We can use an analogous approach to calculate the spectral function \( A(k, E) \). \( A(k, E) \) represents the probability density that an electron with Bloch wave-vector \( k \) has energy \( E \), and is given by \( A(k, E) = -\frac{1}{\pi} Im \sum_{\lambda}(k, \lambda|\left(\frac{1}{z-i\eta}\right)|k, \lambda) \) where \( z = E + i0^+ \). It can be evaluated using the methods of the previous section giving

\[
A(k, E) = -\frac{1}{\pi} Im \left( \sum_{\lambda=1}^{2} \frac{1}{z - \epsilon_{k,\lambda} - \Sigma_{\lambda}(k, z)} \right), \quad (3.28)
\]

where \( \Sigma_{\lambda}(k, E) \) is the self-energy and is written to first order in \( 1/N \). We find that the self-energy is independent of both \( \lambda \) and \( k \) and takes the form

\[
\Sigma_{\lambda}(k, z) = \frac{t'^2}{2N} \left( \frac{1}{z - \epsilon_0 - \frac{t'^2}{2N} G_0(z)} \right). \quad (3.29)
\]

All these equations [(3.24) - (3.29)] remain valid for non-nearest-neighbor hopping; only the form of the graphene density of states has to be changed.

3.4.4 Effects of Electron-Electron Interaction; Spin-Polarized Density of States and Magnetic Moment

Finally, we discuss the effects of including a non-zero Hubbard term \( H_U \) [Eq. (3.20)] in the Hamiltonian. If we treat \( H_U \) by mean-field theory [Eq. (3.21)], then the densities of states for spin-up and spin-down electrons may be different. We can calculate the partial density of states self-consistently as follows. First, we make an initial assumption for the values of \( \langle n_{0\uparrow}\rangle \) and \( \langle n_{0\downarrow}\rangle \). Then the effective on-site energy for an up-spin electron on the hydrogen adatom is obtained by making the replacement

\[
\epsilon_{0,\uparrow} \rightarrow \epsilon_0 + U\langle n_{\downarrow}\rangle, \quad (3.30)
\]

with a corresponding expression for \( \epsilon_{0,\downarrow} \). Given \( \epsilon_{0,\uparrow} \) and \( \epsilon_{0,\downarrow} \), we can compute the local densities of states \( \rho_{00,\uparrow} \) and \( \rho_{00,\downarrow} \) using the appropriate generalizations of Eq. (3.24); we can also obtain the total densities of states \( \rho_{tot,\uparrow} \) and \( \rho_{tot,\downarrow} \) using the corresponding generalizations.
Figure 3.5: (a). Local density of states per spin on the adatom site, $\rho_{00}(E)$, with $U = 0$ for a graphene sample with $N = 500$ graphene unit cells (1000 C atoms) and one adatom. We assume the model described in the text [Eqs.(3.15), and (3.19)]. Black curve: $t' = 5.8$ eV, $\epsilon_0 = 0.4$ eV; blue curve: $t' = 1.0$ eV, $\epsilon_0 = 0.4$ eV; and red curve: $t' = 1.0$ eV, $\epsilon_0 = -0.4$ eV. In all three cases, $t = 2.8$ eV. The Fermi energy is calculated using Eq. (3.31) and gives $E_F = 0.236$ eV. (b). The change in the density of states per spin due to the adatom for the three cases shown in (a). In both (a) and (b), the inset figures are enlargements of the region between -1 eV and +1 eV.

The Fermi energy, $E_F$, is then obtained from the condition

$$2N + 1 = \int_{-3t}^{E_F} \rho_{\text{tot}}(E)dE,$$

where we assume one adatom, $2N$ carbon sites, and $\rho_{\text{tot}}(E) = \rho_{\text{tot},\uparrow}(E) + \rho_{\text{tot},\downarrow}(E)$. Given $E_F$, we then recalculate $\langle n_{0,\uparrow} \rangle$ and $\langle n_{0,\downarrow} \rangle$. The procedure is repeated until successive iterations do not lead to a significant change in $\langle n_{0,\uparrow} \rangle$ and $\langle n_{0,\downarrow} \rangle$. In practice, we require that these quantities change by no more than $\pm 0.001 n_a$ on successive iterations (here $n_a$ is the number of adatoms in the calculation). Typically, about twenty iterations of the self-consistent equations are needed to attain this degree of convergence, as discussed further below.

Once $E_F$ has been found, the total magnetic moment $\mu_T$ of the system is obtained from

$$\frac{\mu_T}{\mu_B} = \int_{-3t}^{E_F} [\rho_{\text{tot},\uparrow}(E) - \rho_{\text{tot},\downarrow}(E)]dE,$$

where $\mu_B$ is the Bohr magneton.
In the limit $U \to \infty$, the mean-field version of the Hubbard model can be done without iteration. In this limit, only one of the quantities $\langle n_\uparrow \rangle$ or $\langle n_\downarrow \rangle$ is non-zero. The reason is that if, say, $\langle n_\uparrow \rangle$ is non-zero, then the energy to put a spin-down electron on the adatom becomes infinite, and hence the number of spin-down electrons must be zero. To be definite, we assume that $\langle n_\downarrow \rangle = 0$. In that case, we just have $\epsilon_0,\uparrow = \epsilon_0$, and $\epsilon_0,\downarrow \to \infty$. The total density of states for the up spins will then be given by Eq. (3.27), while that for the down spins is just that of unperturbed graphene: $\rho_{\text{tot},\downarrow} = N\rho_0(E)$.

In the limit $U \to \infty$ the Fermi energy, $E_F$, is obtained from Eq. (3.31) and may be simplified to

$$\int_0^{E_F} 2N \rho_0(E) dE - \frac{1}{\pi} \text{Im} \ln \left[ \frac{E_F - \epsilon_0 - \frac{t'^2}{2N} G_0(E_F)}{-3t - \epsilon_0 - \frac{t'^2}{2N} G_0(-3t)} \right] = 1. \quad (3.33)$$

Once $E_F$ has been obtained, the magnetic moment $\mu_T$ can be again found using Eq. (3.32). Since both $\rho_\uparrow(E)$ and $\rho_\downarrow(E)$ are available analytically, using Eqs. (3.32) and (3.33), $\mu_T$ is easily computed in closed form.

In Fig. 3.5(a), we plot the local density of states $\rho_{00}(E)$ for parameters appropriate to a hydrogen adatom on graphene with $U = 0$, as calculated from Eq. (3.24). We use the parameters $t = 2.8 \text{ eV}$, $t' = 5.8 \text{ eV}$, and $\epsilon_0 = 0.4 \text{ eV}$, as given by Ref. [78] for a hydrogen adatom. In Fig. 3.5(b), we plot the change in the total density of states produced by a single hydrogen atom, i. e., the quantity $\rho_{\text{tot}}(E) - N\rho_0(E)$ for the three cases of Fig. 3.5(a), calculated using Eqs. (3.23) and (3.27).

Next, we calculate both the spectral function $A(\mathbf{k}, E)$ for $U = 0$ and the spin polarized spectral function $A_\sigma(\mathbf{k}, E)$ for $U = \infty$ as functions of $E$ for several values of $\mathbf{k}$, using the parameters given previously. $A_\sigma(\mathbf{k}, E)$ is obtained using a generalization of Eq. (3.28) in the limit $U \to \infty$ as discussed in the previous section. The resulting spectral functions are shown in Fig. 3.6 through first order in $1/N$. The contribution from the adatom appears as the sharp spike near $E_F = 0.173 \text{ eV}$, while the contribution from the graphene sheet is shown as broadened peaks near the values of $\epsilon_{\mathbf{k},i}$ ($i = 1, 2$) for the three choices of $\mathbf{k}$. The self energy term [Eq. (3.29)] controls the width of the graphene resonances. The integral of the graphene sheet’s contribution to the spectral function will be of order $N$ times larger.
Summary of Numerical Results

| $U$ (eV) | $\epsilon_0$ (eV) | $t'$ (eV) | $\mu_a$ (µB) per adatom | $\mu_T$ (µB) | Charge Transfer (|$|e|$|) | $E_F$ (eV) |
|----------|------------------|------------|-------------------------|-------------|-----------------------------|-----------|
| 0.0$t^a$ | 0.4              | 5.8        | 0.0                     | 0.0         | 0.372                       | 0.372     |
| 4.59$t^b$| 0.4              | 5.8        | 2.67E-4                 | 1.13E-3     | 0.695                       | 0.173     |
| 10.0$t$  | 0.4              | 5.8        | 3.11E-3                 | 7.67E-3     | 0.758                       | 0.236     |
| $\infty$ | 0.4              | 5.8        | 0.300                   | 0.871       | 0.699                       | 0.111     |
| $\infty$ | 0.0              | 5.8        | 0.260                   | 0.927       | 0.738                       | 0.050     |
| $\infty$ | -0.4             | 5.8        | 0.338                   | 0.958       | 0.662                       | 0.050     |
| $\infty$ | -1.0             | 5.8        | 0.360                   | 0.990       | 0.639                       | -0.01     |
| $\infty$ | 0.4              | 1.8        | 0.358                   | 0.506       | 0.641                       | 0.236     |
| $\infty$ | 0.4              | 7.8        | 0.219                   | -0.11       | 0.780                       | 0.236     |

Table 3.1: Magnetic moment on the adatom ($\mu_a$), total magnetic moment on the graphene-adatom system ($\mu_T$) (both in units of µB), and the charge transferred from the adatom to the graphene lattice (in units of an electron charge), for various choices of $U$, on-site energy $\epsilon_0$, and hopping energy $t'$. Note that $U = 4.59t$, $\epsilon_0 = 0.4$ eV, and $t' = 5.8$ eV corresponds to the expected parameters of a hydrogen adatom. When $U \to \infty$, we find a spin polarized state near the Fermi energy. The magnetic moment calculated on the adatom is done using a combination of Eqs. (3.21) and (3.24) and the magnetic moment on the sheet is calculated using Eq. (3.32). (a)- Spin polarized LDOS plotted in Fig. 3.5. (b)- Spin polarized LDOS plotted in Fig. 3.7.

than that of the adatom. Furthermore, the width of the graphene peaks in the spectral function is proportional to the density of adatoms.

Using the mean-field methods described in the previous sections we can calculate a variety of other spin-independent and spin-dependent properties of the adatom-graphene system. These include $\rho_{00,\uparrow}(E)$ and $\rho_{00,\downarrow}(E)$, the local density of states of up and down spin on the adatom; the induced magnetic moment on the adatom ($\mu_a$) and in the entire system of graphene sheet plus adatom ($\mu_T$); and the net charge transfer from the adatom to the sheet, all as functions of the parameters $U$, $\epsilon_0$, and $t'$. The magnetic moment on the adatom site is

$$\mu_a = (\langle n_{\uparrow} \rangle - \langle n_{\downarrow} \rangle) \mu_B. \quad (3.34)$$

$\langle n_{\sigma} \rangle$ is obtained from

$$\langle n_{\sigma} \rangle = \int_{-\infty}^{E_F} \rho_{00,\sigma}(E)dE, \quad (3.35)$$
Figure 3.6: (a)-(c). Spectral function $A(k, E)$ at $U = 0$ for the graphene-adatom system, as calculated using Eqs. (3.28) and (3.29) for three values of $k$ corresponding to $M$, $K$, and $\Gamma$ respectively, assuming a nearest-neighbor tight-binding band. We use $t = 2.8 \, eV$, $t' = 5.8 \, eV$, $\epsilon_0 = 0.4 \, eV$, and $N = 500$. (d). The spin polarized spectral function for the point $M$ and the case $U \to \infty$ in the mean-field approximation, using the same parameters as in (a)-(c). $A_\sigma(k, E)$ for the majority spin component is shown in black and that of the minority component in red. For the minority spin component, $A_\sigma(k, E)$ is just that of the unperturbed graphene sheet, i. e., delta functions at the unperturbed pure graphene energy eigenvalues for all values of $k$. For the case $U = 0$, and for the majority spin at $U = \infty$, the adatom contribution occurs near $E_F$, while the graphene sheet contribution corresponds to broadened peaks near the unperturbed energy eigenvalues $\epsilon_k$ given as the eigenvalues of in Eq. (3.18). For points $\Gamma$ and $M$, the integral of the peak near $E \sim 0$ is of order $1/(2N)$ times those of the main peaks in the spectral function, and thus vanishes as $N \to \infty$. 
where $\rho_{00,\sigma}$ ($\sigma = \uparrow$ or $\downarrow$) is defined using the appropriate generalization of Eq. (3.24). The total magnetic moment is given in Eq. (3.32). The net charge transfer from adatom to the graphene lattice is obtained by first integrating $\rho_{00,\uparrow} + \rho_{00,\downarrow}$ up to the Fermi energy, to obtain the net number of electrons on the adatom, then subtracting this quantity from the adatom valence $Z$ (i.e., for hydrogen, $Z = 1$) to obtain the net charge transfer.

We have carried out these calculations for various values of the adatom on-site energy $\epsilon_0$, Hubbard parameter $U$, and hopping energy $t'$. In Table 3.1 we summarize the results above for parameters appropriate to a hydrogen adatom and summarize the trends when the various adatom parameters are varied. Additional results are shown in Figs. 3.5 and 3.7. As can be seen in Table 3.1 and Fig. 3.7, the parameter values thought to be appropriate
to an $H$ adatom ($U = 4.59t$, $t' = 5.8$ eV, and $\epsilon_0 = 0.4$ eV), lead to a very small magnetic moment on the adatom though there is an increase in both the LDOS and TDOS close to the Fermi energy ($E_F = 0.173$ eV; see Fig. 3.7(a)).

In general, as seen in Table 3.1, for sufficiently large $U$, a nonzero magnetic moment develops on both the adatom and the graphene sheet. The moment on the adatom is of order 0.3 $\mu_B$ in this limit, for the given parameters, while the sum of the moments on the adatom and the sheet approaches $\mu_B$ in this limit. We also find in all of our calculations that a large fraction (typically 0.6—0.7 of the electron) is transferred from the adatom to the graphene sheet for the parameters we consider. For the parameters appropriate to hydrogen adatoms, the model predicts no, or only a very small, induced magnetic moment. A possible explanation is that our model assumes no lattice distortion due to the adatom. But DFT calculations have shown that the surface of graphene is warped due to the addition of an adatom. This warping could change the distance between the adatom and the neighboring carbon atoms, and hence possibly the value of the Coulomb integral.

In Fig. 3.8, we show the total magnetic moment of the system as given by Eq. (3.32) plotted as a function of $U$, for various values of $t'$. In each case shown, $\epsilon_0 = 0.4$ eV and $t = 2.8$ eV. In all the plots, there is an apparent threshold behavior: the moment becomes nonzero only if $U$ exceeds a threshold value which depends on $t'$ as well as on $U$. While these calculations are done using a simple mean-field approximation, they seem to be consistent with other work on related models [82, 91].

3.5 Effects of Varying the Fermi energy on the Magnetic Properties of a Graphene-Adatom System

To determine how the Fermi energy changes the magnetic properties of the graphene-adatom system we undertook calculations in which we varied the Fermi energy for a variety of different values of $\epsilon_0$, $t'$, and $U$. In every case, we find that the total magnetic moment is non-zero only when $E_F$ lies within a limited range. We write this condition as $E_\ell < E_F < E_u$ where $E_\ell$ and $E_u$ are the lower and upper energies within which $\mu_T \neq 0$. Within this range,
the magnitude of $\mu_T$ is controlled by varying the Fermi energy $E_F$, typically by applying a gate voltage to the sample which interacts with the conduction electrons via the electric field effect [92]. If the graphene-adatom system is neutral and no voltage is applied, $E_F$ will be constrained to have a particular value controlled by the charge neutrality condition. Introducing a gate voltage will shift $E_F$ from this neutral value (denoted $E_{F_0}$) and hence change the magnetic moment.

As an illustration of this picture, we show in Fig. 3.9 the total magnetic moment $\mu_T(E_F)$ under various conditions. In each case, we assume all parameters but one are those thought to describe H on graphene [$t = 2.6 \, \text{eV}, \, t' = 7.5 \, \text{eV}, \, \epsilon_0 = 0.16 \, \text{eV}, \, \text{and} \, U = 4.59t$ [91]], and vary the remaining parameter [88, 89, 91]. We assume a single H adatom is placed on a graphene sheet containing $N = 500$ carbon primitive cells, giving 1 H atom per 1000 C atoms. In Fig. 3.9(a), we assume that $t$ and $t'$ are those of the H-graphene system, while each curve represents a different value of the on-site energy $\epsilon_0$. We find, when $E_{F_0} > \epsilon_0$
Figure 3.9: Total magnetic moment versus Fermi energy for an adatom on graphene calculated using Eq. (3.32). In each case, all the parameters but one are appropriate to H on graphene \([t = 2.6 \, eV, \quad t' = 7.5 \, eV, \quad \epsilon_0 = 0.16 \, eV, \quad \text{and} \quad U = 4.59t \) [91]. In (a) each curve represents a different on-site energy \(\epsilon_0\) (given in eV in the legend) with the calculated maximum value for each curve found to be \(\mu_{\text{max}} \approx 1 \times 10^{-6} \mu_B\) for \(\epsilon_0 = -0.4 \, eV\). In (b), each curve represents a different hopping energy \(t'\) (in eV) with the calculated maximum value for each curve found to be \(\mu_{\text{max}} \approx 1 \times 10^{-4} \mu_B\) for \(t' = 5.8 \, eV\). In (c) each curve represents a different Hubbard energy \(U\) (in eV) with the calculated maximum value of \(\mu_{\text{max}} \approx 1 \times 10^{-5} \mu_B\) for \(U = 15.0t\). Similar to Fig. 3.10.
Figure 3.10: Total magnetic moment versus Fermi energy for an adatom on graphene calculated using Eq. (3.32). In each case, all the parameters but one are appropriate to H on graphene, as given in the text. In (a) each curve represents a different on-site energy $\epsilon_0$ (given in eV in the legend). In (b), each curve represents to a different hopping energy $t'$ (in eV), and in (c) each curve represents a different Hubbard energy $U$ (in eV). The maximum calculated magnetic moment in (a) is $\mu_T \approx 0.1\mu_B$, corresponding to $\epsilon_0 = -0.4\ eV$ and $-1.0\ eV$, (b) the maximum value of $\mu_T \approx 0.14\mu_B$ for $t' = 5.0eV$, and (c) a maximum value of $\mu_T \approx 0.2\mu_B$ for $U = 12.0t$. 
and we allow $\epsilon_0$ to become much less then $E_{F_0}$, that the onset energy $E_\ell \to 0$, whereas the upper cutoff energy $E_u$ shows only a minimal dependence on $E_F$.

In Fig. 3.9(b) we plot $\mu_T(E_F)$ versus $E_F$ for several values of $t'$, with other parameters the same as the H-graphene system. As $t'$ is varied we find that both $E_u$ and $E_\ell$ depend strongly on the hopping energy $t'$. In Fig. 3.9(c), we plot $\mu_T(E_F)$ versus $E_F$ for several values of the electron-electron energy $U$, assuming the other parameters are the same as the H-graphene system. As $U$ increases, so do both $E_\ell$ and $E_u$. As $U \to \infty$, $E_u \to \infty$ as well, i.e., $\mu_T$ persists no matter how large $E_F$ in this case.

For all parameters we have considered, we find that the magnitude of the magnetic moment $\mu_T < \mu_B$. In Fig. 3.9(a) the maximum value of $\mu_T \approx 1 \times 10^{-6} \mu_B$, corresponding to $\epsilon_0 = -0.4 \text{ eV}$. In Fig. 3.9(b) the maximum value of $\mu_T \approx 1 \times 10^{-4} \mu_B$ for $t' = 5.8 \text{ eV}$, while in Fig. 3.9(c) a maximum value of $\mu_T \approx 1 \times 10^{-5} \mu_B$ for $U = 15.0t$. As shown previously, as $U \to \infty$, $\mu_T \to \mu_B$.

The maximum value of $\mu_T$ is also very sensitive to the parameters of the Hamiltonian, especially to $\epsilon_0$ and $t'$. For example, for the earlier set of parameters $t = 2.8 \text{ eV}$, $t' = 5.8 \text{ eV}$, $\epsilon_0 = 0.4 \text{ eV}$, and $U = 4.59t$ [78], the maximum $\mu_T$ increases to $\sim 0.14 \mu_B$, primarily, we believe, because the hydrogen energy level is further from the Dirac point where the graphene density of states is larger. These earlier results are plotted in Fig. 3.10.

Note that both parameter choices give the same qualitative result, namely, that by changing the Fermi energy one would be able to turn the magnetic moment on and off again in a reproducible fashion.

### 3.6 Discussion of the Fermi Energy Calculation

The numerical results of Figs. 3.9 and 3.10 can be qualitatively understood as follows. If the system of graphene plus adatom has a net magnetic moment, then the partial densities of states $\rho_\uparrow(E)$ and $\rho_\downarrow(E)$ will be unequal. The total magnetic moment is then obtained by integrating these two densities of states up to $E_F$. If $E_F$ lies below the bottom edge of the lower band, there will be no net magnetic moment. The moment becomes non-zero at
the energy $E_F = E_\ell$ when $E_F$ moves above the bottom of the lower band. It reaches its maximum when $E_F$ lies somewhere between the peaks in $\rho_T(E)$ and $\rho_\downarrow(E)$ (assuming the two bands overlap), and thereafter decreases until it becomes zero at $E_F = E_u$, the energy above which both sub-bands are filled. Thus, for any choice of the parameters $\epsilon_0$, $t'$, and $U$, there should be a finite range of $E_F$, within which $\mu_T \neq 0$.

Of course, this description is an oversimplification because we self-consistently determined $\rho_T(E)$ and $\rho_\downarrow(E)$ which depend on the quantities $\langle n_{0,\sigma} \rangle$ ($\sigma = \pm 1/2$), which themselves depend on $\mu_T$. However, even with the oversimplification, the qualitative description remains correct. The maximum value of $\mu_T$ depends, in part, on how much the two sub-bands overlap. If the overlap is large, maximum of $\mu_T$ will be small, everything else being equal, while a small overlap will tend to produce a larger $\mu_T$. Another reason why $\mu_T$ is reduced below $\mu_B$ is that there is generally a large electron transfer from the adatom onto the graphene sheet [4]. We also note that the energy range, $E_u - E_\ell$, where $\mu_T \neq 0$ is approximately equal to the width of the extra density of states due to the adatom.

The Fermi energy $E_F$ can be controlled experimentally in several ways. One is to apply a suitable gate voltage $V$, which raises or lowers $E_F$ by an amount $eV$, where $e$ is the magnitude of the electronic charge. Another is by chemical doping: if one adds or subtracts charge carriers to the graphene-adatom system by doping with suitable molecules, this will also raise or lower $E_F$ as was done in Ref. [93]. One could also add a small number of vacancies in the graphene, as also done in Ref. [93]. This will reduce the number of charge carriers and hence lower $E_F$. Of course, vacancies would also change the graphene density of states; so the present calculations would have to be modified to treat this situation.

The model used here treats only the effects of adatoms on graphene, but it does qualitatively reproduce the upper energy cutoff found in the experiments of Ref. [93]. For example, Nair et al. [93] found an upper cutoff of around $E_u = 0.5$ $eV$, which we can approximately obtain by assuming an on-site energy $\epsilon_0 = 0.4$ $eV$, $t' = 5.8$ $eV$ and $U = 4.59t$. However, our model does not account for the onset energy found in Ref. [93] of $E_F \sim 0$ since in our model the bottom edge of the lower band occurs at $E_\ell > 0$.

In summary, by using a simple tight-binding model of adatoms on graphene we are able
to calculate the total magnetic moment of graphene with a small concentration adatoms as a function of $E_F$. The model is expected to apply to the case of H adatoms, but could also be applicable to other adatom species, characterized by different model parameters. The Fermi energy $E_F$ can be controlled experimentally by a suitable gate voltage. Our results show that, for realistic tight-binding parameters ($\epsilon_0 = 0.16 \, eV, t' = 7.5 \, eV, U = 4.94t$), the magnetic moment can be switched off at a relatively low voltage ($eV \sim 0.5 \, eV$), in rough agreement with the experiments of Ref. [93]. These results are potentially of much interest since they suggest that the magnetic moment of graphene with adatoms can be electrically controlled.

3.7 Summary of Graphene-Adatom Work

Using a tight-binding model we have calculated the local and total density of states and the spectral function for a system consisting of a single adatom in a $T$ site on graphene. Because the hopping integral from the adatom to a graphene Bloch state has the same magnitude for any $k$, we have shown that these quantities can be calculated analytically. This simplification holds even if we do not make the oft-used linear approximation [75] for the graphene density of states near the Dirac point. It is also valid even if we include non-nearest-neighbor hopping in the tight-binding graphene Hamiltonian. Since our numerical results give both the local and total density of states, we can compute the charge transfer from the adatom to the graphene. Our numerical results show that, for most parameters we consider, this charge transfer is a substantial fraction of an electron (approximately 70% for parameters appropriate to hydrogen).

Because the calculations are at low adatom concentrations, the adatom-induced density of states is linear in concentration. Other work has treated the same system at higher adatom concentrations, but only numerically [78]. In future work, it might be possible to treat the present model analytically at higher concentrations, at least approximately. It would also be of interest to include the effects of lattice distortions, which are known to exist when adatoms bind to graphene [94], and which can lead to a large increase in spin-
orbit interactions \cite{91, 95}. Such spin-orbit interactions would likely have a large effect on
the magnetic properties arising from the adatom.

We have also calculated the magnetic properties induced by the adatom, using a Hubbard
model treated within mean-field theory. For all choices of the Hamiltonian parameters,
we find that there is a critical value of the Hubbard $U$ above which the density of states
near the Fermi energy is spin-polarized and a net induced magnetic moment is formed. The
appearance of this magnetic moment was predicted long ago to occur within mean-field
theory for models with a slowly varying density of states near the Fermi energy \cite{82}. Here,
it is also found to occur in a system with a roughly linear density of states near $E_F$.

Next, we discuss the reliability of the simple mean-field approximation (MFA) used
to study magnetic moment formation. While the approximation is too simple to give all
the details of the magnetic properties, it may give a qualitatively reasonable picture. In
support of this hypothesis, a study of the Kondo Hamiltonian using renormalization-group
techniques for a system with a linear density of states \cite{91} also found a critical threshold for
moment formation, as a function of the model parameters. Since, at large $U$, the Hubbard
model can be approximately transformed into the Kondo model \cite{96}, it seems likely that
there really is a threshold behavior in the Hubbard model with a linear density of state
such as is found here, even though we use a mean field theory to obtain it.

A somewhat counterintuitive result of our calculations is that, as $t'$ increases, the value
of $U$ needed to induce a magnetic moment becomes smaller. Since a larger $t'$ suggests that
it is easier for the electron to hop from the impurity to the graphene, one might expect
that a moment on the impurity atom would be less likely to form. A possible explanation
is that the larger $t'$ also causes the peak in the impurity density of states to shift closer to
the Dirac point, where the graphene density of states is smaller. Thus, there are fewer final
states available for an electron to hop into, and hence, the electron is less likely to hop, thus
increasing the likelihood of moment formation on the impurity.

In our approximation we also calculate the spectral function of our graphene-adatom sys-
tem to first order in $1/N$. The main effect of the adatom is, as expected, simply to broaden
the delta-function peaks that the spectral function would exhibit in an ideal graphene lat-
tice. In our approach, this broadening, and the shape of the spectral line, are computed analytically. To the same order, we find that both the adatom contribution to the spectral function at $E \sim 0$ and the broadening of the graphene spectral lines will vanish as $N \to \infty$.

**Extension to Other Two-Dimensional Systems**

In this work our single-particle Green’s function approach was used with a tight binding Hamiltonian in the limit of no electron-electron correlations, to obtained analytical equations for the LDOS, TDOS, and spectral function for adatoms on the surface of graphene. Using the same model with a finite Hubbard energy $U$, we find that a magnetic moment is induced both on the adatom and nearby on the graphene sheet above a critical value of $U$ which depends on the other model parameters. These results are not only of intrinsic interest but also may be useful in understanding the behavior of a variety of adatoms on graphene. Furthermore, the same analytical approach might also be used to treat adatoms on other 2D systems, such as those based on Si or Ge or the class of two dimensional materials known as dichalcogenides.

While this work included only a single orbital for the adatom, it could be extended to larger absorbed atoms by including additional orbits from these adatoms. This multi-band model could be used to understand the role heavier elements, either magnetic or non-magnetic, have on the magnetic properties of graphene.
Chapter 4

ON THE MAGNETIC FIELD DEPENDENCE OF THE SPIN-DEPENDENT SEEBECK COEFFICIENT OF INSB

4.1 Overview

The spin Seebeck effect refers to the generation of spin currents by an applied temperature gradient, or to the resulting voltage often induced by the so-called inverse spin Hall effect (ISHE). In the longitudinal spin-dependent Seebeck effect, both the spin orientation and the spin current are parallel to the temperature gradient. A number of recent experiments have demonstrated the occurrence of a spin Seebeck effect in a variety of different materials [97], including metallic ferromagnets [98], magnetic insulators [99], and doped non-magnetic semiconductors [100] in strong magnetic fields. Several papers discuss possible explanations for such behavior but, to our knowledge, none discuss the spin-dependent Seebeck effect in n-doped InSb [97, 101–107].

The band structures of InSb and other zinc-blende semiconductors have been extensively investigated, both theoretically and experimentally. Early theoretical studies by Kane [108], Dresselhaus [109], and Parmenter [110] explain the effects of symmetry on the conduction band electronic states. In other early studies, the effects of a magnetic field on the band structure of InSb were investigated by Roth et al. [111, 112] and by Pidgeon et al. [113]. These theoretical and experimental studies led to a better understanding of the beats observed in Shubnikov-de Haas oscillations in III-V semiconductors [114]. Other experiments showed that the lowest conduction band state in InSb has the spherically symmetric $\Gamma_6$ symmetry [109, 115], and that the effective mass of the conduction band electrons is only a
small fraction of the free electron mass [115].

In this chapter, we present a simple model calculation for spin transport in InSb in the presence of a temperature gradient and an external magnetic field with and without spin-orbit interactions. Our model is basically a simple treatment based on the Boltzmann equation, but applied to the bands formed by the Landau levels in an n-type semiconductor when there is a strong magnetic field parallel to the temperature gradient. We will first discuss the electronic band structure of InSb near the Γ point which is the \( k = 0 \) point in the first Brillouin zone and, second, discuss why it is called the spin-dependent Seebeck effect and not the spin Seebeck effect. Third, we will consider the case of no spin-orbit interactions and determine various spin-dependent and spin-independent transport coefficients. Then, after discussion the origins of the Spin Hall effect, we will outline how one would include the spin-orbit Hamiltonian in our calculation using first and second order perturbation theory. The spin-orbit interactions we consider include the effects of strain on the spin-orbit coupling and the cubic in \( k \) Dresselhaus term. The use of first and second order perturbation theory allows one to calculate the energies and wave function of the perturbed system which will allow one to determine various spin-dependent transport coefficients including the spin Seebeck coefficient.

4.2 Band Structure of InSb near the Γ Point

In doped semiconducting materials the number of conduction electrons is often much less then the number of electrons in the system. Therefore, it is often necessary and convenient to only consider electrons near an extremum of a conduction band. Consider Fig. ?? which shows a sketch of a direct band gap semiconductor which is electron doped (a) and hole doped (b). The filled portions of the bands represent the density of states of the conduction band (blue) and density of states of the valence band (orange). If the n-doped semiconductor is doped so that the Fermi energy, \( E_F \), is pushed into the valence band, then only the portion of the density of states, and therefore a portion of the total number of electrons, contribute to the conductivity of the material.
Figure 4.1: Energy vs. Density of States of a electron doped (a) and hole doped (b) semiconductor. Note that the energy gap, $E_g$, is approximately the same in both cases and that the Fermi Energy $E_F$ relative to the energy gap changes as a function of doping. Conduction band density of states labeled in blue and the valence band density of states is labeled in orange.

Since only a small fraction of the electrons contribute to the conduction in doped semiconductors, it is a valid approximation to assume that the number of conduction electrons will be concentrated around the minimum of the conduction band. Therefore, knowledge of the entire band structure is unnecessary [116] and only knowledge of the band structure near the band extrema is necessary. At the same time, the symmetry of the crystal is often enough to accurately determine the energy spectrum near the critical points. This negates the need to solve the full Schrödinger equation [116].

One can often determine what points in $k$ space are critical points by looking at the symmetry of the crystal as was done by many authors [108–110, 116]. For the case of n-doped InSb the relevant critical point in $k$ space is the Γ point, which is located at the center of the Brillouin zone. Early authors used the symmetry of the Γ point to determine the energy spectrum for $k$ values near Γ. This early work was pioneered by Dresselhaus...
and Parmenter and later expanded by Kane in what is known as $k \cdot p$ theory.

One can understand the approximations made in $k \cdot p$ theory using the following argument. First, we know that the Bloch wave functions, $\phi_{nk}$, are exact solutions to the full Schrödinger equation [8] and could be used to find the energy of the system for any wave vector $k$. However, since we care only about wave vectors near a specific point (or points) in $k$ space we can use the method of Luttinger and Kohn [117] to write the wave function near this critical $k_0$ point as [116]

$$\varphi_{nk} = \frac{1}{\sqrt{V}} \phi_{nk_0} e^{ik \cdot x} \quad (4.1)$$

where $V$ is the crystal volume and the Bloch wave function $\phi_{nk_0}$ is evaluated at the extremum $k_0$ (which we take to be the $\Gamma$ point) and is an eigenfunction of the operator $H_0 = \frac{p^2}{2m} + V(x)$ with energy $E_n(k_0)$. Let us define the difference in wave vector $K$ between the wave vector $k$ and the critical point $k_0$ as $K = k - k_0$. Then, the Bloch wave function $\phi_{nK}$ can be expanded in terms of the Luttinger-Kohn wave functions as

$$\phi_{nK} = \sum_{n'} c_{n'k} \varphi_{n'k} \quad (4.2)$$

where the periodicity of the wave functions is preserved (see Bir in Ref. [116]) and the coefficients $c_{n'}$ define the transformation between the Bloch wave function and the Luttinger-Kohn wave functions [116] which are atomic-like wave functions that describe the bands nearest the conduction band minimum [117].

If we multiply the Schrödinger equation by Eq. (4.2) and multiply on the left by $\varphi_{nk}$ we can write, after integration over $K$,

$$\sum_{n'} \left( E_n(k_0) + \frac{\hbar^2 k^2}{2m} - E \right) \delta_{n,n'} + \frac{\hbar k \cdot p_{nn'}}{m} \right) c_{n'} = 0 \quad (4.3)$$

where we use the fact that $H_0(p) \phi_{nk} = H_0(p + \hbar k) \phi_{nk}$ and defined $p_{nn'}$ as the matrix element between Bloch wave functions $\phi_{nk_0}$ as [116]

$$p_{nn'} = \frac{1}{V} \int \phi_{nk_0}^* P \phi_{n'k_0} dx \quad (4.4)$$
where \( p = -i\hbar \nabla \).

Since the matrix element \( p_{nn'} \) contains inter-band matrix elements, we can apply a transformation that partially diagonalizes the system\(^7\) which allows us to write, up to second order in the wave vector \( \mathbf{k} \), the energy of the system as

\[
E(\mathbf{k} + \mathbf{k}_0) = E_0(\mathbf{k}_0) + \frac{\hbar}{m} \sum_{\alpha} k_\alpha p_{n_k,n_\mathbf{k}_0}^{\alpha} + \sum_{\alpha\beta} \frac{\hbar^2}{2m_{\alpha\beta}} k_\alpha k_\beta \tag{4.5}
\]

where \( \alpha, \beta = x, y, z \) and \( m_{\alpha\beta} \) is the effective mass tensor given by

\[
\frac{1}{m_{\alpha\beta}} = \frac{1}{m^2} \sum_{n' \neq n} \frac{p_{nn'}^{\alpha} p_{n'n}^{\beta} + p_{nn'}^{\beta} p_{n'n}^{\alpha}}{E_n(\mathbf{k}_0) - E_{n'}(\mathbf{k}_0)} + \frac{1}{m} \delta_{\alpha\beta}. \tag{4.6}
\]

In Eq. (4.5) we ignored the contribution from the spin-orbit interaction. To include the spin-orbit interaction we need to include a term proportional to both the spin polarization \( \sigma \) and the momentum of the particle \( p \). The only term of this form found in the relativistic corrections to the Schrödinger equation given by Pauli is\([42, 116]\)

\[
H_{SO} = \frac{\hbar}{4mc^2} (\sigma \cdot [\nabla V \times p]) \tag{4.7}
\]

where \( V \) is the periodic potential of the crystal.

To include the spin-orbit Hamiltonian in the above derivation, we simply replace \( p \) by \( \pi \) where \( \pi \) is defined as

\[
\pi = p + \frac{\hbar}{4mc^2} [\sigma \cdot \nabla V]. \tag{4.8}
\]

This allows us the write the energy of the system as

\[
E(\mathbf{k} + \mathbf{k}_0) = E_0(\mathbf{k}_0) + \frac{\hbar}{m} \sum_{\alpha} k_\alpha \pi_{n_k,n_\mathbf{k}_0}^{\alpha} + \sum_{\alpha\beta} \frac{\hbar^2}{2m_{\alpha\beta}} k_\alpha k_\beta \tag{4.9}
\]

with a similar change to the effective mass tensor given in Eq. (4.6) (i. e. \( p \to \pi \)).

To get an idea of how \( \mathbf{k} \cdot \mathbf{p} \) theory works we will give three examples that make successively better approximations for the conduction band of InSb at the \( \Gamma \) point. In each of the approximations used below, we will determine the energy as a function of \( k_\alpha \) using the known symmetry properties of the zinc-blende crystal structure without inversion symme-

\(^7\)See Bir in Ref. [116] for the mathematical details.
try. The lack of inversion symmetry stems from the fact that unit cell of InSb contains two atoms (one indium atom and one antimony atom) and therefore a reflection of the unit cell about a plane passing through the center of the unit cell is not a symmetry operation.

First, we will note that in the case of n-doped InSb the conduction band minimum is taken as the critical point $k_0$ and is known as the symmetry point $\Gamma$. We take the $\Gamma$ point to have zero energy (i.e. $E(k_0) = 0$) and, due to inversion asymmetry of the zinc-blende crystal, we take the velocity at the critical point $k_0$ to be equal to zero. This allows us to write the energy near the conduction band minimum as

$$E(k) = \sum_{\alpha\beta} \frac{\hbar^2}{2m_{\alpha\beta}} k_\alpha k_\beta$$

(4.10)

where $\alpha, \beta = x, y, z$ giving the conduction band minimum an ellipsoidal shape in $k$-space. For InSb it was experimentally determined by Dresselhaus et al. that the conduction band minimum is, in fact, spherically symmetric via cyclotron resonance experiments on InSb [115] (i.e. that $m_{\alpha,\beta} = m^*$ for all $\alpha$ and $\beta$).

If we allow for slightly larger values of $k_\alpha$ and use the symmetry of the zinc-blende crystal InSb (which has a spherically symmetric $\Gamma_6$ ground state) we find that the energy is given as

$$E(k) = Ak^2 \pm \sqrt{B^2k^4 + C^2 (k_x^2k_y^2 + k_x^2k_z^2 + k_y^2k_z^2)}$$

(4.11)

where the constants $A, B, C$ and $D$ are defined by

$$A = \frac{L + 2M}{3}$$

$$B = \frac{L - M}{3}$$

$$C^2 = \sqrt{D^2 - 3B^2}$$

$$D = \frac{N}{\sqrt{3}}$$

(4.12)

and the constants $L, M$ and $N$ relate momentum matrix elements between different con-
duction and valence bands as

\[ L = \frac{\hbar^2}{2m} + \frac{\hbar^2}{m^2} \sum_n \frac{|\langle X|p^x|n\rangle|^2}{E_0 - E_n} \]

\[ M = \frac{\hbar^2}{2m} + \frac{\hbar^2}{m^2} \sum_n \frac{|\langle X|p^y|n\rangle|^2}{E_0 - E_n} \]

\[ N = \frac{\hbar^2}{m^2} \sum_n \frac{\langle X|p^z|n\rangle\langle n|p^y|Y\rangle + \langle X|p^y|n\rangle\langle n|p^z|Y\rangle}{E_0 - E_n} \]

where the wave functions \( X, Y \) and \( Z \) are Bloch wave functions whose symmetries are discussed in Ref. [108, 109, 116]. The energy given in Eq. (4.11) is second order in the wave vector \( k \) and reduced to the previous result [Eq. (4.10)] in the limit that all the inter-band matrix elements are small.

If one extends this calculation to third order in \( k \), which is necessary if one considers larger and larger wave vectors \( k \), then one would include a term known as the Dresselhaus spin-orbit coupling energy, given as [109]

\[ E_D = \gamma_D \left( \sigma_x k_x (k_y^2 - k_z^2) + \sigma_y k_y (k_z^2 - k_x^2) + \sigma_z k_z (k_x^2 - k_y^2) \right) \]

(4.14)

where \( \gamma_D \) is the Dresselhaus spin-orbit coupling strength which itself depends on various band parameters. In this instance we find that [118]

\[ \gamma_D = \frac{2\hbar^3}{3m_{cv}} \frac{\eta}{\sqrt{2m_e E_g(1 - \eta/3)}} \]

(4.15)

where \( \eta = \Delta_{SO}/(\Delta_{SO} + E_g) \) and \( E_g \) is the energy gap, \( \Delta_{SO} \) is the energy gap between the spin-split bands, \( m_{cv} \) has units of mass and relates to the interaction between the conduction and valence bands, and \( m_e \) is the bare electron mass.

One could continue to calculate higher order corrections in \( k \cdot p \) theory to any arbitrary order in the wave vector \( k \). However, for the purposes of this calculation, we limit ourselves to terms third order in the wave vector \( k \) and will only discuss terms linear in the wave vector \( k \) when we include the effects of strain on the energy spectrum.

The calculated energy terms given above now include the effects of electron spin and
only will be modified by including the Zeeman interaction of an electron in a magnetic field in a later part of the chapter. Since spin and spin-orbit interactions are now part of our calculated energy we will now discuss the naming conventions for the various spin-related effects found in metals and semiconductors while paying particular attention to whether the effect is a bulk effect or a spin-injection effect.

4.3 Nomenclature of Seebeck effects

In semiconductors and metals spin phenomena can be roughly categorized into three types [97]: (1) independent electron effects, (2) collective effects, and (3) relativistic effects. The first class consists of phenomena in which the two spin types can be considered as separate entities which show little interaction. This independence gives rise to spin-dependent electrical and thermal conductivities and spin-dependent Seebeck effects [97]. In the first part of this chapter we will consider independent electron effects when we calculate the spin-dependent Seebeck effect for the longitudinal configuration (magnetic field, spin current, and temperature gradient all parallel) [6]. The second class of effects comes from the collective dynamics of the magnetic order parameter that couples a single electron spin via spin-transfer torque, spin-pumping or spin-orbit interactions which we will discuss in the later part of this chapter during our calculation of the transverse spin Seebeck effect [7]. Finally, the third class of phenomena comes from the relativistic correction to the electron energy via spin-orbit coupling and generally refers to thermal Hall effects such as the Nerst effect which exist in normal metals and represents the Hall voltage induced by a heat current [97].

The remainder of the chapter is split into two parts. First we review, with no spin-orbit interactions, the relevant macroscopic transport equations describing the heat, electronic, and spin transport. Then we present a theory for these transport coefficients based on a microscopic Hamiltonian combined with the Boltzmann equation. The Hamiltonian includes the Landau Hamiltonian for electrons in a magnetic field and the Zeeman interaction between the spins and the magnetic field. The Boltzmann equation is then linearized, and solved to yield various thermoelectric and spin-dependent coefficients. Finally, we present
Figure 4.2: Schematic of the idealized experimental configuration, showing the orientation of the magnetic field and thermal gradient, and the positions of the non-magnetic contacts (red) used to measure the spin-dependent Seebeck coefficient in InSb (tan). The thermal gradient and applied magnetic field are oriented along $z$. The voltage drop along $z$ can also be measured by attaching leads to the non-magnetic contacts [97].

numerical solutions of this model for the various transport coefficients as a function of magnetic field at a temperature $T = 4.5K$ and present explicit expressions for the various Onsager coefficients as a function of the various numerical parameters. In the second half of this chapter we include the effects of the spin-orbit interaction and calculate the transverse spin Seebeck coefficient as a function of a magnetic field. After this discussion we end with brief concluding remarks.

4.4 Spin-Dependent Transport Coefficients with No Spin-Orbit Interactions

4.4.1 Macroscopic Transport Equations

We begin by writing down the appropriate macroscopic transport equations for the system of interest, which we visualize as a doped semiconductor such as n-InSb in a magnetic field $\mathbf{B}$ taken parallel to the $z$ axis. In this case, there are three current densities to consider: the heat current density $J_Q$, and the charge current densities $J_+$ and $J_-$ for spin up and spin down charge carriers.

These currents are expected to be linearly related to corresponding fields, which will be $-\nabla T$, and $-\nabla \mu_\pm$, where $T$ is the temperature and the $\mu_\pm$ are the electrochemical potentials for spin up and spin down charge carriers. As noted by Brechet and Ansermet [119] (see also Bauer et al. [97] and Uchida et al. [120]), the linear Onsager relations between these
currents and fields may be written as

\[
\begin{pmatrix}
J_Q \\
J_+ \\
J_-
\end{pmatrix} =
\begin{pmatrix}
LQQ & L_Q+ & L_Q- \\
L_Q+ & L++ & L_{+-} \\
L_Q- & L_{-+} & L_{-+}
\end{pmatrix}
\begin{pmatrix}
-\nabla T \\
-\nabla \mu_+ \\
-\nabla \mu_-
\end{pmatrix}.
\] (4.16)

Instead of the currents \( J_+ \) and \( J_- \), it may be more convenient to consider the charge current density \( J_e = J_+ + J_- \) and the spin current density \( J_S = (\hbar/2q)(J_+ - J_-) \) (where \( q = -e \) is the charge of the current carriers and we assume a spin \( \hbar/2 \) per carrier). Similarly, rather than the \(-\nabla \mu_\pm\), it is more convenient, following Valet and Fert [121], to introduce the quantities \( \mu_{av} \) and \( \Delta \mu \) via the relation

\[
\mu_\pm = \mu_{av} \pm \Delta \mu + qV.
\] (4.17)

Here \( \mu_{av} \) is the average of the two chemical potentials at zero applied voltage, \( V \) is the electrostatic potential, and \( \Delta \mu = \frac{1}{2}(\mu_+ - \mu_-) \).

We can now write down the linear transport equations in terms of these new fields and currents. The result is

\[
\begin{pmatrix}
J_Q \\
J_e \\
J_S
\end{pmatrix} =
\begin{pmatrix}
LQQ & L_Qe & L_QS \\
L_Qe & L_{ee} & L_{eS} \\
L_QS & L_{Se} & L_{SS}
\end{pmatrix}
\begin{pmatrix}
-\nabla T \\
\mathcal{E} \\
-\frac{\hbar}{2q} \nabla (\Delta \mu)
\end{pmatrix},
\] (4.18)

where the various \( L \) coefficients are all certain linear combinations of the coefficients in Eq. (4.16) and \( \mathcal{E} = \mathbf{E} + \frac{\nabla \mu}{e} \) is the effective electric field.

Eq. (4.18) applies if the spin polarization is parallel to the direction of the spin current. If the spin polarization is not parallel to the direction of spin current flow, then there are three spin current vectors, to be called \( J_{S,i} \) with \( i = x, y, \) and \( z \), corresponding to current densities of the \( x, y, \) and \( z \) components of electron spin. In this case, Eq. (4.18) should be replaced by a \( 5 \times 5 \) matrix equation, corresponding to the five current densities \( J_Q, J_e, \) and the three \( J_{S,i} \). Since we will not consider this situation in the present section, we will not write down this equation explicitly.
4.4.2 Theory for Transport Coefficients in InSb

Next, we present a theory for some of the above transport coefficients in an n-type semiconductor, such as Te-doped InSb, in a magnetic field. Our goal is to model experiments carried out on a sample geometry similar to that shown in Fig. 4.2. In Fig. 4.2, we assumed that the sample is a rectangular prism having edges $L_x$, $L_y$, and $L_z$ ($L_x, L_y \ll L_z$). The top face is assumed to lie parallel to the $xz$ plane and non-magnetic leads are attached to either end of the sample, as shown, so that any electrical current would flow in the $z$ direction. A uniform magnetic field $B$ and a uniform temperature gradient $\nabla T$ are assumed to be applied in the $z$ direction.

I. Electronic Energies and Wave Functions with no Spin-Orbit Interactions

The conduction band of InSb is non-degenerate, and the low-lying electronic states in this band have the spectrum of a free electron (of effective mass $m^*$) in a magnetic field. The spin-independent part of the effective-mass Hamiltonian describing these states is thus

$$H_0 = \frac{1}{2m^*} \left[ +(-i\hbar \frac{\partial}{\partial x} + qBy)^2 - \hbar^2 \frac{\partial^2}{\partial y^2} - \hbar^2 \frac{\partial^2}{\partial z^2} \right], \quad (4.19)$$

where we have used SI units and a gauge such that the vector potential $A = (-By, 0, 0)$, where $B = \nabla \times A$ is the applied magnetic field.

The solutions of the spin-independent Hamiltonian given in Eq. (4.19) are standard. The total energy is a function of a wave vector $k_z$ and the Landau level index $n$, and can be written as

$$E_n(k_z) = \frac{\hbar^2 k_z^2}{2m^*} + \left( n + \frac{1}{2} \right) \hbar \omega_c, \quad (4.20)$$

where $\omega_c = eB/m^*$ is the cyclotron frequency. Each level has a degeneracy per spin $\sigma_z$ of

$$N_{n,\sigma_z} = \frac{L_x L_y B}{\Phi_0}, \quad (4.21)$$

where $\Phi_0 = \hbar/2e$ is the magnetic flux quantum.

In the absence of spin-orbit interaction, the spin-dependent part of the electronic Hamiltonian, denoted $H_s$, consists of a Zeeman interaction between the conduction electron and
the applied magnetic field, which may be written as
\[ H_s = g \mu_B B \cdot \sigma. \] (4.22)
Here \( g \) is the electronic g-factor, which is assumed independent of the magnetic field strength, \( \mu_B \) is the Bohr magneton, and \( \sigma \) is the vector of the three Pauli spin matrices for a spin-1/2 particle. The eigenvalues of \( H_0 + H_s \) are characterized by quantum numbers \( n \), \( k_z \), and \( \sigma_z = \pm 1/2 \), and are given by
\[ E_{n,\sigma_z}(k_z) = E_n(k_z) + g \mu_B B \sigma_z, \] (4.23)
with a spin \( \sigma_z \) parallel to \( z \) and a degeneracy given by Eq. (4.21).

II. Electrical, Thermal, and Spin Currents

Next, we will obtain the various electronic transport coefficients for an n-type semiconductor such as InSb, using the Boltzmann equation. In the presence of a magnetic field, the conduction band is broken up into many one-dimensional bands, labeled by a Landau level index \( n \) and a spin index \( \sigma_z \) (\( \sigma_z = \pm \)). Each band is also highly degenerate, with degeneracy \( N_{n,\sigma_z} \) as given in Eq. (4.21). The Boltzmann equation for an electron of spin \( \sigma_z \) in band \( n \) can be written in the standard way (see, e.g., Ref. [8]) as
\[ \frac{\partial g_{n,\sigma_z}}{\partial t} + \mathbf{v}_{n\sigma_z}(k_z) \cdot \nabla_r g_{n,\sigma_z} + \frac{\mathbf{F}}{\hbar} \cdot \nabla_{k_z} g_{n,\sigma_z} = \left( \frac{\partial g_{n,\sigma_z}}{\partial t} \right)_{\text{coll}}. \] (4.24)
Here \( g_{n,\sigma_z}(r, k_z, t) \) is the probability that an electron in a state \( k_z \) in the \( n^{th} \) band with spin \( \sigma_z \) at a position \( r \) is occupied at time \( t \), and \( \mathbf{v}_{n\sigma_z}(k_z) \) is the velocity of a Bloch electron in the state described by \( k_z \), \( \sigma_z \) and \( n \). \( \mathbf{F} \) is the force on an electron due to an applied field.

As is conventional, we make the relaxation time approximation so that the collision term is rewritten as
\[ \left( \frac{\partial g_{n,\sigma_z}}{\partial t} \right)_{\text{coll}} \sim -\frac{\delta g_{n,\sigma_z}(r, k_z, t)}{\tau}, \] (4.25)
where \( \delta g_{n,\sigma_z} \) is the deviation of \( g_{n,\sigma_z} \) from its equilibrium value \( g_{n,\sigma_z}^0 \) and \( \frac{1}{\tau} \) is the collision
rate. The function $g_{n,\sigma_z}^0$ is set equal to the Fermi function given by

$$
g_{n,\sigma_z}^0(k_z) = \frac{1}{e^{\beta(E_{n,\sigma_z}(k_z) - \mu)} + 1},
$$

(4.26)

where $\beta = 1/k_B T$, $T$ is the temperature, $k_B$ is Boltzmann’s constant, and $\mu$ is the chemical potential.

We seek a steady state solution and thus the first term on the left hand side of Eq. (4.24) vanishes. We also linearize the Boltzmann equation by assuming that both $\nabla r g_{n,\sigma_z}$ and $F$ are small, so that the factor $g_{n,\sigma_z}$ in both the second and the third terms of Eq. (4.24) can be approximated as $g_{n,\sigma_z}^0$. Combining these conditions, we obtain the linearized steady-state Boltzmann equation in the relaxation time approximation which, after simplification, is

$$
-\frac{\delta g_{n,\sigma_z}(k_z)}{\tau} = \frac{E_{n,\sigma_z}(k_z) - \mu}{T} \left( -\frac{\partial g_{n,\sigma_z}}{\partial E} \right) \nabla T \cdot \mathbf{v}_{n,\sigma_z}(k_z) + \mathbf{F} \cdot \mathbf{v}_{n,\sigma_z}(k_z) \left( \frac{\partial g_{n,\sigma_z}}{\partial E} \right),
$$

(4.27)

where we evaluate $E$ at $E = E_{n,\sigma_z}(k_z)$.

We are interested in the case of an applied temperature gradient and effective electric field oriented primarily along the $z$ axis (See Eq. (4.18)). We can now express the electric, heat, and spin currents in terms of $\delta g_{n,\sigma_z}(k_z)$, as obtained from Eq. (4.27). Two of these expressions are given, for a spherical band, by, e. g., Ref. [8]. These general expressions need to be modified to take account of the degeneracy of the Landau bands as we do below. The mathematical form of the spin current density, $J_S$, is similar to that of the electrical current density, $J_e$.

To be explicit, we can write out the current densities in the system as follows:

$$
J_e = \frac{L_z}{V} \sum_{n,\sigma_z} \int \frac{dk_z}{2\pi} (-e) N_{n,\sigma_z} \mathbf{v}_{n,\sigma_z}(k_z) \delta g_{n,\sigma_z}(k_z),
$$

(4.28)

$$
J_Q = \frac{L_z}{V} \sum_{n,\sigma_z} \int \frac{dk_z}{2\pi} N_{n,\sigma_z} \Delta E_{n,\sigma_z} \mathbf{v}_{n,\sigma_z}(k_z) \delta g_{n,\sigma_z}(k_z),
$$

(4.29)

$$
J_{S,i} = \frac{L_z}{V} \sum_{n,\sigma_z} \int \frac{dk_z}{2\pi} \mu_B \langle \sigma_{n,i} \rangle N_{n,\sigma_z} \mathbf{v}_{n,\sigma_z}(k_z) \delta g_{n,\sigma_z}(k_z),
$$

(4.30)

where we take the integral over $k_z$ from $\pm \infty$ and $\Delta E_{n,\sigma_z} = E_{n,\sigma_z}(k_z) - \mu$.

In Eqs. (4.28) - (4.30), $J_Q$ is the heat current, $\mathbf{v}_{n,\sigma}(k_z) = \hbar^{-1} \nabla_k E_{n,\sigma_z}(k_z)$ is the velocity
of a Bloch electron in the band labeled by \((n, \sigma_z)\), and \(\langle \sigma_{n,i} \rangle\) is the expectation value of the \(i\)th component of spin in the band \((n, \sigma_z)\) \((i = x, y, z)\). In the absence of spin-orbit interaction, only \(J_{S,z}\), that is, the current density associated with the \(z\) component of spin, is non-zero.

For an electron in the conduction band the velocity, \(v_{n,\sigma_z}(k_z) = v_{n,\sigma_z}(k_z)\hat{z}\) is given by

\[
v_{n,\sigma_z}(k_z) = \frac{\hbar k_z}{m^*} \nonumber = \pm \hbar \sqrt{\frac{2m^*}{\hbar^2} (E_{n,\sigma_z}(k_z) - E_{n,\sigma_z}^0)},
\]

where the + and − signs apply when \(k_z > 0\) and \(k_z < 0\), respectively, and \(E_{n,\sigma_z}^0\) is defined as the minimum energy for the band \((n, \sigma_z)\) given by

\[
E_{n,\sigma_z}^0 = \left( n + \frac{1}{2} \right) \hbar \omega_c + \sigma_z g \mu_B B.
\]

In order to calculate the various transport coefficients in Eqs. (4.28) - (4.30), we need the chemical potential \(\mu\). \(\mu\) can be calculated given the conduction electron density \(\rho = N_c/V\), where \(N_c\) is the total number of conduction electrons in volume \(V\). For the present case, the chemical potential \(\mu\) is obtained from

\[
\rho = \frac{B}{\pi \Phi_0} \sum_{n,\sigma_z} \int_0^\infty g_{n,\sigma_z}^0(k_z) dk_z
\]

where Eq. (4.33) is an implicit equation for \(\mu(T, B)\).

Since the experiments of Ref. [100] are done at a very low temperature \((T = 4.5K)\), we have approximated \(\mu\) (or equivalently, the Fermi energy \(E_F\)) by its value at \(T = 0\). In this case, \(g_{n,\sigma_z}^0\) is just a step function, and \(E_F\) is given implicitly by

\[
\rho = \sum_{n,\sigma_z} \frac{B}{\pi \Phi_0} \left( \frac{2m^*}{\hbar^2} \left( \mu - E_{n,\sigma_z}^0 \right) \right)^{\frac{1}{2}},
\]

where \(E_{n,\sigma_z}^0\) is defined in Eq. (4.32) and the sum runs only over Landau bands with nonzero electron occupation.
Figure 4.3: Calculated Fermi energy at $T = 0K$ plotted as a function of an applied magnetic field along the $z$ direction as indicated in Fig. 4.2. We also show the first three Landau bands ($n = 0, 1, 2$); each band is labeled by its band index $n$ and spin $\sigma_z$ as $(n, \sigma_z)$, where $\sigma_z = \pm$. Straight lines correspond to the minima of the various Landau sub-bands, as labeled in the Figure. Scalloped curve represents the $T= 0$ Fermi energy $E_F$ as a function of magnetic field. In this figure, $E_F$ is calculated neglecting spin-orbit coupling.

III. Transport Coefficients

We obtain the transport coefficients of interest by using Onsager’s linear relationship between the currents and the forces generating the currents [122]. For the present problem, this relation is given by Eq. (4.18). These may be written in condensed form as

$$J_i = \sum_j L_{ij} F_j,$$

(4.35)

where $i = e, Q, S$ runs over the three currents in the system and $j$ runs over the forces acting on the conduction electrons. In this chapter, we consider only longitudinal spin currents, i.e., we assume that only $\langle \sigma_z \rangle \neq 0$. The explicit form of the measured transport coefficients can then be obtained by combining Eq. (4.18) with Eqs. (4.27) - (4.31).

For example, the electrical conductivity, $\sigma_e$, is given by the Onsager coefficient $L_{ee}$ (see
Figure 4.4: The calculated electrical conductivity $\sigma_e$, given in Eq. (4.41), plotted as a function of the inverse magnetic field $1/B$ at $T = 4.5K$, and neglecting spin-orbit interactions. The maxima in the conductivity occur when the Fermi energy crosses the bottom of the Landau band as plotted in Fig. 4.3. The highest-field maximum occurs at approximately $B = 1.2T$, which corresponds to the Fermi energy crossing the $(0, -)$ Landau level. This curve is calculated neglecting spin-orbit interaction and using the $T = 0$ Fermi energy.

Similarly, the thermal conductivity, $\kappa$, is the coefficient between the heat current $J_Q$ and the negative temperature gradient $-\nabla T$ when the electrical current $J_e = 0$. $\kappa$ is given by [8]

$$\kappa = \frac{L_{QQ}L_{ee} - L_{Qe}L_{eQ}}{L_{ee}}$$

(4.36)

where the Onsager coefficients are given below, $\kappa$ is shown in Fig. 4.5.

The thermopower $\alpha$ is generally defined as the ratio of the $z$ component of the electric field to the negative of the thermal gradient (also assumed to be in the $z$ direction) under the condition of zero electrical current in the $z$ direction. We write this condition as $\mathcal{E} = \alpha(-\nabla T)_{J_e=0}$ [8]. It is readily shown that the $\alpha$ can be expressed in terms of the Onsager coefficients as

$$\alpha = -\frac{L_{eQ}}{L_{ee}}$$

(4.37)
Figure 4.5: Calculated thermal conductivity, $\kappa$, given in Eq. (4.36), plotted as a function of $1/B$ at $T = 4.5K$. The maxima in $\kappa$ occur, like those of $\sigma_e$, when the field-dependent Fermi energy crosses the bottom of a Landau level. This curve is calculated assuming no spin-orbit interaction and the values of the $T = 0K$ Fermi energy.

We can also calculate the coefficient $L_{SQ}$, which describes spin current parallel to the magnetic field and driven by a temperature gradient. A possible geometry for measuring this coefficient is shown in Fig. 4.2, as already mentioned. In this geometry, the n-type InSb is placed between two non-magnetic contacts in an open circuit (no charge current), and a temperature difference is maintained between the two contacts.

The analysis of spin and thermal transport in this configuration has been discussed in Ref. 123 for a ferromagnetic metallic wire, and can also be used for the present case. As discussed there, the results depend on the boundary conditions at the ends of the wire, which are likely to fall between two possible limiting cases. In our notation, these are (i) $\Delta \mu = 0$ at each end of the wire; and (ii) $J_S = 0$ at the two ends. For case (i), we can solve Eqs. (4.18) taking $J_e = 0$ and $\Delta \mu = 0$ to obtain $E = (L_{eQ}/L_{ee})\nabla T$ and

$$J_S = \left( L_{SQ} - \frac{L_{Se}L_{eQ}}{L_{ee}} \right) (-\nabla T) \quad (4.38)$$
In our notation, this is equivalent to the result obtained in Ref. 123 for position-independent temperature gradient and boundary condition (i). For boundary condition (ii), one can solve Eq. (4.18) under the conditions \( J_e = 0, J_S = 0 \) to obtain

\[
\mathcal{E} = \frac{L_{SS} L_{eQ} - L_{eS} L_{SQ}}{L_{ee} L_{SS} - L_{eS} L_{Se}} \tag{4.39}
\]

and

\[
-\frac{\hbar}{2q} \nabla (\Delta \mu) = \frac{L_{ee} L_{SQ} - L_{Se} L_{eQ}}{L_{ee} L_{SS} - L_{eS} L_{Se}} \tag{4.40}
\]

Thus, various observable quantities (spin current density, induced electric field) are sensitive to the spin-dependent Seebeck coefficient \( L_{SQ} \). The results would be modified when spin-flip scattering is included, as described in Ref. 123. The thermally induced spin accumulation (i.e., \( \Delta \mu \)) or spin current can also be detected non-locally, by allowing the spin to diffuse into a non-magnetic material, as discussed by Slachter et al. [124].

Before discussing the numerical results, we present the Onsager coefficients which are integrated as functions of the magnetic field strength \( B \). In our model, the Onsager coefficients can be written as

\[
L_{ee} = \frac{L_z}{V} \sum_{n,\sigma} \int_{-\infty}^{\infty} \frac{dk_z}{2\pi} e^2 N_{n,\sigma} [v_{n,\sigma}(k_z)]^2 \tau \frac{\partial g_{n,\sigma}^0(E, T)}{\partial E}; \tag{4.41}
\]

\[
L_{eQ} = \frac{L_z}{V} \sum_{n,\sigma} \int_{-\infty}^{\infty} \frac{dk_z}{2\pi} e N_{n,\sigma} [v_{n,\sigma}(k_z)]^2 \tau \frac{\Delta E}{T} \frac{\partial g_{n,\sigma}^0(E, T)}{\partial E}; \tag{4.42}
\]

\[
L_{Se,i} = -\frac{L_z}{V} \sum_{n,\sigma} \int_{-\infty}^{\infty} \frac{dk_z}{2\pi} \mu_B \langle \sigma_i(k_z) \rangle N_{n,\sigma} [v_{n,\sigma}(k_z)]^2 \tau \frac{\partial g_{n,\sigma}^0(E, T)}{\partial E}; \tag{4.43}
\]

\[
L_{SQ,i} = -\frac{L_z}{V} \sum_{n,\sigma} \int_{-\infty}^{\infty} \frac{dk_z}{2\pi} \mu_B \langle \sigma_i(k_z) \rangle N_{n,\sigma} [v_{n,\sigma}(k_z)]^2 \frac{\Delta E}{T} \frac{\partial g_{n,\sigma}^0(E, T)}{\partial E}; \tag{4.44}
\]

\[
L_{QQ} = \frac{L_z}{V} \sum_{n,\sigma} \int_{-\infty}^{\infty} \frac{dk_z}{2\pi} N_{n,\sigma} \frac{(\Delta E)^2}{T} [v_{n,\sigma}(k_z)]^2 \tau \frac{\partial g_{n,\sigma}^0(E, T)}{\partial E}, \tag{4.45}
\]

where \( L_{eQ} = L_Qe \) and \( \Delta E = E_{n,\sigma_z}(k_z) - \mu \). The derivation of the Onsager Coefficients is shown in Appendix A.

In Eqs. (4.41) - (4.45), the derivative \( \partial g_{n,\sigma_z}^0(E, T)/\partial E = -\beta e^{\beta (E-\mu)}/[e^{\beta (E-\mu)} + 1]^2 \), with \( \beta = 1/(k_B T) \), and \( E = E_{n,\sigma_z}(k_z) \). During numerical calculations the integrals given above are converted to integrals over energy using the relationship \( dk_z = dE/[dE/dk_z] \). All
the integrals are dominated by the energy range within $k_B T$ of the Fermi energy, because $\partial g_{n,\sigma z}^0/\partial E$ is strongly peaked around $E = E_F$. In practice, the integrands all become vanishingly small beyond an energy of $\sim 3k_B T$ on either side of $E_F$. In all the above expressions, $v_{n,\sigma z}(k_z)$ is obtained from Eq. (4.31).

### 4.4.3 Numerical Results with No Spin-Orbit Interaction

We now turn to numerical results based on the present simplified model. We first calculate the chemical potential $\mu(T, B)$ at $T = 0K$, assuming parameters appropriate to the conduction band of InSb and the experiments of Ref. [100], as given in Table 4.1. The resulting Fermi energy is shown in Fig. 4.3 as function of $B$, assuming a conduction electron density of $\rho = 3.7 \times 10^{15} \text{ cm}^{-3}$, as used in the experiments of Ref. [100]. The results show, as already obtained in Ref. [100], that $\mu(T = 0, B)$ is a non-monotonic function of $B$, with discontinuous changes in slope wherever the minimum of one of the spin sub-bands rises through the Fermi energy and becomes unoccupied.

Given the Fermi energy, or at finite temperature the chemical potential $\mu(T, B)$, we can calculate a variety of transport coefficients. Here we calculate the components of electrical and thermal conductivities, and of the thermopower, parallel to the field, under the appropriate experimental conditions as described above. We also calculate the transport coefficient $L_{SQ}$ [Eq. (4.18)], which represents the spin current density in the $z$ direction per unit applied temperature gradient in the $z$ direction. All the coefficients are functions of both the applied magnetic field $B$ and the temperature $T$. The integrals in the transport

<table>
<thead>
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<th>Quantity</th>
<th>Value</th>
<th>Ref.</th>
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<tr>
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<td>[125]</td>
</tr>
<tr>
<td>$m^*$</td>
<td>$0.013m_e$</td>
<td>[115]</td>
</tr>
<tr>
<td>$\tau$</td>
<td>$\approx 1 \times 10^{-12} \text{ s}$</td>
<td>[100]</td>
</tr>
</tbody>
</table>

Table 4.1: Numerical parameters used in the calculation of the Onsager coefficients given in Eqs. (4.41) to (4.45). The estimate $\tau \sim 10^{-12} \text{ s}$ is estimated from the electron mobility presented in Ref. [100].
coefficients are all dominated by energies within $k_B T$ of $E_F$, since the energy derivative of the Fermi function, which is a factor in each of the integrals, is strongly peaked near $E_F$.

The results of these calculations are shown in Figs. 4.4 - 4.7. In each case, we have plotted the transport coefficients at $T = 4.5K$ as functions of the inverse magnetic field. The various numerical parameters used in the calculations are given in Table 4.1. We plot the transport coefficients in this manner in order to show that the positions of the peaks in these quantities vary periodically with $1/B$. The oscillations are related to the de Haas-van Alphen oscillations normally seen in the magneto-transport coefficients of metals [126].

### 4.5 Spin Seebeck Coefficient With Spin-Orbit Interaction

While excluding the spin-orbit interaction allowed us to calculate a number of interesting transport coefficients, we are unable to calculate the transverse spin-dependent Seebeck coefficient which was experimentally observed by Jaworski et al. [100]. To calculate the transverse spin Seebeck coefficient one must include the effects of the spin-orbit interaction...
which creates an effective magnetic field in the system. It is known experimentally and theoretically that the spin-orbit interaction can have a substantial affect on the energetics of the system and in particular, on the energy levels within InSb [100, 109].

In our case, we will include the spin-orbit interaction by using an approximation first introduced by Dresselhaus. This approximation is based on the version of $\mathbf{k} \cdot \mathbf{p}$ perturbation theory originally introduced by Kane for any semiconductor lacking inversion symmetry [108], which allows spin-orbit coupling to be included to arbitrary accuracy. The Dresselhaus spin-orbit interaction, or the "Dresselhaus term," depends on the wave vector $\mathbf{k}$ as $k^3$. A second form of the spin-orbit interaction that we include in our calculations is strain-induced spin-orbit interaction, which is linear in wave vector $\mathbf{k}$, and depends on the strain tensor $\tilde{\epsilon}$ to linear order. Such strains are thought to significantly affect the band structure at low temperatures [116, 118, 127, 128].
Dresselhaus Spin-Orbit Coupling

Dresselhaus spin-orbit coupling occurs in any bulk material that lacks inversion symmetry [109]. Therefore, in zinc-blende crystals, such as InSb, which contain two different atoms per primitive cell, there should always be a Dresselhaus term in the Hamiltonian. Zinc-blende crystals do indeed lack an inversion center, or, equivalently, are called noncentrosymmetric.

Strain-Induced Spin-Orbit Coupling

Since phonons play a significant role in the transport properties of InSb at low temperatures \((T < 20K)\) [129, 130], we will include the effects of strain at low temperatures as well by introducing the strain-induced spin-orbit interaction, which is thought to affect the energy levels of many semiconductors at low temperatures [116, 118]. The early work by Bir and Pikus [127, 128] shows that one should only include strain-induced terms when (1) the calculation is done at low temperatures, and (2), there exists a strong coupling between the phonon and electron baths. In fact, the application of strain, either by mechanical means or by lattice vibrations (phonons), can change the symmetry of the crystal structure and therefore will change the calculated energy in \(\mathbf{k} \cdot \mathbf{p}\) perturbation theory. The effect of strain on the spin-orbit interaction comes from the relative change in positions of atoms in the lattice which directly affects the potential \(V(x)\) seen by the conduction electrons. Therefore, both the periodic potential of the system and the spin-orbit interactions are affected by strain.

4.5.1 Electronic Energies and Wave-functions with Spin-Orbit Interactions

When including the spin-orbit interaction we start from the Hamiltonians given in the previous sections as \(H_0\) and \(H_s\) which we rewrite here for clarity. The free-particle Hamiltonian given by \(H_0\) is

\[
H_0 = \frac{1}{2m^*} \left[ + (i\hbar \frac{\partial}{\partial x} + qBy)^2 - \hbar^2 \frac{\partial^2}{\partial y^2} - \hbar^2 \frac{\partial^2}{\partial z^2} \right], \tag{4.46}
\]
and the Zeeman Hamiltonian is given by

\[ H_s = g\mu_B B \cdot \sigma. \]  \hspace{1cm} (4.47)

Since the wave-functions and associated energies are already known for these two Hamiltonians we will determine the effect of adding the additional Hamiltonians, given by

\[ H_{SO} = \frac{1}{2} \Omega_{SO} \cdot \sigma, \]  \hspace{1cm} (4.48)

where \( \Omega_{SO} \) is the sum of the Dresselhaus spin-orbit coupling \([109]\) \( \Omega_D \) and the strain-induced spin-orbit coupling \([116, 118, 131]\) \( \Omega_s \).

The components of \( \Omega_D \) are given by

\[ \Omega_{Dz} = 2\gamma_D k_z (k_x^2 - k_y^2), \]  \hspace{1cm} (4.49)

and those of \( \Omega_s \) by

\[ \Omega_{sz} = 2C_3 (\epsilon_{xx} k_x - \epsilon_{yy} k_y) + 2D k_z (\epsilon_{xx} - \epsilon_{yy}). \]  \hspace{1cm} (4.50)

The \( x \) and \( y \) components of \( \Omega_D \) and \( \Omega_s \) are given by cyclic permutations of Eqs. (4.49) and (4.50). The spin-orbit coefficients \( C_3 \) and \( \gamma_D \) depend on the band gap energy, the spin-orbit splitting energy, and the effective mass of an electron, and will be estimated below; the spin-orbit coefficient \( D \) will be ignored as it results from higher order corrections to \( \mathbf{k} \cdot \mathbf{p} \) theory. We estimate values of the spin-orbit coefficients by using the experimentally and theoretically determined values of the spin-orbit splitting energy \( \Delta_{SO} \), conduction band effective mass \( (m^*) \), and band gap \( (E_g) \) as

\[ \gamma_D = \frac{2\hbar^3}{3m_{cv}} \frac{\eta}{\sqrt{2m_e E_g (1 - \eta/3)}} \]  \hspace{1cm} (4.51)

and

\[ C_3 = \frac{2\hbar c_2\eta}{3\sqrt{2m_e E_g (1 - \eta/3)}} \]  \hspace{1cm} (4.52)

where \( \eta = \Delta_{SO}/(\Delta_{SO} + E_g) \), \( c_2 \) is the inter-band deformation potential for acoustic phonons, \( m_e \) is the mass of an electron, and \( m_{cv} \) is the effective mass arising from the conduction-
Values for the Spin-Orbit Properties of InSb

<table>
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<tr>
<th>Quantity</th>
<th>Value</th>
<th>Ref.</th>
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</thead>
<tbody>
<tr>
<td>$\Delta_{SO}$</td>
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<td>[132]</td>
</tr>
<tr>
<td>$m^*$</td>
<td>0.013$m_e$</td>
<td>[115]</td>
</tr>
<tr>
<td>$\tau$</td>
<td>$\approx 1 \times 10^{-12} \text{ s}$</td>
<td>[100]</td>
</tr>
<tr>
<td>$E_g$</td>
<td>0.81 eV</td>
<td>[132]</td>
</tr>
<tr>
<td>$c_2$</td>
<td>$7.705 \times 10^{-14} eV$</td>
<td>[113]</td>
</tr>
<tr>
<td>$m_{cv}$</td>
<td>$\approx 0.34m_e$</td>
<td>[132]</td>
</tr>
<tr>
<td>$\epsilon_{xz} = \epsilon_{yz}$</td>
<td>0.01</td>
<td></td>
</tr>
</tbody>
</table>

Table 4.2: Numerical parameters used in the calculation of the spin-dependent transport coefficients. The estimate $\tau \sim 10^{-12} \text{ s}$ is inferred from the electron mobility quoted in Ref. [100], the estimate for $m_{cv}$ comes from the mass of the heavy hole electron, and the inter-band scattering potential $c_2$ is extracted from the work of Pidgeon et al [113]. The chosen value of $\epsilon_{xz}$ corresponds to 1% strain since we are assuming only a small displacement of the atoms within the unit cell.

We will determine the energies of the spin Hamiltonian via first and second order perturbation theory by using the unperturbed wave functions of $H|\Phi(x)\rangle = E(k_z)|\Phi(x)\rangle$, where $H$ is the sum of the Hamiltonians given in Eqs. (4.46) and (4.47). This wave function, which is the product of a free particle wave function in the $x$ and $z$ directions, a harmonic oscillator in the $y$ direction, and the spin states of the Pauli Matrix $\sigma_z$, will be used to determine the energy for the spin part of the Hamiltonian which we consider to be a small perturbation.

While our work to include the effects of spin-orbit interaction using first and second order perturbation theory is still ongoing, we can describe the origins of the Hall Effect and spin-Hall effect which we will use to calculate the transverse spin Seebeck coefficient.

4.5.2 The Hall Effect and Spin-Hall effect

The ordinary Hall effect, first quantified by E. H. Hall in 1879 [133], describes the effects of placing an electrical current in a perpendicular magnetic field. Hall found that when a current was placed along the $x$ direction of a thin gold leaf (a conductor) and an external magnetic field in the $z$ direction that a voltage was induced in the $y$ direction and that valence band interaction [118]. The calculated and measured values are indicated in Table 4.2 and give values for $\gamma_D = 0.84 eV \cdot m^3$ and $C_3 = 9.3 \times 10^{-4} eV \cdot nm$ [118].

While our work to include the effects of spin-orbit interaction using first and second order perturbation theory is still ongoing, we can describe the origins of the Hall Effect and spin-Hall effect which we will use to calculate the transverse spin Seebeck coefficient.
this voltage depended linearly on the strength of the magnetic field and strength of the applied current. In Fig. 4.8 we sketch a typical geometry for the Hall Effect including the relative orientations of the current, magnetic field, and generated electric field. The physical significance of the Hall effect is apparent when one considers the current to be a stream of electrons moving with the same velocity [134]. In a magnetic field, any moving electron, with charge $q$, experiences a force proportional to the cross product of the velocity and the magnetic field. This can be expressed formally as

$$F = qv \times B.$$  \hspace{1cm} (4.53)

In a neutral material, we expect that his magnetic force $F$ will counter act the induced force due created by the electric field $E$ set up by the moving charges as $F = qE$. The velocity $v$ of the electron can be expressed in terms of the charge current density $j = nqv$ allowing us to rewrite the above relationships as

$$E = R (j \times B)$$ \hspace{1cm} (4.54)
where the Hall coefficient \( R = \frac{-1}{nq} \) where \( n \) is the density of electrons and \( q \) is the charge of the charge carriers. (For electrons, \( q = -e \), where \( e \) is the magnitude of the electrons charge, and hence \( R \) is negative when the charge carriers are electrons.) While this derivation of the Hall coefficient \( R \) is not rigorous it does give a physical idea of why one would expect a perpendicular electric field to develop when a current interacts with a perpendicular magnetic field.

The above physical picture gives rise to what is known as the ordinary Hall effect. Which characterizes the response of a current to a perpendicular magnetic field. In some materials, particularly ferromagnetic materials, an additional contribution to the Hall effect comes from the magnetization of the sample. For example, in a ferromagnetic material, the total magnetic field is given by \( B = H + \mu_0 M \) where \( H \) is the external magnetic field, \( \mu_0 \) is the magnetic permeability of vacuum, and \( M = \sum_i m_i \) is the magnetization of the material expressed as a sum over the magnetic moments, \( m_i \) of each atom \( (i = 1 \ldots N) \). For example, in nickel, which is ferromagnetic, the anomalous Hall effect is several hundred times larger then the ordinary Hall effect [135]. In either case, the preferential movement of electrons to one side of the material over the other creates an electrical current \( j_e = \sigma E \) perpendicular to the applied current and perpendicular to the applied magnetic field. Using the geometry of Fig. 4.8 we find that an electrical current \( j_{e,y} \) is generated in the \( y \) direction due to an applied current \( j_{e,x} \) and magnetic magnet field \( B_z \) in the \( z \) direction.

While the ordinary and anomalous Hall effects are interesting effects in metals and semiconductors, in which they are often used to determine the density of electrons in the system under investigation [134], we also know that electrons have a spin moment. This spin moment could be influenced by the transverse electric field as well. This interaction between the electron’s magnetic moment and the transverse electric field gives rise to the spin Hall Effect, which was first postulated by Hirsch [136]. In fact the same mechanism that gives rise to the anomalous Hall effect is believed to give rise to the spin Hall effect [136]. That is, even without an external magnetic field, the same scattering mechanism(s) are expected to cause spin up electrons to move preferentially in one direction and spin down electrons to move in the other [136], leading to the build up of spin magnetic moment on opposite
faces of the particular sample.

If we consider the material in Fig. 4.8 to be a piece of paramagnetic material or a doped semiconductor, we would find that an applied current \( j_{e,x} \) would create a perpendicular spin current \( j_{s,y} \) if the magnetization of the material lies along the \( z \) direction (this could be achieved by placing a small external magnetic field along the \( z \) axis to align the spin states and is given by \( M = (n_{\uparrow} - n_{\downarrow})\mu_B \) where \( n_{\uparrow} \) is the density of electrons with spin up). This spin current \( j_{s,y} \) is effectively the build up of the a magnetic moments on the edges of the sample [136].

I. Inverse Spin Hall Effect

In the ordinary Hall effect, it is clear why the inverse Hall effect should work (an applied electrical current in the \( y \) direction generates an electrical current in the \( x \) direction) since, without spin, the system should be rotationally symmetric. To observe the inverse of the spin Hall effect (known as the Inverse Spin Hall Effect (ISHE)) one would have to apply a spin current to a doped semiconductor or paramagnetic material and observe the corresponding electrical current.

Mathematically, the inverse spin Hall effect can be written as

\[
\mathbf{J}_e = \theta (\mathbf{J}_s \times \mathbf{B}) \\
= \theta (\mathbf{J}_s \times (\mathbf{H} + \mu_0 \mathbf{M})) \\
= \mu_0 \theta (\mathbf{J}_s \times \mathbf{M}) \\
= \mu_0 \mu_B \theta \left( \mathbf{J}_s \times \sum_i n_i \langle \sigma_i \rangle \right)
\]

(4.55)

where \( \theta \) is the inverse spin Hall coefficient (traditionally known as the spin Hall angle), \( m_i = \mu_B \langle \sigma_i \rangle \), \( n_i \) is the occupation number for the \( i^{th} \) state labeled by \( k_z \), and in the second line we assumed \( \mathbf{J}_s \parallel \mathbf{H} \).

Dividing both sides of Eq. (4.55) by the electrical conductivity one finds that the electric
field induced by the inverse spin hall effect is given by

\[ E = \frac{\mu_0 \mu B \theta}{\sigma_e} \left( J_s \times \sum_i n_i \langle \sigma_i \rangle \right) \]  

(4.56)

where \( \sigma_e \) is the electrical conductivity (given by the Onsager coefficient \( L_{ee} \)). Noting that the spin current is in the \( z \) direction we can write

\[ E_y = \frac{\mu_0 \mu B \theta}{\sigma_e} J_{s,z} \langle \sigma_x \rangle \]  

(4.57)

where \( \langle \sigma_x \rangle = \sum_{k_z} n_{k_z} \langle \sigma_x(k_z) \rangle \) and \( \sigma_x(k_z) \) can be calculated by taking the expectation value of the Pauli spin matrix \( \sigma_x \) using the wave function for the perturbed system using first and second order perturbation theory. If we require that no electrical current flow in the \( z \) direction and require no difference in spin-dependent chemical potential at the edges of the sample [107] then we find that the transverse spin Seebeck coefficient \( \alpha_s \), which we define through \( E_y = \alpha_s (-\nabla T_z) \), is

\[ \alpha_s = \frac{\mu_0 \mu B \theta}{\sigma_e} \langle \sigma_x \rangle \left( L_{SQ} - L_{Se} \frac{L_{eQ}}{L_{ee}} \right). \]  

(4.58)

In calculating the transverse spin Seebeck coefficient we once again use the Onsager coefficients given in Eqs. (4.41) to (4.45). The energy of the system will be calculated using first and second order perturbation theory and therefore the velocity of the system can be determined by \( v_{n\sigma}(k_z) = \hbar^{-1} \nabla_{k_z} E_n(k_z) \) where \( E_N(k_z) \) is the calculated energy using first and second order perturbation theory. The velocity then, will have the following form:

\[ v_{n\sigma}(k_z) = \frac{\hbar k_z}{m^*} + \sigma \frac{d\lambda_n(k_z, B)}{dk_z} \]  

(4.59)

where \( \lambda_n(k_z, B) = E_{n,\sigma}^1(k_z) + E_{n,\sigma}^2(k_z) \), \( E_{n,\sigma}^1(k_z) \) is the first order perturbation theory correction to the energy, and \( E_{n,\sigma}^2(k_z) \) is the second order correction to the energy using perturbation theory. In future work, I hope to make this very qualitative discussion more qualitative.
4.6 Discussion and Conclusions

In this chapter, we have given simple models for the Seebeck coefficients in InSb. In our model, the electronic energy levels of n-type InSb in a magnetic field are given as Landau levels and the various electronic transport coefficients, including the longitudinal spin Seebeck coefficient, are obtained from a simple Boltzmann equation approach for each Landau subband. The oscillations of this coefficient in a magnetic field occur when the Fermi energy crosses the minima of the various Landau subbands as the magnetic field is varied.

While our model holds, in principle, for any temperature $T$, we have carried out the calculations of the transport coefficients only at low $T$ ($T \sim 4.5$ K) and specifically calculated the chemical potential at $T = 0K$ (See Fig. 4.3). While the difference between the chemical potential at $T = 0$ and $T = 4.5K$ is small, it could affect both the magnitude and position of the Landau level crossings. This change could give quantitatively different results, but the qualitatively picture of the oscillations would remain the same.

In the second part of this chapter we discussed our attempt to model the transverse spin Seebeck coefficient. In the first part of this chapter, we omitted the spin-orbit interaction, which is known to have a large affect on the band structure of InSb and similar compound semiconductors. The spin-orbit interaction couples the spatial momentum to various components of the electronic spin. In particular, some forms of this interaction couple momenta in one direction with spin components in other directions. Such coupling could lead to expectation values of the spin vector which are tilted relative to the electronic momentum. This could, in turn, produce a nonzero value of $J_{S,x}$ and $J_{S,y}$ along the $z$ direction. If the spin vector is tilted relative to the direction of spin current, this will lead to a transverse electric field via the inverse spin Hall effect (ISHE) [137]. While this is not the only way to produce a transverse electric field, it is the only way to produce such a field within our simple model.

By including spin-orbit interactions of both the Dresselhaus and strain-induced forms using first and second order perturbation theory we hope to show that the transverse spin-dependent Seebeck is enhanced when the Fermi energy crosses the second lowest Landau
level. The inclusion of Dresselhaus spin-orbit coupling, which is a bulk effect, is necessary to describe the effect of spin-orbit interactions on the electrons in InSb. The inclusion of the strain-induced spin-orbit interactions comes from the interplay between the electron bath and phonon bath at lower temperatures. At low temperatures electron-phonon coupling is important in InSb and can modify the band structure by introducing linear-in-k terms to the energy dispersion relation.

4.6.1 Extension of Transport Calculations to other Systems

While our model uses $\mathbf{k} \cdot \mathbf{p}$ theory specifically to determine the electronic energies of an electron doped semiconductor, one could use the basic theory found here to calculate the transport coefficients in other materials as well, assuming one can write down the energy of the current carries in such systems. If this can be done, then one could use the Boltzmann equation approach to determine the distribution of electrons in this new system by allowing for additional relaxation mechanisms such as spin-flip scattering or spin-spin scattering (which are known to exist in magnetic systems). Additional work in magnetic insulators, for instance, would allow for a better understand of the Seebeck effect in the magnetic insulator known as YIG (Yttrium- Iron- Garnet) as well as a better understanding of spin-dependent transport phenomena in magnetic insulators.
Chapter 5
CONCLUSIONS

We briefly conclude this thesis by highlighting the main results of our research for each of the given chapters and then briefly commenting on future research projects related to the topics presented here.

In chapter 2 our investigation into the dispersion relations of surface plasmons on chains of metallic particles lead to the possibility of tuning the dispersion relations by the application of an anisotropic liquid crystal host or external magnetic field. We found that the orientation of the liquid crystal director axis relative to the metallic chain direction controlled the frequencies range of the dispersion relations and that one could use this control to create, for example, a band-pass filter using chains of metallic particles. With the application of a magnetic field under the appropriate experimental geometry one could create conditions in which one-way wave guiding is possible. That is, if a linearly polarized wave of fixed frequency and wave number was transmitted along the wave then its backscattered wave would be suppressed due to the symmetry breaking of the magnetic field. This realization of a one-way wave guide is unique in its approach and should be easy to construct.

In chapter 3 our investigation into the effects of placing a low concentration of adatoms on to the surface of graphene allowed us to analytically calculate the density of states, local density of states, and spin-polarized spectral function for the graphene-atom system using mean-field theory to describe the electron-electron interaction. By varying the parameters in this tight-binding approach we are also able to determine the parameter dependence of magnetic moment formation caused by the presence of the adatom. We are also able to show that the magnitude of the magnetic moment can be controlled with an external gate.
voltage. This switchable magnetic moment at low adatom concentrations is a direct result of the near linear density of states of the graphene-adatom system near the Fermi energy.

In chapter 4, by selectively including and excluding spin-orbit interactions, we are able to determine the magnetic field dependence of various transport coefficients in an n-doped semiconductor. Specifically, we implore a simple Hamiltonian that include the effects of an external magnetic field (Landau Hamiltonian) and the Zeeman splitting between the magnetic field and the spin moment of the electron. Without spin-orbit interaction we are able to calculate the electrical conductivity, thermal conductivity, thermopower, and spin-dependent Seebeck coefficient. By including spin-orbit interactions via the Dresselhaus Hamiltonian and the strain-induced spin-orbit Hamiltonian we hope to calculate a non-zero value of the spin polarization in the $x$ and $y$ directions. This tilted spin polarization leads to a transverse spin Seebeck effect as well due to the inverse spin hall effect. The origins of the oscillations recently observed in experiments are also observed to coincide with Landau level crossings of the Fermi energy.

As noted at the end of chapter 2, the work on surface plasmon dispersion relations can easily be extended to magnetic nanoparticle systems by including the affect of a frequency dependent permeability tensor. Or, as recent experimental work by several groups on metamaterials suggests, the possibility of developing systems in which the frequency dependence of the permeability tensor comes from the structure of the material, and not necessarily the magnetic nature of the nanoparticles. In either case, the possibility of transmitting information via the magnetic coupling of surface plasmons will lead to future research in the area of non-electrical transmission of information.

Additional work on the graphene-adatom system to include the effects of spin-orbit interactions in a tight-binding model would also be a natural extension of the research presented in chapter 3. Early work to calculate the effects of spin-orbit interactions on graphene using DFT and a tight-binding fit showed that spin-orbit interactions introduces a small (meV) energy gap in the energy spectrum and density of states of the graphene adatom system. Including the effects of spin-orbit interactions in a tight binding model may lead to a better understanding of its magnetic properties, specifically the switching of
the magnetic moment, since the density of states near the Fermi energy is critical for this
switching effect. An extension of this work to other 2D systems which contain two different
atoms per unit cell and therefore would create an intrinsic energy gap in the system and
therefore, provide different and possible interesting effects when adatoms are introduced to
the surface.

The extension of our transport calculations to other systems, specifically magnetic insu-
lators, should allow for better insight into the transport phenomena and magnetic field
dependence of these systems in a model that is easily understood and of general applicabil-
ity. One could also extend the calculations done here by introducing additional energy terms
via $\mathbf{k} \cdot \mathbf{p}$ theory or include additional scattering mechanisms within Boltzmann transport
theory. In either case one could investigate the effects of different scattering mechanisms or
Hamiltonians on the transport properties within the simple theory set forth in chapter 5.
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Appendix A
DERIVATION OF THE ONSAGER COEFFICIENTS

To determine the functional form of the Onsager coefficients we first need to write down the current equation as a linear combination of the various forces in our material. In the case of InSb, the forces we consider (for the case of no spin-orbit interaction) are the forces due to the effective electric field, $\mathcal{E}$, and the force due to the temperature gradient, $-\nabla T$. For the case of the electrical current we can write down the general form by assuming that a linear relationship exists between the currents and forces as

$$J_e = L_{ee}\mathcal{E} + L_{eQ}(-\nabla T) \quad (A.1)$$

where $L_{ee}$ and $L_{eQ}$ are the Onsager coefficients that relate the generating force to the current. In what follows we will only show the derivation of the Onsager coefficient known as $L_{ee}$ which represents the relationship between the electrical current and the effective electric field. However one could easily extend this approach to find other Onsager coefficients used in the calculations of chapter 4.

The electrical current can also be written in terms of a distribution function which, via the Boltzmann equation, determines how the electrical current is influenced by the forces acting on the system. The electrical current caused by the non-equilibrium distribution of electrons is given by Ashcroft and Mermin as [8]

$$J_e = \frac{L_z}{V} \sum_{n,\sigma_z} \int \frac{dk_z}{2\pi} (-e)N_{n,\sigma_z}v_{n,\sigma_z}(k_z)\delta g_{n,\sigma_z}(k_z) \quad (A.2)$$

where the integral over $k_z$ ranges from $\pm\infty$, $N_{n,\sigma}$ is the degeneracy of the $(n, \sigma)$ band.
[Eq. (4.21)], \( L_z \) is the length of the sample in the \( z \) direction, \( V \) is the volume of the sample, \( e \) is the magnitude of the electrons charge, and \( v_{n,\sigma}(k_z) \) is the velocity of the electron. \( \delta g_{n,\sigma}^0(k_z) \) is the non-equilibrium distribution function given by the Boltzmann equation in the relaxation time approximation as

\[
-\frac{\delta g_{n,\sigma}^0(k_z)}{\tau} = \frac{E_{n,\sigma}(k_z)}{T} - \mu \left( -\frac{\partial g_{n,\sigma}^0}{\partial E} \right) \nabla T \cdot v_{n,\sigma}(k_z) + F \cdot v_{n,\sigma}(k_z) \left( \frac{\partial g_{n,\sigma}^0}{\partial E} \right)
\]  

(A.3)

where \( E_{n,\sigma}(k_z) \) is the energy of the \((n,\sigma)\) band, \( \mu \) is the chemical potential, \( T \) is the temperature, and \( F = -eE \). In Eq. (A.3) the function \( g_{n,\sigma}^0(k_z) \) is the equilibrium distribution function which we will take to be equal to the Fermi function.

By combining Eqs. (A.2) and (A.3), we can write out the current equation in terms of the effective electric field and temperature gradient. Then, by comparing the combined equation with Eq. (A.1), we can extract the coefficient of \( E \) to get the Onsager coefficient that connects the electrical current to the effective electrical field. This Onsager coefficient is \( L_{ee} \) in our notation and given by

\[
L_{ee} = \frac{L_z}{V} \sum_{n,\sigma_z} \int_{-\infty}^{\infty} \frac{dk_z}{2\pi} e^2 N_{n,\sigma_z}[v_{n,\sigma_z}(k_z)]^2 \tau \frac{\partial g_{n,\sigma_z}^0(E,T)}{\partial E}.
\]  

(A.4)

In the same manner, by extracting the coefficient between the electrical current and the negative temperature gradient one can determine the coefficient \( L_{eQ} \) as well.

By writing down the heat and spin currents in a manner similar to the electrical current one can determine the Onsager coefficients used to describe the linear relationship between the heat and spin currents and the forces in the manner described above. We note that the derivative of the Fermi function, which is a key part of every Onsager coefficient, is a narrowly peaked function at the temperatures we are considering. Therefore, during the numerical calculations presented here, we converted the integrals over \( k_z \) to integrals over energy, using the chain rule and the energy of the system, and only integrated over a region in energy space near the Fermi energy. The energy range used in this calculation was \( \Delta E = \pm 2k_bT \) where \( k_b \) is Boltzmann’s constant.