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Electronic and vibrational properties of two-dimensional materials constructed from graphene and molecular components

By

Liang Zheng Tan

A dissertation submitted in partial satisfaction of the requirements for the degree of Doctor of Philosophy in Physics in the Graduate Division of the University of California, Berkeley

Committee in charge:

Professor Steven G. Louie, Chair
Professor Feng Wang
Professor Mark Asta

Fall 2014
Electronic and vibrational properties of two-dimensional materials constructed from graphene and molecular components

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Liang Zheng Tan
Abstract

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Liang Zheng Tan

Doctor of Philosophy in Physics

University of California, Berkeley

Professor Steven G. Louie, Chair

In the first part of this dissertation, we study the effects of electron-phonon coupling on the electronic properties of two-dimensional graphene-based materials and molecular lattices. We develop a theoretical model of magneto-phonon resonances in graphene under high magnetic fields, for phonons at both Γ and K points. Multiphonon excitations in molecular lattices are treated within the cumulant expansion, leading to an accurate description of phonon satellite structures in tunneling experiments. The second half of this dissertation deals with the electronic structure of graphene-based materials and two-dimensional electron gases under external long wavelength potential variations. We show how a graphene-like electronic structure can be created in molecular lattices self-assembled on metal surfaces. We show how velocity renormalization, new Dirac points, and band gap openings can occur when modulated electric and magnetic fields are applied to graphene or bilayer graphene.
I dedicate this dissertation to my teachers.
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Chapter 1

Introduction

The subject of condensed matter physics in general concerns itself with ordinary matter — that is, matter consisting of electrons and nuclei. Solid state physics in particular is the study of the solid phase of ordinary matter, which is defined by the discrete translational symmetries of the positions of electrons and nuclei. Being subatomic particles, these constituents of matter are in principle bound by the laws of quantum mechanics. However, the fact that the masses of nuclei are \( \sim 10^4 \) times heavier than the mass of an electron allows a drastic simplification in the quantum mechanical treatment. In the Born-Oppenheimer approximation, the electrons are considered to equilibrate on time scales much faster than that of the nuclei. Operationally, the positions of the nuclei are taken as parameters of the quantum mechanical electronic problem. This gives rise to a notion of crystal structure: one can treat the positions of nuclei as classical variables, and from them calculate all macroscopic properties that result from the electronic band structure. This is the approach taken by \textit{ab-initio} computer codes (1) for the calculations of various electronic properties, using the tools of density functional theory (2).

A central question in solid state physics is then the relationship between crystal structure and electronic properties. An excitation of the crystal structure, corresponding to a movement of nuclei, is a phonon. Slight changes in crystal structure give rise to slight changes in electronic energy levels. Loosely speaking, this allows phonons to couple to electrons in the crystal, giving rise to the electron-phonon interaction. The electron-phonon interaction manifests itself in many intricate ways in measurements of the electronic properties of materials.

The subject of the first part of this dissertation is how the electron-phonon interaction affects the electronic properties of two dimensional materials. Our main material under consideration is graphene, a two-dimensional honeycomb network of carbon atoms. Compared to other prototypical two-dimensional materials like semiconductor quantum wells, graphene is distinguished by its linear energy-momentum dispersion relation and the chiral (pseudospin) nature of its quasiparticle excitations near the \( K \) points of the Brillouin zone (termed "valleys"). There are two such inequivalent points (\( K \) and \( K' \)) in the Brillouin zone. The pseudospin is a result of the crystal structure having two sublattices, and is a...
particularly convenient concept for analyzing the electronic properties at the valleys. The consequences of these properties will be explored throughout this dissertation, where we consider either graphene directly, or materials inspired by or modified by graphene. Chapter 2 is an introduction to the basic properties of graphene, such as its electronic structure, and electron-phonon interactions. We will make use of the material developed in Chapter 2 throughout this dissertation.

In Chapters 3 and 4 we study how the electron-phonon interaction affects the absorption spectra of graphene in high magnetic fields. The effects of the electron-phonon interaction are the most evident when the frequency of the phonon matches the energy of some electronic excitations. Under these conditions of resonance, new features, such as splittings and broadenings of absorption peaks, are observed in the absorption spectrum. The role of the magnetic field is to quantize the electronic energy levels; by changing the strength of the magnetic field, one can control the energy of electronic transitions, and the presence or absence of a resonant condition. In Chapter 3 we consider the resonance with the phonon at the Brillouin zone center ($\Gamma$), while Chapter 4 is concerned with the phonon at the $K$ point of the Brillouin zone. In both cases, the electronic structure plays an important role in determining the absorption spectrum. In the former, unequal electronic occupation of the two valleys result in a characteristic splitting of the absorption peaks. To a lesser extent, a similar behavior can also be observed in the $K$-phonon resonance. The fact that graphene has two inequivalent valleys explains how a magneto-phonon resonance can occur with a phonon of non-zero wavevector ($K$). Ordinarily, such phenomena can only be observed with phonons of the same wavevector as light (i.e. those close to the Brillouin zone center).

In Chapter 5 we consider a different manifestation of electron-phonon interactions — phonon satellite peaks. These are features in tunneling experiments where the tunneling electron emits a number of phonons, resulting in peaks in the measured differential conductance. Unlike Chapters 3 and 4, this phenomenon does not depend on any resonant condition between phonon frequencies and electronic excitation energies. In fact, phonon satellite peaks at arbitrarily high multiples of the phonon frequency should always be present (albeit with rapidly diminishing intensity), corresponding to the emission of multiple phonons. In Chapter 5, we will outline a method for calculating these phonon satellite peaks. We will apply these techniques to two-dimensional molecular lattice arranged on graphene. Here, graphene plays only a secondary role in decoupling the molecules from the underlying substrate, and the molecular electronic and vibrational structures are the main factors determining the tunneling spectra.

Returning to the theme of the relation between crystal structure and electronic properties, one might consider multi-atom complexes, such as molecules, instead of atoms or nuclei, as the individual structural units of crystal lattices. For example, the CVB molecules of Chapter 5 can be seen as units of a supramolecular lattice. Such systems are often called superlattices. In the second half of this thesis (Chapters 6, 7), we consider the electronic properties of superlattices and how they can be controlled by their structural properties. We take the point of view that the behavior of electrons in superlattices can be described in terms of an effective theory, instead of deriving their behavior from the more fundamental
Schrödinger’s equation.

Chapter 6 is dedicated to superlattices constructed from molecular components arranged on metal surfaces. These metal surfaces host free electron-like surface state states, which are then modified by the presence of the molecules. In this chapter, we consider how graphene-like electronic band structures can be created in these systems. We also study the properties of artificial defects — missing molecules or "grain-boundaries" of the molecular superlattice. In these systems, a practical concern is the magnitude of the energy scale of the effective theory. For example, the special graphene-like properties might not be experimentally measurable if they are present only at small energy scales. This leads to the question of how to design such superlattices in order to maximize the energy scale. We address this question by a systematic exploration of the design space of supramolecular superlattices.

The focus of Chapter 7 is on systems created by modifying graphene instead of two-dimensional electron gases. We consider the effect of electric and magnetic fields on the electronic properties of graphene, under the assumption that these potentials vary on length scales much larger than the graphene lattice constant. This allows an effective Hamiltonian description based on the Dirac equation with scalar and vector potentials. The symmetries of the Dirac equation result in a mathematical transformation that relates the properties of magnetic graphene superlattices and electrostatic graphene superlattices. We also consider bilayer graphene superlattices, which are described by an effective theory different from both two-dimensional electron gases and single layer graphene, and have electronic properties different from either.
Chapter 2

Basic properties of graphene

2.1 Electronic structure of graphene

Graphene is a two-dimensional honeycomb network of carbon atoms. It has a hexagonal lattice with lattice vectors \( a_1 = (a, 0) \) and \( a_2 = (-a/2, \sqrt{3}a/2) \). The primitive reciprocal lattice vectors are \( g_1 = (2\pi/a)(0, 2/\sqrt{3}) \) and \( g_2 = (2\pi/a)(1, 1/\sqrt{3}) \). Graphene has two carbon atoms per unit cell, located at positions \((2a_1 + a_2)/3\) and \((a_1 + 2a_2)/3\). These two atoms belong to two sublattices, denoted \( A \) and \( B \) respectively. The carbon 2s and 2p atomic orbitals hybridize into an \( sp^2 \) \( \sigma \) bonding network and a delocalized \( p_z \) \( \pi \) bonding network.

The low energy electronic excitations of graphene involve the \( \pi \) bonds instead of the \( \sigma \) bonds, which are comparatively stronger and higher in energy.

In the simplest tight-binding approximation, we take into account only nearest neighbor hopping between \( p_z \) orbitals, that is, hopping of electrons from sublattice \( A \) to \( B \) and from \( B \) to \( A \). Then, the tight binding Hamiltonian is

\[
\mathcal{H}_0 = \gamma_0 \sum_{<i,j>} c_i^\dagger c_j + h.c.
\]

(2.1)

We have set the on site energy to zero, and the nearest neighbor hopping parameter is \( \gamma_0 \). The creation operator at sublattice \( j \), lattice vector \( R \) is denoted by \( c_{j,R}^\dagger \). Making a Fourier transform,

\[
c_{j,k}^\dagger = \sum_R e^{ik \cdot R} c_{j,R}^\dagger
\]

(2.2)

\[
\mathcal{H}_0 = \gamma_0 \sum_k c_{B,k}^\dagger c_{A,k}(1 + e^{-ik \cdot a_1} + e^{-k \cdot a_2}) + h.c.
\]

(2.3)

we arrive at an expression for the Hamiltonian in reciprocal space. As will be shown below this Hamiltonian contains electronic excitations of arbitrarily low energies. In fact, graphene
2.2. LANDAU LEVELS IN GRAPHENE

is a semimetal and these low energy excitations take place at two distinct points in the Brillouin zone, \( K = (g_1 + g_2)/3 \) and \( K' = -K \). Expanding Eq. 2.3 near the \( K \) point, we obtain

\[
H_0 = \gamma_0 \sum_k c_{B,k}^\dagger c_{A,k} \frac{\sqrt{3}}{2} a(k_x' - i k_y') + h.c. \tag{2.4}
\]

where \( k = k' + K \), \( k' \ll 2\pi/a \). Writing \( H_0 = \Psi^\dagger H_0 \Psi \), with \( \Psi^\dagger = (c_{A,k'}^\dagger, c_{B,k'}^\dagger) \), the low energy Hamiltonian can be expressed as

\[
H_0 = \hbar v_0 (\sigma_x k_x' + \sigma_y k_y') \tag{2.5}
\]

where \( \hbar v_0 = \gamma_0 a \sqrt{3}/2 \). This equation is known as the Dirac equation and has eigenenergies and wavefunctions

\[
\psi_{s,k'} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ e^{i \theta_{k'}} \end{pmatrix} \tag{2.6}
\]

and

\[
E_s(k') = s\hbar v_0 k' \tag{2.7}
\]

respectively. Here \( s = \pm 1 \) is the band index and \( \theta_{k'} \) is the angle between \( k' \) and the \( +k_x \) direction. The linearly dispersing bands give rise to a vanishing density of states at the Fermi level. This, together with the chiral nature of the excitations in Eq. 2.6, results in many unusual properties of graphene that will be explored more fully in the following chapters.

2.2 Landau levels in graphene

Unlike a conventional two-dimensional electron gas (2DEG) with Landau levels equally spaced in energy, the \( n \)-th Landau level of graphene in a magnetic field \( B \) has energy \( E_n = sgn(n)v_0 \sqrt{2e\hbar B|n|} \), with \( v_0 \approx 10^6 \text{m/s} \) the Fermi velocity of graphene (3). The \( n = 0 \) Landau level has a four-fold degeneracy due to spin and valley degrees of freedom in graphene. In the presence of electron-electron interactions, this degeneracy can be lifted. This will be addressed in Chapt. 3.

The optically-allowed transitions between Landau levels are given by the selection rules \(-(|n| + 1) \rightarrow |n| \) and \(-|n| \rightarrow |n| + 1 \) (4). In the following chapters, we will be concerned with the transitions \( 0 \rightarrow 1 \) and \(-1 \rightarrow 0 \) only. The energy of these transitions is \( E_{01} = v_F \sqrt{2e\hbar B} \).

2.3 Phonons in graphene

Electrons in graphene couple strongly to two distinct phonon modes, here referred to as \( K \) and \( \Gamma \). Respectively, these are the highest energy transverse optical (TO) phonons with
2.4. ELECTRON-PHONON INTERACTION IN MAGNETIC FIELDS

phonon wave vector $K$, and the highest energy transverse and longitudinal optical (LO) phonons at the $\Gamma$ point. The $K$ phonons belong to the $A'_1$ representation (non-degenerate) while the $\Gamma$ phonons belong to the $E_{2g}$ representation and are doubly degenerate.

The energy of the $K$ phonons is $\omega_K = 151\text{meV}$, obtained from theory (5) and experiments (6). The energy of the $\Gamma$ phonons at the $\Gamma$ point is $\omega_{\Gamma} = 196\text{meV}$. Near the $K$ and $\Gamma$ points, both phonon modes show some dispersion, related to the Kohn anomaly (7).

The electron-phonon interaction can be treated simply within the tight binding approximation, in a similar spirit to Eq. 2.1. Allowing displacements of the carbon atoms $u_j(R) = u_j e^{iq \cdot R}$ of some wavevector $q$, for sublattices $j = A, B$, the full Hamiltonian is

$$H = \sum_R \gamma(t_3 + u_B(R) - u_A(R)) c_{B,R}^\dagger c_{A,R}^\dagger + \gamma(t_2 + u_B(R + a_1) - u_A(R)) c_{B,R+a_1}^\dagger c_{A,R}^\dagger + \gamma(t_1 + u_B(R - a_2) - u_A(R)) c_{B,R-a_2}^\dagger c_{A,R}^\dagger + h.c. \quad (2.8)$$

where the nearest neighbor hopping parameter $\gamma(r)$ is now distance dependent and the nearest neighbor vectors are $t_1 = a(0, -1/\sqrt{3})$, $t_2 = a(1/2, 1/(2\sqrt{3}))$, $t_3 = a(-1/2, 1/(2\sqrt{3}))$. Expanding $H$ to first order in atomic displacement, and writing $H = H_0 + H_{e-ph}$, the electron-phonon interaction is described by

$$H_{e-ph} = \frac{\partial \gamma}{\partial r} \sum_k c_{B,k+q}^\dagger c_{A,k}^\dagger (t_3 \cdot (u_B - u_A))$$

$$+ t_2 \cdot (u_B e^{iq \cdot a_1} - u_A) e^{-i(k+q) \cdot a_1}$$

$$+ t_1 \cdot (u_B e^{-iq \cdot a_2} - u_A) e^{i(k+q) \cdot a_2} \quad (2.9)$$

Analysis of Eq. 2.9 for the $K$ phonon is performed in (8), while the $\Gamma$ phonon is analyzed in (9). A symmetry based treatment of the electron-phonon interaction can be found in (10).

2.4 Electron-phonon interaction in magnetic fields

In anticipation of Chapt. 4, where we explore the consequences of the electron-phonon interaction in high magnetic fields, we show here the electron-phonon matrix elements in the Landau level (LL) basis. For the $K$ phonon, they can be written as:

$$H_e^{ph} = \sum_{jnn',kk',q} g_{kk'q}^j c_{j+1,n',k'}^\dagger c_{j,n,k}^\dagger (a_{j,q}^\dagger + a_{j,q}). \quad (2.10)$$

Here, $c_{j,n,k}^\dagger$ is the electron creation operator in valley $j = 0, 1$ (corresponding to the $K$ or $K'$ valley), for the LL $n$ and wavevector $k$ in the Landau gauge, and $a_{j,q}^\dagger$ is the $K$ or $K'$ phonon
creation operator of wavevector $\vec{q}$ relative to the $K$ or $K'$ point. The addition of the valley index $j + 1$ is understood to be modulo 2. The matrix elements are:

$$
g^{\text{in}}_{jnn'}^{k\vec{q}} = \frac{2\beta \hbar v_0}{b^2} \sqrt{\frac{\hbar}{2N_c M \omega_K}} C i e^{2\pi i/3} \delta_{k,k'+q_x} e^{i q_y (k - q_x/2)} l_B^2 \\
(J_{|n'|-1,|n|-1}(\vec{q}) - \text{sgn}(n)\text{sgn}(n')J_{|n'|,|n|}(\vec{q}))
$$

with

$$
J_{n',n}(\vec{q}) = \left(\frac{n'}{n!}\right)^{1/2} e^{-q^2 l_B^2/4} \left(\frac{q_x l_B + i q_y l_B}{2}\right)^{n'-n} L_{n'}^{n'-n} \left(\frac{q^2 l_B^2}{2}\right) \text{ when } n' \geq n \geq 0
$$

$$
J_{n',-1}(\vec{q}) = 0
$$

$$
J_{n',n}(\vec{q}) = J_{n',n'}^*(-\vec{q})
$$

In these equations, $b = a/\sqrt{3}$ is the C-C bond length, and $\beta = -(b/\gamma)(d\gamma/db)$ is a dimensionless coupling parameter. $N_c$ is the number of unit cells, $M$ is the mass of a carbon atom, $\omega_K$ is the $K$-phonon frequency and $l_B = \sqrt{\hbar/(eB)}$ is the magnetic length. The constant $C$ takes the value of 1/2 if $|n| > 0$ and $|n'| > 0$, and $1/\sqrt{2}$ otherwise. $L_n^m(u)$ denotes the Laguerre polynomial and $\text{sgn}(n) = 1$ when $n \geq 1$ and $\text{sgn}(n) = -1$ otherwise.
Chapter 3

Γ-phonon magneto-resonance in graphene

Magneto-phonon resonances occur when the frequency of a phonon mode is comparable to energy differences between Landau levels of a system. The interaction between these two types of elementary excitations, phonons and electron-hole pairs, results in measurable and characteristic changes to the optical spectrum of a material. When the electron-phonon coupling is negligible, for example, when there are no phonon modes close in energy to the electron-hole pair energies, the absorption spectrum consists of single sharp peaks corresponding to energies of each dipole allowed transition between Landau levels. As the electronic transition energies start to approach the phonon energies (through the process of increasing magnetic field, for example), the magneto-phonon resonances begin to change the lineshape of these peaks. Depending on the nature of the phonon and the electronic ground state, the absorption spectrum can look very different in the vicinity of the magneto-phonon resonance. In this chapter, we will examine magneto-phonon resonances for the Γ phonon mode in graphene, while the next chapter is dedicated to the resonance with the K phonon mode.

3.1 Introduction

As we have seen in Chapt. 2, due to the spin and valleys degeneracies, the $n=0$ LL form a quartet with the symmetry SU(4). Refined experimental investigations, using different types of transport measurements have shown that this symmetry is in fact broken (11–16). This gave rise to an intense debate among theorists to identify the nature of the broken phase as reviewed by Kharitonov (17) and more recently by Abanin et al. (18) and Roy et al. (19). At present, there is not clear consensus about the nature of the broken phase induced by electron-electron and electron-phonon interactions in that matter.

Such a broken phase should also be observed in infra-red magneto-optical transitions involving the $n=0$ LL (i.e transitions from $n=-1$ to $n=0$ or from $n=0$ to $n=1$
equivalent to a cyclotron resonance (CR) transition) with an energy \( E_{01} = v_F \sqrt{2e\hbar B} \). We (20) reported on the magnetic field dependence of this transition revealing its interaction with the \( K \)-phonon in (20). We note that, besides this specific interaction, we were lead to assume that the basic broadening \( \gamma_{01}(B) \) of the transition had an additional component proportional to \( B \) in contrast to all theoretical models (21). This could be already a sign of the breaking of the valley degeneracy. In the present work, we use the \( \Gamma \)-phonon at the Brillouin zone center as a probe of the valley symmetry breaking. In the absence of valley symmetry breaking, the \( \Gamma \)-phonon does not affect the infra-red absorption spectrum because the electron-phonon matrix elements are of opposite signs for the \( K \) and \( K' \) valleys (4). However, one expects to see peculiar effects in the presence of valley symmetry breaking when the energy \( E_{01}(B) \) is larger than that of the \( \Gamma \)-phonon (\( \hbar \omega_{\Gamma} = 0.196 \text{eV} \)). It turns out, indeed, that when that condition is reached, a new optical transition develops at an energy higher than the main line. This is interpreted as a signature of the breaking of the SU(4) symmetry. A model has been established to reproduce these findings and applied to the different phases which have been proposed. Only the CDW certain phase is compatible with the experimental results.

In the experiment, precise infra-red transmission measurements were performed on multi-layer epitaxial graphene samples, at 1.8 K, under magnetic fields up to 35 T. The TR spectra of the sample S5 are displayed in Fig. 3.1 (top panel) for different values of \( B \). For energies larger than that of the \( \Gamma \)-phonon (\( B \geq 27 \text{T} \)), the transmission starts decreasing again due to an increase of the broadening of the \( E_{01} \) transition which results, for higher fields, in a splitting of the line. This is clearly seen in Fig. 3.1 where the evolution of the CR line is displayed for high fields.

This evolution is also seen in other samples and in particular for sample S4 grown on different SiC substrate with a similar number of effective layers \( N_{\text{eff}} \). Therefore we observe a new transition occurring at an energy higher than that of the CR line, growing in intensity when increasing the magnetic field. This behavior cannot be explained, in a SU(4) symmetric picture. In order to characterize more clearly these findings, one can treat the data, as a first step and in a very rough way, extracting from the transmission data the real part of the effective diagonal component of the conductivity \( \sigma_{xx}(\omega, B) \) (22). We have deconvoluted this result with two Lorentzians of equal width, extracting the evolution of the two extrema with the magnetic field. The resulting energies are displayed in Fig. 3.2 (top panel) for samples S4 and S5.

Though the procedure adopted in this initial analysis is quite rough, it provides important information: (i) The evolution of the lower energy line varies at low fields like \( B^{1/2} \) (function \( F2(B) \) in Fig. 3.2) with a coefficient proportional to the Fermi velocity \( v_F \) and ends at higher fields with a similar dependence (function \( F1(B) \)) but with a smaller value of \( v_F \) which is, by itself, a sign of some interaction occurring at an energy close to that of the \( \Gamma \)-phonon; (ii) The second component of the de-convolution appears at energies larger than that of the \( \Gamma \)-phonon; (iii) In principle, in the SU(4) symmetric picture, it is not possible to explain the occurrence of an additional transition, growing in intensity with \( B \), at higher energies than the main transition line; (iv) It is therefore clear that the \( \Gamma \)-phonon plays a crucial role.
3.1. INTRODUCTION

Figure 3.1: Evolution of the $E_{01}$ transition for different values of the magnetic field beyond 27 T for sample S5.
though it should not, indicative that the SU(4) symmetry is broken. We then have some guide
lines to develop a theory which can explain quantitatively the experimental observations. In
addition we note that results for samples S4 and S5 are quite similar within the experimental
errors. Knowing that the active layers which contribute to the \( E_{01} \) transition should have a
filling factor \( \nu \leq 2 \) ( \( \nu = N_s \Phi_0 / B, \Phi_0 \) being the flux quantum and \( N_s \) the carrier density)
and that there is no reason why, in samples S4 and S5, the carrier density for active layers
should have the same sequence, the model describing the experimental findings should not
be very dependent on the doping of active layers.

### 3.2 Theory of the \( \Gamma \)-phonon magneto-resonance

To illustrate how the electron-phonon interaction and the valley symmetry breaking give
rise to the observed features in the transmission spectrum, we first introduce a simplified
model for the interaction of the \( \Gamma \) phonon with the \( E_{01} \) transition line, before discussing the
full SU(4) calculation. The simplified model provides a minimal description of the valley
symmetry breaking by neglecting the spin degree of freedom in the \( n = 0 \) LL. We assume
that \( K \) and \( K' \) sublevels of the \( n = 0 \) LL are separated in energy by \( \Delta V \), and have different
filling factors \( \nu_K \) and \( \nu_{K'} \). Considering just the \( n = 0 \) to \( n = 1 \) transitions, the interaction
with the \( \Gamma \) phonon is captured by the Hamiltonian

\[
H = \begin{pmatrix}
E_{01} - \Delta V/2 & 0 & g\sqrt{\nu_K} \\
g\sqrt{\nu_K} & E_{01} + \Delta V/2 & -g\sqrt{\nu_{K'}} \\
-g\sqrt{\nu_{K'}} & -g\sqrt{\nu_K} & \hbar \omega \Gamma
\end{pmatrix}.
\]  

(3.1)

The optical conductivity is calculated using the Green’s function formalism introduced by
Toyozawa (23). The conductivity components are

\[
\text{Re} \sigma_{xx}(\hbar \omega) = \frac{1}{\omega} \text{Im} M_1^\dagger G(\hbar \omega) M_x
\]  

(3.2)

where the Green’s function is \( G = (\hbar \omega - H - i\eta)^{-1} \), with \( \eta \to 0^+ \). The optical matrix
elements for the simplified model are \( M_1^\dagger = (\sqrt{\nu_K}, \sqrt{\nu_{K'}}, 0) \). The simplified model explains
the splitting of the main transition line in the two limits \( E_{01} \approx \hbar \omega \Gamma \) and \( E_{01} \gg \hbar \omega \Gamma \). In
the absence of valley splitting (\( \Delta V = 0 \) and \( \nu_K = \nu_{K'} \)), the eigenstates of Eq. 3.1 are
valley-symmetric and valley-antisymmetric combinations of \( E_{01} \) transitions, i.e.

\[
\frac{1}{2} \left(c_{1,K}^\dagger c_{0,K} + c_{1,K'}^\dagger c_{0,K'}\right) |\text{GS}\rangle
\]

\[
\frac{1}{2} \left(c_{1,K}^\dagger c_{0,K} - c_{1,K'}^\dagger c_{0,K'}\right) |\text{GS}\rangle
\]

(3.3)

respectively, where \( |\text{GS}\rangle \) denotes the ground state and \( c_{n,K}^\dagger \) are creation operators at LL \( n \) and
valley \( K \). The valley-symmetric combination is infra-red active but does not interact with
the \( \Gamma \) phonon, while the valley-antisymmetric combination is infra-red inactive and interacts
3.2. THEORY OF THE $\Gamma$-PHONON MAGNETO-RESONANCE

Figure 3.2: Top: CR energies, resulting from the de-convolution of the experimental transmission traces, as a function of $\sqrt{B}$ for samples S4 (full dots) and S5 (open dots). The full lines are a linear fit of the data for the low energy transition at low ($F_2(B)$) and high ($F_1(B)$). Bottom: Comparison of the variation of experimental CR energies for sample S5 (open dots), with that calculated for the CDW phase (open squares), as a function of $\sqrt{B}$. The size of the open squares mimics the relative oscillator strength of the optical transition.
with the $\Gamma$ phonon. The symmetry breaking valley splitting term $\Delta V$ allows both eigenmodes to interact with the $\Gamma$ phonon while remaining infra-red active, inducing a splitting of the main transmission line in the vicinity of the $\Gamma$ phonon frequency. Away from the $\Gamma$ phonon frequency ($E_{01} \gg \hbar \omega_{\Gamma}$), $E_{01}$ transitions at $K$ and $K'$ interact weakly with the phonon and the splitting of the main transmission line is controlled directly by the energy difference $\Delta V$.

### 3.2.1 Description of the ground state

We reintroduce the spin degree of freedom and the $n = -1$ to $n = 0$ transitions in order to obtain a quantitative understanding of the experiment. We consider different theoretical models of the $n = 0$ LL SU(4) symmetry breaking, taking into account the effects of $\nu \neq 0$ and disorder by introducing Gaussian broadening into a mean field theory. Different symmetry-breaking phases are represented in the mean field theory by different orderings and filling factors of the four sublevels of the $n = 0$ LL. We consider four candidate symmetry-breaking phases that have been proposed in the literature (17): Ferromagnetic (F), Charge Density Wave (CDW), Canted Antiferromagnetic (CAF) and Kekulé-distortion (KD), and calculate the optical conductivity using Eq. 3.2 with the appropriate Hamiltonian $H$ for each phase (Figs. 3.3). Treating these phases on the same footing, we find that each phase results in characteristic features in the evolution of the transmission spectrum as a function of the magnetic field. By examining the intensities and positions of the transmission lines, we identify the symmetry broken phase in our experiment as the CDW type. This phase has unequal occupation numbers of the $n = 0$ LL at the $K$ and $K'$ valleys, corresponding to a density modulation of the graphene $A$ and $B$ sublattices in real space. Unlike the ideal disorder-free CDW discussed in (17), both $K$ and $K'$ valleys have non-zero occupation number in our calculation, due to disorder-induced broadening (Fig. 3.3). Nevertheless, the mechanism giving rise to the splitting of the $E_{01}$ transmission line remains essentially the same as illustrated by the simple model (Eq. 3.1) above.

We assume that the ground state is a single Slater determinant of the form:

$$|GS\rangle = \prod_{j=1}^{4} \prod_{m_j=1}^{N_j} \Psi_{j,m_j}^+ |0\rangle$$

(3.4)

the index $j$ runs over the 4-dimensional spin/valley space and $m_j$ describe the "guiding center" degree of freedom. The state $(j, m_j)$ is represented by the wavefunction $\xi_j \phi_{m_j}(\vec{r})$ where $\xi_j$ is a four-component spinor and $\phi_{m_j}(\vec{r})$ is the orbital part of the wavefunction. These wavefunctions belong to the $n = 0$ landau level (LL) of graphene. The occupation numbers $N_j$ count the number of $j$ states that are occupied in this ground state.

For a given symmetry broken phase, we assume that the system is polarized along a certain direction in $j$-space. For instance, with increasing order of energies, $j = 1, 2, 3, 4$ corresponds to ($K', \uparrow, K', \downarrow, K', \uparrow, K', \downarrow$) in the charge density wave (CDW) phase. The remaining degrees of freedom, $\phi_{m_j}(\vec{r})$ and $N_j$, are treated as variational parameters, subject to the constraint $N_1 + N_2 + N_3 + N_4 = N$. We minimize the energy of the ground state
Figure 3.3: Schematic of the spin and valley sublevels of the $n = 0$ LL, showing their filling factors and ordering corresponding to different broken symmetry phases. Top: charge density wave (CDW), bottom: canted antiferromagnet (CAF). Arrows denote the spin orientation.
3.2. THEORY OF THE $\Gamma$-PHONON MAGNETO-RESONANCE

$E_{GS} = \langle GS|H_0 + H_{e-e} + H_{\text{disorder}}|GS \rangle$. Here $H_0$ is the single part of the Hamiltonian without disorder, $H_{e-e}$ the interaction term and $H_{\text{disorder}}$ the disorder potential. Because we assume a single Slater determinant, we can apply mean-field theory and obtain single-particle energy levels $E_{j,m_j}$.

In a system with finite disorder, the energy levels $E_{j,m_j}$ are clustered about mean values $E_j = \text{avg} E_{j,m_j}$. We remove the $m_j$ degrees of freedom by replacing the energy levels $E_{j,m_j}$ by broadened energy levels centered at $E_j$. There is a Fermi level $E_F$ which fixes the occupation numbers $N_j$ when the graphene layer is doped with a total filling factor $\nu$. Assuming the broadening be of Gaussian type with a width $\gamma_0$ the Fermi level is determined by solving the following equation:

$$\nu = \sum_j \text{erf} \left( \frac{E_F - E_j}{\sqrt{2} \gamma_0} \right)$$

from which one can calculate the individual filling factors $\nu_j = (1 + \text{erf} \left( \frac{E_F - E_j}{\sqrt{2} \gamma_0} \right))/2$ for each level $E_j$. These $E_j$ will be used, later on, as fitting parameters dependent on the broken-symmetry phase under consideration. Note that in this approach all optical transitions to or from the $n = 0$ LL are allowed.

We have now to describe these optical transitions.

3.2.2 Description of the optical transitions

We first consider the transitions from the $n = 0$ LL to $n = 1$ LL. The Hamiltonian of the magneto-excitons, including their interaction with the $\Gamma$-phonon, denoted $H_\circ$ (reminding that it describes the optical transitions allowed in the $\sigma^+$ polarization), is:

$$H_\circ = \begin{pmatrix}
h\omega_{01} - E_1 & 0 & 0 & 0 & g_1 \sqrt{\nu_1} \\
0 & h\omega_{01} - E_2 & 0 & 0 & g_2 \sqrt{\nu_2} \\
0 & 0 & h\omega_{01} - E_3 & 0 & g_3 \sqrt{\nu_3} \\
g_1^* \sqrt{\nu_1} & g_2^* \sqrt{\nu_2} & g_3^* \sqrt{\nu_3} & g_4^* \sqrt{\nu_4} & h\omega_{ph}
\end{pmatrix} .$$

(3.6)

where $h\omega_{01}$ is the energy of the $E_{01}$ transition from the $n = 0$ LL to $n = 1$ LL in the absence of interactions and $h\omega_{ph}$ that of the $\Gamma$-phonon. This Hamiltonian describes the excitations from the 4 sublevels $\{E_j, j = 1..4\}$ of the $n = 0$ LL to the $n = 1$ LL. The matrix elements $\{g_j, j = 1..4\}$ respectively describe their interaction with the $\Gamma$-phonon, and is dependent on the wavefunction character of the 4 sublevels (i.e., dependent on the broken-symmetry phase). In general, $g_j \propto g_{ph} \sqrt{B}/\sqrt{2}$, with a prefactor dependent on $j$ and the broken-symmetry phase. In the following, $g_{ph}$ will be taken real and used as a fitting parameter.
Similarly, the Hamiltonian describing the magneto-excitons for the transitions from the
\( n = -1 \) LL to the \( n = 0 \) LL (allowed in the \( \sigma^- \) polarization) is written as:

\[
H = \begin{pmatrix}
\hbar \omega_{01} + E_1 & 0 & 0 & g_1 \sqrt{1 - \nu_1} \\
0 & \hbar \omega_{01} + E_2 & 0 & g_2 \sqrt{1 - \nu_2} \\
0 & 0 & \hbar \omega_{01} + E_3 & g_3 \sqrt{1 - \nu_3} \\
g_1^* \sqrt{1 - \nu_1} & g_2^* \sqrt{1 - \nu_2} & g_3^* \sqrt{1 - \nu_3} & \hbar \omega_{01} + E_4
\end{pmatrix}.
\] (3.7)

The total Hamiltonian \( H \) describing the magneto-excitons is therefore:

\[
H = \begin{pmatrix}
H \otimes 0 & 0 \\
0 & H \otimes 0
\end{pmatrix}.
\] (3.8)

We will also need to introduce the optical matrix elements \( M_x \) and \( M_y \) for corresponding transitions. In the present case they are written, in the basis of \( H \), as:

\[
M_x = \{ \sqrt{\nu_1}, \sqrt{\nu_2}, \sqrt{\nu_3}, 0, -\sqrt{1 - \nu_1}, -\sqrt{1 - \nu_2}, -\sqrt{1 - \nu_3}, -\sqrt{1 - \nu_4}, 0 \} \quad \text{and} \quad M_y = iM_x.
\]

The Green’s function for the magneto-excitons, is obtained as

\[
G = (\hbar \omega + i\gamma_{01})^{-1} (I - H)^{-1}
\]

(3.9)

We calculate now the real part of the diagonal component of the conductivity (Re\( \sigma_{xx} \)) for the different phases proposed to explain the SU(4) symmetry breaking \( (17) \) and compare the results to the experimental findings.

### 3.2.3 Conductivity in the different phases

Before entering into the details characterizing the different phases, one has to define the different fitting parameters which will be used in this section. First the broadening \( \gamma_{01} \) entering the Green function is the one entering the Eq.3.9. In our previous work \( (20) \), we were lead to assume that the magnetic field dependence of this parameter had, in addition to the standard \( \sqrt{B} \) dependence \( (21) \), a component proportional to \( B \) not explained at that time. Since we are going to introduce later on the symmetry breaking, we have re-visited the analysis of the spectra at lower fields imposing a field dependence only proportional to \( \sqrt{B} \).

We have taken \( \gamma_{01} (\text{eV}) = (3 + 0.8\sqrt{B(T)})10^{-3} \) for all samples. The second fitting parameter to be used is \( \gamma_0 \) characterizing the broadening of the Landau levels in Eq.3.5. We have taken \( \gamma_0 = \gamma_{01}/2 \) because the broadening of the \( E_{01} \) transition should have contributions from both the \( n = 0 \) and \( n = 1 \) Landau levels. The Fermi velocity which determines the evolution of \( \hbar \omega_{01} \) (Eq.3.6) at lower fields has been taken as: \( v_F = 1.01 \times 10^6 \text{ms}^{-1} \). Finally one has to evaluate the parameter of the electron-\( \Gamma \)-phonon interaction \( g_{ph} \). Following the
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approach of Goerbig et al. (4) $g_{ph} \simeq 2$ meV/T$^{1/2}$ but considering other DFT calculations (5) $g_{ph}$ could be significantly larger ranging from 2 to 2.5 meV/T$^{1/2}$. We will use in the following the value $g_{ph} = 2.3$ meV/T$^{1/2}$ to compare theoretical results for different phases. However, considering other DFT calculations (5) $g_{ph}$ could be significantly larger ranging from 2 to 2.5 meV/T$^{1/2}$, a degree of freedom which will be used to fit the experimental data. The other fitting parameters are dependent on the phases and will be discussed in the following.

3.2.4 Charge density wave (CDW) phase

The CDW phase is characterized, at filling factor $\nu = 0$, by two electronic LL full in one valley (say $K'$ for instance) and two LL empty in the other valley ($K$). We will introduce a valley asymmetry $\Delta V$ mainly determined by electron-electron interactions (17) and a Zeeman splitting $\Delta S$. Therefore the sequence of sublevels take the following form:

$$
E_1(K' \uparrow) = -\Delta V/2 - \Delta S/2
$$
$$
E_2(K' \downarrow) = -\Delta V/2 + \Delta S/2
$$
$$
E_3(K \uparrow) = \Delta V/2 - \Delta S/2
$$
$$
E_4(K \downarrow) = \Delta V/2 + \Delta S/2
$$

(3.10)

In this case, the parameters governing the electron-$\Gamma$phonon interaction $g_1$, $g_2$ on one hand and $g_3$, $g_4$ in the other hand are of opposite sign. That is,

$$
\langle GS_{CDW} + \Gamma\text{phonon}|H_{e-\text{ph}}\Psi_{Ks,1}^\dagger\Psi_{Ks,0}|GS_{CDW}\rangle = g_{ph}\sqrt{B}/\sqrt{2}
$$
$$
\langle GS_{CDW} + \Gamma\text{phonon}|H_{e-\text{ph}}\Psi_{K's,1}^\dagger\Psi_{K's,0}|GS_{CDW}\rangle = -g_{ph}\sqrt{B}/\sqrt{2}
$$

(3.11)

The results obtained for this phase are presented in Fig. 3.4, assuming $\Delta V$ proportional to $B$, for two extreme values of the carrier density with $g_{ph} = 2$ meV/T$^{1/2}$. The results are not very dependent on $N_s$. This is because the disorder induced broadening reduces the dependence of the sublevel filling factors ($\nu_{K\uparrow}$, etc.) on the carrier density. The value of $\Delta S = 0.15$ meV $B$ corresponds to a value of the g-factor of 2.6 to be compared with other report (24) giving a value $2.7 \pm 0.2$. The splitting of the transition is directly governed by the amplitude of $\Delta V$ whereas the introduction of $\Delta S$ modifies only the relative amplitude of the two transitions. In all cases both $\Delta V$ and $g_{ph}$ need to be finite to observe the effect. We finally note that, in this case, $\Delta V > \Delta S$ in coherence with (20).

However there is no clear consensus about the field dependence on $\Delta V$ (17). Therefore one can alternatively assume that $\Delta V$ is proportional to $\sqrt{B}$. The corresponding results are displayed in Fig. 3.5 keeping all other parameters fixed. We obtained essentially the same results than in Fig. 3.4. Within the experimental errors we will not be able to differentiate between the two magnetic field variations of $\Delta V$.

The CDW state is compatible with the experimental results as we will see in the following.
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Figure 3.4: CDW phase with $\Delta V \propto B$: evolution of the $\sigma_{xx}$ component of the conductivity for different values of the magnetic field between 25 T and 35 T for a) a carrier density $N_s = 0.5 \times 10^{11}$ cm$^{-2}$ and b) $N_s = 1 \times 10^{12}$ cm$^{-2}$. In both cases $g_{ph} = 2.3$ meV/T$^{1/2}$.

Figure 3.5: CDW phase with $\Delta V \propto \sqrt{B}$: evolution of the $\sigma_{xx}$ component of the conductivity for different values of the magnetic field between 25 T and 35 T for a) a carrier density $N_s = 0.5 \times 10^{11}$ cm$^{-2}$ and b) $N_s = 1 \times 10^{12}$ cm$^{-2}$. In both cases $g_{ph} = 2.3$ meV/T$^{1/2}$. 
3.2.5 Kekulé-distortion (KD) phase

In this phase (17), the \( K \) and \( K' \) valleys hybridize into linear combinations \( \overline{K}, \overline{K}' \). At \( \nu = 0 \), both spin \( \uparrow \) and spin \( \downarrow \) electrons occupy one of these valley-combinations, say \( \overline{K} \). The \( \nu = 0 \) ground state for the KD phase is \( \Psi_{\overline{K},0}^+ \Psi_{\overline{K'},0}^+ |0\rangle \). Therefore, the "natural" basis for this phase, where the density matrix is diagonal, is \{ \( \overline{K} \uparrow, \overline{K} \downarrow, \overline{K'} \uparrow, \overline{K'} \downarrow \} \) in contrast to the basis \{ \( K \uparrow, K \downarrow, K' \uparrow, K' \downarrow \} \) used in the CDW phase. Therefore the sequence of sublevels take the following form:

\[
\begin{align*}
j = 1 : \overline{K} \uparrow \\
j = 2 : \overline{K} \downarrow \\
j = 3 : \overline{K'} \uparrow \\
j = 4 : \overline{K'} \downarrow
\end{align*}
\] (3.12)

It is easy to derive, via a change of basis, that the electron-light matrix elements do not change with respect to the CDW phase, and the electron-phonon matrix elements vanish by symmetry. That is,

\[
\begin{align*}
\langle GS_{KD} + \Gamma \text{phonon}\ | H_{e-ph} \Psi_{\overline{K'},1}^+ \Psi_{\overline{K},0}^+ | GS_{KD} \rangle &= 0 \\
\langle GS_{KD} + \Gamma \text{photon}\ | H_{e-light} \Psi_{\overline{K'},1}^+ \Psi_{\overline{K},0}^+ | GS_{KD} \rangle &= 1
\end{align*}
\] (3.13)

The structure of the Hamiltonian (Eq.3.8) becomes only diagonal and no splitting is observed when calculating the conductivity. Therefore the KD phase does not explain the experimental results.

3.2.6 Ferromagnetic (F) phase

In the F phase (17), the ground state, at filling factor \( \nu = 0 \), is composed in both valleys \( K \) and \( K' \) of a single full LL with the same spin. In analogy with the CDW phase, we will introduce a valley asymmetry \( \Delta_V \) and a Zeeman splitting \( \Delta_S \). Therefore the sequence of energy levels take the following form:

\[
\begin{align*}
E_1(K' \downarrow) &= -\Delta_V/2 - \Delta_S/2 \\
E_2(K \downarrow) &= \Delta_V/2 - \Delta_S/2 \\
E_3(K' \uparrow) &= -\Delta_V/2 + \Delta_S/2 \\
E_4(K \uparrow) &= \Delta_V/2 + \Delta_S/2
\end{align*}
\] (3.14)

Note that, in this case, \( \Delta_S \) should be larger than \( \Delta_V \) to preserve the ferromagnetic nature of the state. In the present case the parameters governing the electron-\( \Gamma \)-phonon interaction (Eq.3.6,3.7) \( g_1, g_3 \) on one hand and \( g_2, g_4 \) in the other hand are of opposite sign.

The results are displayed in Fig. 3.6 where we have taken for \( \Delta_S \) the same evolution that \( \Delta_V \). The conductivity does not show any significant splitting.
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Figure 3.6: Ferromagnetic phase with $\Delta V \propto B$: evolution of the $\sigma_{xx}$ component of the conductivity for different values of the magnetic field between 25 T and 35 T for a carrier density $N_s = 5.0 \times 10^{11} \text{cm}^{-2}$ and $g_{ph} = 2.3 \text{meV/T}^{1/2}$. 

\begin{figure}
\centering
\includegraphics[width=0.5\textwidth]{figure3.6}
\caption{Ferromagnetic phase with $\Delta V \propto B$: evolution of the $\sigma_{xx}$ component of the conductivity for different values of the magnetic field between 25 T and 35 T for a carrier density $N_s = 5.0 \times 10^{11} \text{cm}^{-2}$ and $g_{ph} = 2.3 \text{meV/T}^{1/2}$.}
\end{figure}
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Figure 3.7: CAF phase with $\Delta_1 \propto \sqrt{B}$ and $\Delta_2 \propto \sqrt{B}$: evolution of the $\sigma_{xx}$ component of the conductivity for different values of the magnetic field between 25 T and 35 T for a) a carrier density $N_s = 0.5 \times 10^{11}$ cm$^{-2}$ and b) $N_s = 1 \times 10^{12}$ cm$^{-2}$. In both cases $g_{ph} = 2.3$ meV/T$^{1/2}$.

of the main line. In fact there is an eigenvalue of the corresponding Hamiltonian larger than that of the main line but it remains optically inactive. Therefore here also, the F phase does not explain the experimental results.

3.2.7 Canted anti-ferromagnetic (CAF) phase

The CAF phase for the ground state is described by a spin in direction $\theta_K$ in valley $K$ and a spin in direction $\theta_{K'}$ in valley $K'$. (The directions $\theta_K$ and $\theta_{K'}$ are in general not opposite to each other except in the special case of the anti-ferromagnetic phase). The direction $\theta_K$ is oriented at an angle $\theta$ relative to the magnetic field $B$ and the direction $\theta_{K'}$ at an angle $-\theta$ with respect to it. (In the anti-ferromagnetic phase, $\theta = \pi/2$). Here the Zeeman splitting should vary like $\Delta_S \propto \cos \theta$ and if $\theta$ is close to $\pi/2$ this term should not play a dominant role. We choose the following order of states:

$$
E_1(K, \theta_K) = -\Delta_1/2 - \Delta_2/2
$$
$$
E_2(K', \theta_{K'}) = -\Delta_1/2 + \Delta_2/2
$$
$$
E_3(K, \pi + \theta_K) = \Delta_1/2 - \Delta_2/2
$$
$$
E_4(K', \pi + \theta_{K'}) = \Delta_1/2 + \Delta_2/2
$$

(3.15)

where the introduction of $\Delta_1$ reflects the CAF pattern of spin. We assume in addition that the asymmetry between valleys is reflected by $\Delta_2$ (favoring here the $K$ valley). To preserve the CAF phase $\Delta_2$ should be smaller than $\Delta_1$. Similar to the F phase, the parameters governing the electron-Γ-phonon interaction (Eq.3.6,3.7) $g_1$, $g_3$ on one hand and $g_2$, $g_4$ in the other hand are of opposite sign.
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The results are displayed in Fig. 3.7 where we have taken, $\Delta_1$ and $\Delta_2$ proportional to $\sqrt{B}$. The results are not very dependent on the carrier concentration. We observe indeed a splitting of the transition when both $\Delta_2$ and $g_{ph}$ are different from zero: in fact the splitting is governed by $\Delta_2$. In the present case we do not have, a priori, a guide for choosing the values of $\Delta_1$ and $\Delta_2$. In order to be consistent with experimental results, we have taken for $\Delta_1$ a value which provides an upper transition energy close to that observed.

However the evolution of the spectra does not reflect the experimental observations: whatever is the choice of parameters, the intensity of the high energy transition never reaches that of the main transition in contrast to the CDW phase where it should become dominant at fields higher than 35 T. To be more quantitative we compare in Fig. 3.8 the real part of the conductivity at 35 T obtained in the CDW and CAF phases with the rough estimate of the experimental one deduced from the data on sample S5. De-convoluting these spectra with two Lorentzians we find, for the experiment, a ratio of the CR weights of $0.9 \pm 0.05$ to be compared to the value 0.9 for the CDW phase and 0.4 for the CAF phase. We therefore do not think that the CAF phase could explain the experimental results, despite the fact that when following the evolution of the extremum energies as a function of the field $B$ one

Figure 3.8: Comparison of the real part of the conductivity for sample S5 (open dots) with that obtained in the CDW phase (continuous line) and the CAF phase (dash line). All spectra have been normalized in amplitude at the maximum of the main transition line.
finds similar results compatible with the experimental ones displayed in Fig. 3.1 of the main text.

3.3 Fitting the experimental transmission curves

We are now going to fit the experimental data displayed in Fig. 3.1 using the CDW phase model. We keep the value of $\Delta_S = 0.15$ meV/T. The fitting parameters are then $\Delta_V$ and $g_{ph}$.

Results of the fit for sample S5 are displayed in Fig. 3.9 for two values of the parameter $g_{ph}$ showing that, within the experimental errors both fits are acceptable.

One can in the same way fit the data for sample S4 and results are displayed in Fig. 3.10.

For both samples, the discrepancy, at low fields, between experimental data and the model reflects the contribution of the $K$-phonon absorption (20) not taken into account in the present model.

To conclude, we are able to reproduce the high field evolution of the infra-red magneto-transmission of multi-layer epitaxial graphene with the charge density wave model describing the SU4 symmetry breaking of the $n = 0$ LL. The transmission spectra depend sensitively on the ordering of the SU(4) sublevels in energy. Depending on the type of graphene sample and its disorder and screening properties, different phases might be realized, giving rise different orderings of the sublevels. We identify the symmetry broken phase in these samples as a CDW, with different occupation numbers at valleys $K$ and $K'$. 
3.3. FITTING THE EXPERIMENTAL TRANSMISSION CURVES

Figure 3.9: Fit of the experimental data for sample S5 with the conductivity model derived for the CDW phase using $\Delta V = 0.24$ meV/T and Left panel $g_{ph} = 2.3$ meV/T$^{1/2}$ (left panel) or $g_{ph} = 2.4$ meV/T$^{1/2}$ (right panel)
3.3. FITTING THE EXPERIMENTAL TRANSMISSION CURVES

Figure 3.10: Fit of the experimental data (open dots) for sample S4 with the conductivity model derived for the CDW phase (continuous lines) using $\Delta V = 0.24$ meV/T and $g_{ph} = 2.4$ meV/T$^{1/2}$. 
Chapter 4

$K$-phonon magneto-resonance in graphene

4.1 Introduction

Magneto-phonon resonances are frequently observed with zone-center ($\Gamma$) phonons. This is because electron-hole pairs excited by a photon have negligible center-of-mass momentum, and can decay via emission of phonons with close to zero wavevector. The $K$-phonon magneto-resonance in graphene involves a non-zero wavevector phonon. This unusual behavior is made possible by the electronic valley degree of freedom in graphene.

Before proceeding to the theory of the $K$-phonon magneto-phonon resonance, we briefly review some important experimental facts. Infrared transmission measurements performed on multilayer epitaxial graphene samples (Fig. 4.1) show that there is a strong change in the optical spectrum when $E_{01}$ is close to $\omega_K$. This happens at a magnetic field of $B = 17 T$. As the cyclotron transition corresponding to $E_{01}$ is tuned across $\omega_K$ by increasing the magnetic field, the absorption peak splits into two and broadens significantly when $E_{01} > \omega_K$. This behavior is reproducible across multiple samples.

These features can be analyzed semi-quantitatively by fitting the $E_{01}$ transition with a single Lorentzian line, for each value of magnetic field. In principle, a detailed analysis of the spectra requires the use of multilayer dielectric model including all layer dielectric properties of the sample. This has been done in (20). However, a simple fit to a Lorentzian is sufficient to illustrate the salient features of the spectra.

This fit provides, for each value of $B$, two independent parameters $E_{01}(B)$ and $\Gamma_{01}(B)$, corresponding to the energy and width of the transition, which are plotted in Fig. 4.1b as a function of $B^{1/2}$. The variation of $\Gamma_{01}(B)$ shows clearly an extra bump beyond 17 T whereas that of $E_{01}(B)/B^{1/2}$ exhibits a downwards kink at the same field. The evolution of $\Gamma_{01}(B)$ is decomposed in two parts: one named $\gamma_{01}(\text{meV}) = 2.3 + 0.6\sqrt{B} + 0.24B$ (full dots) and an extra contribution to $\Gamma_{01}$ represented by stars in the top panel of Fig. 4.1b. The $\sqrt{B}$ dependence of $\gamma_{01}$ is attributed to scattering with short range impurities (21); the linear variation with $B$ is not predicted by scattering mechanisms considered in previous studies.
4.2. THEORY OF K-PHONON MAGNETO-PHONON RESONANCE

Figure 4.1: (a) Relative transmission spectra of sample S1, for different magnetic field values. (b) Bottom panel: variation of cyclotron transition energy $E_{01}/B^{1/2}$ as a function of $B^{1/2}$ (open blue circles). Top panel: variation of the fitted linewidth $\Gamma_{01}(B)$ of the transition $E_{01}(B)$ as a function of $B^{1/2}$ (open red circles). This variation is de-convoluted in two parts, one named $\gamma_{01}(B)$ (green dots) and the remaining part (stars) which is assigned to the $K$-phonon contribution.

(21) and will be discussed later. The shape of the extra contribution to $\Gamma_{01}$ has a threshold at around 17 T ($\sim 150$ meV) with a maximum amplitude of about 2 meV for all samples, within the experimental uncertainties, before decreasing at higher fields. In that energy range the only likely excitations in graphene which could play a role are the zone-boundary $K$-phonons (6). Note that, at this threshold energy, the evolution $E_{01}/B^{1/2}$ (bottom panel of Fig. 4.1b) is the signature of interactions because, in the absence of such interactions, it should be an horizontal line.

4.2 Theory of $K$-phonon magneto-phonon resonance

The mechanism for the interaction of the cyclotron transition with the $K$-phonon is not a priori clear for the reason of conservation of wavevector, i.e., a state corresponding to an optical cyclotron transition which has wavevector 0 cannot decay into a state with a phonon of wavevector $\overrightarrow{K}$ without simultaneously emitting another entity of wavevector $-\overrightarrow{K}$. Given that this interaction must necessarily involve the electron-phonon interaction, and that the low-energy electronic states at the two valleys of graphene are separated in reciprocal space by a wavevector $\overrightarrow{K}$, we propose that an intervalley intra-LL electron scattering process (creation of a zero-energy intervalley electron-hole pair) is responsible for the observed phenomenon (Fig. ??).
Figure 4.2: Cyclotron resonant excitations $|\eta_1(j,k)\rangle$ (a) and $|\eta_2(j,k)\rangle$ (b) involving the $n = 0$ Landau levels, at either the $K$ or $K'$ valley, with the excitation energy $E_{ex} = E_{01}$. (c) Excited state $|\xi(j,k)\rangle$ corresponding to intervalley transfer of an electron within the $n = 0$ LL from $K$ to $K'$ and creation of a phonon with wavevector $\mathbf{K} + \mathbf{q}$, which has excitation energy $E_{ex} = \hbar\omega_{\mathbf{K} + \mathbf{q}}$. (d) At resonance, i.e. $E_{01} = \hbar\omega_{\mathbf{K} + \mathbf{q}}$, $|\eta_1\rangle$ and $|\eta_2\rangle$ may be transformed to $|\xi\rangle$ via an emission of a $\mathbf{K} + \mathbf{q}$ phonon as indicated by the dashed brown lines. The mixing between the three excited states, mediated by the electron-phonon interaction, is the strongest when the resonance condition is satisfied ($E_{01} = \hbar\omega_{\mathbf{K} + \mathbf{q}}$).
To explain the observed spectral features, we shall consider the coupling of the photo-excited (cyclotron transition) states (denoted as $|\eta_1(j,k)\rangle$ and $|\eta_2(j,k)\rangle$ for the $0 \rightarrow 1$ and $-1 \rightarrow 0$ LL transitions respectively) with an excited state of the system containing an intervalley, intra-Landau level electron-hole pair excitation and a $K$-phonon of wavevector $\vec{K} + \vec{q}$ (denoted as $|\xi_{\vec{q}}(j,k)\rangle$). See Fig. 4.2. Here $j$ is the valley index and $k$ is the quantum number which describes the degenerate states within a LL. As illustrated in Fig. 4.2, at cyclotron transition energy $E_{01}$ near $\hbar \omega_{\vec{K} + \vec{q}}$, $|\eta_1(j,k)\rangle$ and $|\eta_2(j,k)\rangle$ are connected to $|\xi_{\vec{q}}(j,k)\rangle$ via an emission of $\vec{K} + \vec{q}$ phonons. The electron-phonon coupling in the system can then strongly mix these states at resonance and lead to significant changes in the absorption spectrum.

### 4.2.1 Choice of reduced Hilbert space

In second quantized notation, the cyclotron transitions of interest are:

$$|\eta_1(j,k)\rangle = c_{j,1,k}^\dagger c_{j,0,k}|0\rangle$$
$$|\eta_2(j,k)\rangle = c_{j,0,k}^\dagger c_{j,-1,k}|0\rangle.$$  \(4.1\)

Here, $|0\rangle$ is the ground state. We now consider candidate states $|\xi\rangle$ to be included in the model, such that the experimental spectra could be explained by their interactions with the cyclotron transition states. Such states have to satisfy two conditions: (i) they can couple directly to $|\eta_1\rangle$, $|\eta_2\rangle$ via the electron-phonon interaction Eq. 2.10 (i.e. $\langle \xi | H_{e-ph} | \eta_{1,2} \rangle \neq 0$), and (ii) in order to describe the resonance at $E = \hbar \omega_{K}$ the states $|\xi\rangle$ must have energy $\langle \xi | H | \xi \rangle \approx \hbar \omega_{K}$.

Based on the form of the electron-phonon interaction, it is evident that $|\xi\rangle$ must contain a $K$-phonon as well as intervalley electronic transitions. Condition (ii) implies that these transitions must be between LL of the same LL index because the electronic part of $|\xi\rangle$ must have the same energy as $|0\rangle$. We therefore consider the states

$$|\xi_{\vec{q}}(j,k)\rangle = c_{j,1,0,k-q_x}^\dagger c_{j,0,k} a_{j,\vec{q}}^\dagger|0\rangle.$$  \(4.2\)

Note that the single phonon states $a_{j,\vec{q}}^\dagger|0\rangle$ satisfy condition (ii) but not condition (i). In Eq. 4.2, the inter-valley transitions are between the $n = 0$ LL because this is the only partially empty LL in the experiment.

Another class of states that can couple to the cyclotron transition states is \{ $b^\dagger |\xi_{\vec{q}}(j,k)\rangle$, $b^\dagger b^\dagger |\xi_{\vec{q}}(j,k)\rangle$, $\ldots \}$, which contain one or more acoustic phonons in addition to $|\xi_{\vec{q}}(j,k)\rangle$. Here, $b^\dagger$, $b^\dagger$ create acoustic phonons.

### 4.2.2 Integration over the phonon continuum

Because of the dispersion of optical phonons at the $K$ point (25), and the coupling to acoustic phonons, the energies of the states that can couple to $|\eta_1\rangle$, $|\eta_2\rangle$ form a continuum, bounded below by $\omega_{K}$. In this section, we perform an integration over this continuum. We
4.2. THEORY OF $K$-PHONON MAGNETO-PHONON RESONANCE

start with a Hamiltonian of a general form that describes two degenerate states interacting with a continuum of states. For a given $(j,k)$,

$$H_1 = \begin{pmatrix}
E_{01} & 0 & u_1(\omega_K) & u_1(\omega_K + \delta) & u_1(\omega_K + 2\delta) & \ldots \\
0 & E_{01} & u_2(\omega_K) & u_2(\omega_K + \delta) & u_2(\omega_K + 2\delta) & \ldots \\
u_1(\omega_K) & u_2(\omega_K) & \omega_K & v & v & \ldots \\
u_1(\omega_K + \delta) & u_2(\omega_K + \delta) & v & \omega_K + \delta & v & \ldots \\
u_1(\omega_K + 2\delta) & u_2(\omega_K + 2\delta) & v & v & \omega_K + 2\delta & \ldots \\
\vdots & \vdots & \vdots & \vdots & \vdots & \ddots
\end{pmatrix}.$$  (4.3)

The first two columns (rows) represent the cyclotron transition states $|\eta_1 \rangle$, $|\eta_2 \rangle$. The rest of the columns (rows) represent the continuum of states that contain phonons. Here, $\delta > 0$ is a small positive energy. The function $u_i(\omega)$ (may be obtained from Eqs. 2.10, 2.11) describes the interaction between $|\eta_i \rangle$ and a $|\xi \rangle$ state of the continuum of energy $\omega$, while $v$ describes the interaction within the continuum.

We now treat the problem in two successive approximations. The first one assumes that the phonons have no dispersion, which allows us to introduce an effective coupling constant $V$ and work in a restricted Hilbert space having effectively one phonon. The second assumption takes into account the dispersion of phonons as a correction to the first approximation. This is done by introducing a self energy term in the Green’s function (see next section for the treatment of the Green’s function).

An effective Hamiltonian in our restricted Hilbert space for dispersion-less phonons can be written as:

$$H = \begin{pmatrix} E_{01} & 0 & V_1 \\ 0 & E_{01} & V_2 \\ V_1^* & V_2^* & \omega_K \end{pmatrix}.$$  (4.4)

where the values of $V_1$ and $V_2$ are chosen such that $H$ and $H_1$ have the same eigenvalues when $\delta = 0$. We have found that $V_1 = -V_2 = V = \sqrt{\sum_{q'} g_{qq'} g_{1q'}^*}$ (see below for explicit expressions of this parameter.)

We then introduce the effects of the phonon continuum using second-order L"{o}wdin perturbation theory (26). This is done by introducing a self energy $\Sigma_{\text{ph}}(\omega)$ in our Green’s function treatment of the optical response functions in the restricted Hilbert space of $H$ (23). The condition imposed by the model is that the Green’s functions $(\omega - H - \Sigma_{\text{ph}}(\omega) - i0^+)^{-1}$ and $(\omega - H_1 - i0^+)^{-1}$ are equal in the space spanned by $|\eta_1 \rangle$, $|\eta_2 \rangle$. Explicit expressions for the different components of $\Sigma_j(\omega)$ are given in the next section.

In the definition of the parameter $V$, the prime (‘) on the sum indicates that not all $\vec{q}$ vectors have to be summed over, because only a fraction $0 < f < 1$ of the total number of
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\begin{align*}
\sqrt{\mathcal{F}} &= 1, \\
n=0 &
\sqrt{\mathcal{F}} = \sqrt{1 - \nu}, \\
n=1 &
\sqrt{\mathcal{F}} = 0
\end{align*}

a) b) c)

\begin{align*}
\sqrt{\mathcal{F}} &= \sqrt{\mathcal{V} - \mathcal{S}}, \\
n=0 &
\sqrt{\mathcal{F}} = \sqrt{2 - \nu}, \\
n=1 &
\sqrt{\mathcal{F}} = 0
\end{align*}

\begin{align*}
\sqrt{\mathcal{F}} &= \sqrt{\mathcal{V}}, \\
n=0 &
\sqrt{\mathcal{F}} = 0
\end{align*}

\begin{align*}
\sqrt{\mathcal{F}} &= \sqrt{\mathcal{V}}, \\
n=0 &
\sqrt{\mathcal{F}} = 0
\end{align*}

|ξ⟩ states are available, depending on the filling factor. Then,

\[ V = \sqrt{\sum_{\mathbf{q}}' g_{1\mathbf{q}} g_{1\mathbf{q}}^*} = \sqrt{f \sum_{\mathbf{all} \mathbf{q}} g_{1\mathbf{q}} g_{1\mathbf{q}}^*} = A \sqrt{\mathcal{F}} \] (4.5)

The constant \( A^2 = \sum_{\text{all} \mathbf{q}} g_{1\mathbf{q}} g_{1\mathbf{q}}^* = \frac{9 \sqrt{3} \alpha^2 \gamma^2 \beta^2}{4 \pi a^3 M_2 K} \) can be obtained from Eq. 2.11. In reality this has to be corrected by the introduction of electron-electron interactions (25). To obtain the value of \( f \), we examine the occupation numbers of the \( n = 0 \) LL of the \( K \) and \( K' \) valleys. \( f \) is dependent on the relative magnitudes of the valley (\( \Delta_V \)) and spin (\( \Delta_S \)) spittings of the \( n = 0 \) LL, that is determined by the occupations of the spin and valley sublevels of the \( n = 0 \) LL.

Let us define \( \nu \) to be the filling factor, including spin and orbital degeneracies. For example, \( \nu = 0 \) at charge neutrality and \( \nu = 2 \) if the carrier concentration is such that the LL \( n = 0 \) is fully occupied. For the case of \( \Delta_V > \Delta_S \), filling factor \( \nu < 1 \) (Fig. 4.3a), we have \( \sqrt{\mathcal{F}} = 1 \) for the spin up transitions, and \( \sqrt{\mathcal{F}} = \sqrt{1 - \nu} \) for the spin down transitions. Whereas for \( \Delta_V > \Delta_S \), filling factor \( 1 < \nu < 2 \) (Fig. 4.3b), we have \( \sqrt{\mathcal{F}} = \sqrt{2 - \nu} \) for the spin up transitions, and \( \sqrt{\mathcal{F}} = 0 \) for the spin down transitions.

On the other hand, if \( \Delta_V < \Delta_S \), the expressions are the same as the case of \( \Delta_V < \Delta_S \) when the filling factor is \( 1 < \nu < 2 \), but when \( \nu < 1 \): we have \( \sqrt{\mathcal{F}} = \sqrt{\nu} \) for the spin up transitions, and \( \sqrt{\mathcal{F}} = 0 \) for the spin down transitions (Fig. 4.3c). Therefore, in that case, for undoped graphene layer, the interaction disappears.

Figure 4.3: a) Schematic diagram of the Landau levels when \( \Delta_V > \Delta_S \) and \( \nu < 1 \); b) Schematic diagram of the Landau levels when \( \Delta_V > \Delta_S \) and \( 1 < \nu < 2 \) and c) Schematic diagram of the Landau levels when \( \Delta_V < \Delta_S \) and \( \nu < 1 \).
4.2.3 Green function formalism for evaluation of optical conductivity

The optical conductivity is calculated using the Green’s function formalism introduced by Toyozawa (23). The conductivity components are

\[ \text{Re } \sigma_{ij}(\hbar \omega) \propto \text{Im} \langle 0 | M_i G(\hbar \omega) M_j | 0 \rangle \] (4.6)

where \(|0\rangle\) is the ground state of the system, and \(M_i, M_j\) are row and column vectors containing optical matrix elements. \(G\) is the retarded Green’s function written here as \(G(\hbar \omega) = [\hbar \omega - H - \Sigma(\omega) + i\epsilon]^{-1}\). In order to facilitate the discussion of the self energy \(\Sigma_{ph}(\omega)\), we express the Green’s function matrix in the basis of eigenstates of the model Hamiltonian \(H\) (Eq. 4.4).

\[ G' = \begin{pmatrix} G_{11}' & 0 & 0 \\ 0 & G_{22}' & 0 \\ 0 & 0 & G_{33}' \end{pmatrix} \]

\[ G'_{jj} = \frac{1}{\omega - \varepsilon_j - i\epsilon}, \ s = 0^+ \] (4.7)

The primed (’) quantities are expressed in the basis of the eigenstates of \(H\). The eigenvalues \(\varepsilon_j\) of the Hamiltonian \(H\) (Eq. 4.4) are

\[ \varepsilon_1 = E_{01} \]
\[ \varepsilon_{2,3} = \frac{1}{2} \left( E_{01} + \hbar \omega_K \pm \sqrt{(E_{01} - \hbar \omega_K)^2 + 8V^2} \right) \] (4.8)

The Green’s function matrix \((G)\) in the original basis (i.e., the same basis as Eq. 4.4) can be recovered by a unitary transformation \(G = U G' U^{-1}\).

\[ U = \begin{pmatrix} \frac{1}{\sqrt{2}} & -V \sqrt{2V^2 + (E_{01} - \varepsilon_2)^2} & -V \sqrt{2V^2 + (E_{01} - \varepsilon_1)^2} \\ \frac{1}{\sqrt{2}} & \sqrt{2V^2 + (E_{01} - \varepsilon_2)^2} & \sqrt{2V^2 + (E_{01} - \varepsilon_1)^2} \\ 0 & \frac{E_{01} - \varepsilon_2}{\sqrt{2V^2 + (E_{01} - \varepsilon_2)^2}} & \frac{E_{01} - \varepsilon_1}{\sqrt{2V^2 + (E_{01} - \varepsilon_1)^2}} \end{pmatrix} \] (4.9)

Then, for instance, the \(\sigma_{xx}\) component of the optical conductivity is related to \(\langle 0 | M_x^1 G M_x | 0 \rangle = \langle 0 | M_x^1 U G' U^{-1} M_x | 0 \rangle\), where \(M_x^1 = (M_{1x}, M_{2x}, 0)\) is a row vector containing the optical matrix elements.

4.2.4 Discussion of \(\Sigma_{ph}\)

We introduce self energy terms into the diagonal elements of \(G'\)

\[ G'_{jj} = \frac{1}{\omega - \varepsilon_j - i\epsilon^+} \rightarrow \frac{1}{\omega - \varepsilon_j - \Sigma_j(\omega)} \] (4.10)
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Figure 4.4: Top panel: Imaginary part of the self-energy ($\Sigma_2$ or $\Sigma_3$ in Eq. 4.11) with $\nu = 0$. Bottom panel: Real part of the self-energy with $\nu = 0$ as deduced from Kramers-Kronig transformation of the Imaginary part. The behavior of the real part of the self-energy, as a function of energy, is quite similar to that of $E_{01}/B^{1/2}$ when adding the contribution of the non re-normalized value of the transition energy $\epsilon_{01}(B)/\sqrt{B} = v_F\sqrt{2e\hbar} = 36.8\text{meV}/T^{1/2}$.

From second-order Löwdin perturbation theory, we have found

$$\begin{align*}
\text{Im} \Sigma_1 &= 0 \\
\text{Im} \Sigma_2 &= \Sigma(\omega, \omega_K) \\
\text{Im} \Sigma_3 &= \Sigma(\omega, \omega_K)
\end{align*}$$

(4.11)

where the imaginary part of the self energy has the form

$$\text{Im} \Sigma(\omega) = \theta(\omega - \omega_K)(u(\omega))^2$$

(4.12)

Here, $u(\omega) = |u_1(\omega, \omega_K)| = |u_2(\omega, \omega_K)|$. In the basis of Eq. 4.4, the Green’s function can be written as

$$G = \begin{pmatrix}
G_{11} & G_{12} & G_{13} \\
G_{21} & G_{22} & G_{23} \\
G_{31} & G_{32} & G_{33}
\end{pmatrix}$$

(4.13)

$$\begin{align*}
G_{11} &= G_{22} = \frac{1}{2} \left( \frac{1}{\omega - E_{01} - i0^+} + \frac{1}{\omega - E_{01} - i0^+ - \Sigma(\omega)} \right) \\
G_{12} &= -\frac{1}{2} \left( -\frac{1}{\omega - E_{01} - i0^+} + \frac{1}{\omega - E_{01} - i0^+ - \Sigma(\omega)} \right).
\end{align*}$$

(4.14)

$\text{Im} \Sigma(\omega)$ has a threshold at $\omega_K$ that arises irrespective of the form of the coupling matrix element $u$. In this model, the threshold is always located at the lower bound of the energies.
of the continuum of states. We have chosen, motivated by the experimental data (see top panel of Fig. 4.1b), for \( u^2 \) the form

\[
(u(\omega))^2 = D \exp(-R(\omega/\omega_K - 1))
\]  

(4.15)

Using the sum rule for \( \text{Im}(G) \) together with the constraint that \( H_1 \) must reduce to \( H \) in the limit where \( R \to \infty \) (the limit where the continuum collapses to a single energy \( \omega_K \)), the value of \( D \) can be fixed at \( D = \frac{\pi RV}{\hbar \omega_K} \). The model is not sensitive to the exact functional form of Eq. 4.12 as long as the qualitative features such as the exponential decay and the presence of a threshold at \( \omega = \omega_K \) are preserved. We then have two independent parameters to describe the interaction, \( V^2 \) and \( R \). As derived in Eq. 4.5, \( V^2 = A^2 f \) and we will use the value \( A^2( \text{meV}^2) = 1.94 \times B(T) \) (25). The energy range of \( u(\omega) \) contains contribution from the \( K \)-phonon dispersion and multi-acoustic phonon processes. The only remaining fitting parameter is \( R \). In the interpretation of the continuum as states containing multiple acoustic phonons, the exponential factor in Eq. 4.15 describes the decreasing probability of multiple acoustic phonon emission far from the threshold energy. With this simplified model, and knowing the experimental results, we have chosen the value \( R = 3 \) as sketched in Fig. 4.4 which in turn is coherent with the value of the linear \( B \) term used for \( \gamma_{01}(B) \). This also gives reasonable values for \( \text{Re} \Sigma(\omega) \) (bottom panel Fig. 4.4) as compared to the experimental values. Of course the extension in energy corresponding to this \( R \) value is quite high but it does not play a role in the actual fitting process limited to about 200 meV (see Fig. 4.5). Though, within the experimental errors, the fit of data is acceptable with \( R = 3 \), it could be also accepted for \( R \) values, as well as the \( \gamma_2 \) values of \( \gamma_{01}(B) \) differing by 15 per cent. Knowing that the spin splitting \( \Delta S/B \simeq 0.12 - 0.15 \text{ meV/T} \) and that the the introduction of \( \Delta V \propto B \) should result in an extra broadening of the \( E_{01} \) transition, the introduction of the \( \gamma_2 \)-term is explained naturally by the fact that it should be larger than \( \Delta S/B \).

We note finally that the introduction of the interference term \( G_{12} \) (Eq. 4.14) (which corresponds to interference effects between the cyclotron transitions at the two valleys) is essential to reproduce the experimental results.

### 4.3 Comparison with experiment

In Fig. 4.5 we compare the experimental data with the calculated results from the model with \( \Delta V > \Delta S \). We have taken \( \hbar \omega_K = 151 \text{ meV} \) and \( R = 3 \). The Fermi velocity \( v_{F01} = 1.012 \times 10^6 \text{ ms}^{-1} \) for the transitions between the \( n = 0 \) LL and \( n = \pm 1 \) LL has been determined experimentally from the positions of the cyclotron transition lines. The same parameters have been used for all the graphene samples. The good agreement between theory and experiment, for all samples, lends strong support to the physical mechanism proposed for the phenomenon. It is, however only obtained when assuming \( \Delta V > \Delta S \) (Fig. 4.6).

An interpretation of the linear term in \( \gamma_{01}(B) \) is that it may be a broadening resulting from the breaking of the valley degeneracy (Fig. 4.6), consistent with the prediction that \( \Delta V \propto B \), according to several theoretical models (Ref. (17) and references therein) as well as
Figure 4.5: Comparison, for different values of the magnetic field, of experimental data for sample S1 (open black dots) with the theoretical curves (red lines) using the proposed K-phonon interaction model. As a guide for the eye, upward arrows show the evolution of the main cyclotron resonance line whereas downward arrows point the structure corresponding to the emission of $K$-phonons.
4.3. COMPARISON WITH EXPERIMENT

Figure 4.6: (a), (b) The spin and valley sublevels of the $n = 0$ LL, for the case when $\Delta V > \Delta S$ and $\Delta V < \Delta S$ respectively. In the former case, intervalley electronic transitions are possible for both spin orientations. In the latter case, only one spin orientation supports intervalley electronic transitions, owing to the Fermi factor. The effective coupling strength is therefore different in the two cases giving rise to different predictions for the transmission spectra. (c) A comparison between experimental spectra and theoretical simulations for $\Delta V > \Delta S$ and $\Delta V < \Delta S$ for values of magnetic field $B = 18.5\,\text{T}$ and $B = 23.0\,\text{T}$ respectively.
transport measurements (13; 16). In this picture, the values of $E_{01}$ at the two valleys differ by $\Delta V$ (27), resulting in a broadening of the main line by a similar amount. An inspection of the linear term in $\gamma_{01}(B)$ shows that it is greater than the value of $\Delta S$ due to Zeeman splitting. This is consistent with our conclusion that $\Delta V > \Delta S$ in the experiments (Fig. 4.6).
Chapter 5

Phonon satellites

5.1 Introduction

Phonon satellites, or vibronic peaks (in the case of molecular systems), are replicas of electronic bands that arise from strong coupling to vibrational modes. These features can be observed in the differential conductance ($\frac{dI}{dV}$) measured by scanning tunneling spectroscopy (STS). The $n$th-phonon replica is $n$ phonon quanta higher in energy than the electronic band, and corresponds to the emission and reabsorption of $n$ virtual phonons.

In this chapter, we focus on molecular systems, with negligible band dispersion. Here, the restriction to molecular systems is made for reasons of simplicity and computational efficiency. The theory is similar for molecular systems and extended systems. The equations for extended systems can be obtained by including integrals over the Brillouin zone in the appropriate equations in the present chapter.

In the absence of electron-phonon coupling, the electronic spectrum of a molecular system consists of $\delta$-function peaks, corresponding to the different molecular orbitals. Each molecular orbital peak gives rise to a series of vibronic peaks when the electron-phonon coupling is taken into account. The vibronic peak spacing can be readily calculated from the phonon energies obtained via density functional theory. On the other hand, the intensities of the vibron satellite peaks has a more complicated dependence on the details of the electron-phonon interaction of the system. In addition, the energy scale of electronic transitions in molecular systems can be of the same order of magnitude as the phonon frequencies. The lack of a clear hierarchy of energy scales limits the utility of perturbation theory. A full understanding of the vibron satellite structure therefore depends not only on a correct determination of the molecular and vibrational structure, but also on accurate numerical values of the electronic excitations of the system.

The cumulant approximation is a method suitable for calculating high-order phonon satellites. The theory behind the cumulant approximation is developed in Section 5.2. In Section 5.3, we apply this theory to a molecular lattice of CVB molecules, which is a system with strong electron-phonon coupling. We show that the electron spectral functions calculated within our ab initio framework are in good agreement with STS measurements.
5.2. CUMULANT APPROXIMATION

5.2.1 Background to the cumulant approximation

We write the Hamiltonian in the form $H = H_e + H_{ph} + H_{e-ph}$, where $H_e$ and $H_{ph}$ describe the electronic and vibrational parts of the system respectively, and $H_{e-ph}$ describes the interaction between them. There are a variety of methods that approximate $H_{e-ph}$ to various orders in the vibron coordinates, and treat $H_{e-ph}$ in various orders of perturbation theory Refs. (29–34). Ab-initio calculations at the lowest order in perturbation theory were reported in Refs. (31; 35–37), in the context of inelastic tunneling spectroscopy (IETS) of single molecules. Model calculations of vibronic satellite peaks based on a rate-equation approach were reported in Refs. (38; 39).

The cumulant method employed here can be understood as a high-order perturbation theory. The exponential resummation implicit in this method captures vertex corrections absent in low-order perturbation theory (40). Unlike the Migdal approximation, which contains only the zero-phonon peak and the first satellite peak as solutions, the cumulant method can be used to access the higher order vibron satellites. The cumulant method has been shown to be successful in systems with strong electron-boson coupling. Ab initio calculations using the cumulant expansion have reproduced the plasmon satellites of a variety of systems (41; 42). Model calculations using the cumulant expansion have been used to understand phonon assisted resonant tunneling in GaAs (43; 44).

We solve for the vibron satellite peak positions and intensities by calculating the tunneling conductance $\frac{dI}{dV}$ as a function of the bias voltage $V$ between the CVB-graphene sample and the STM tip. We neglect energy-dependent tunneling matrix elements (45). In this approximation, the tunneling conductance is proportional to the local density of states, which in turn can be expressed as the imaginary part of the Green’s function:

$$\frac{dI}{dV} \propto \rho(\vec{r}, E)$$

$$= -2\Im G(\vec{r}, \vec{r}; E)$$

The Green’s function is calculated in the 1st order cumulant approximation. We derive the Green’s function from the following Hamiltonian:

$$H_e + H_{ph} = \sum_j E_j c_j^{\dagger} c_j + \sum_\nu \omega_\nu a_\nu^{\dagger} a_\nu$$

$$H_{e-ph} = \sum_{ij\nu} M_{ij\nu} c_i^{\dagger} c_j (a_\nu^{\dagger} + a_\nu)$$

where $c_j^{\dagger}$, $c_j$ and $a_\nu^{\dagger}$, $a_\nu$ are electron and phonon creation and annihilation operators respectively, $E_j$ the energies of orbital $j$, $\omega_\nu$ the frequencies of phonon mode $\nu$, and $M_{ij\nu}$ the
5.2. CUMULANT APPROXIMATION

The Green’s function in the time domain is written as

\[ G(t) = G_0(t)e^{G_0^{-1}(t)(G_1(t) + G_2(t) + \ldots)} \]  \hspace{1cm} (5.3)

where the terms \( G_n(t) \) contain the \( n \)th powers of the electron-phonon coupling, and \( G_0(t) \) is the zeroth-order Green’s function. Here, we use the 1st order cumulant approximation,

\[ G(t) \approx G_0(t)e^{G_0^{-1}(t)G_1(t)} \]  \hspace{1cm} (5.4)

which is known to give the exact solution to Eq. 5.2 when there is only a single electronic orbital (46). In Eqs. 5.3, 5.4, it is understood that the Green’s functions are matrices with rows and columns corresponding to different molecular orbitals.

5.2.2 Diagonal approximation

In order to derive the LDOS, we require the Green’s functions in the frequency domain (Eq. 5.1). However, Eqs. 5.3, 5.4 cannot be cast into a computationally convenient form for the numerical evaluation of the Green’s functions in the frequency domain because of their matrix structure. On the other hand, the computation simplifies if the off-diagonal elements of \( G_n(t) \) are neglected. We will now proceed to elaborate on this approximation and show that it is justified in a practical case (Sec. 5.3).

We start by evaluating the Green’s functions in the time domain. The non-interacting electron and phonon Green’s functions for unoccupied orbital \( j \) and phonon mode \( \nu \) are:

\[ G_0(j, t) = -i\theta(t)e^{-iE_jt} \]
\[ D_0(\nu, t) = -i[\theta(t)e^{-i\omega_\nu t} + \theta(-t)e^{i\omega_\nu t}] \]  \hspace{1cm} (5.5)
In terms of the non-interacting electron and phonon Green’s functions, the first-order Green’s function (Fig. 5.1) has the following diagonal elements:

\[ G_1(t)_{jj} = \sum_{i\nu} |M_{ij\nu}|^2 \int_{-\infty}^{\infty} dt_1 dt_2 G_0(j, t) D_0(\nu, t_2 - t_1) G_0(j, t - t_2) \]

\[ = G_0(j, t) \sum_{i\nu} |M_{ij\nu}|^2 \left[ -\frac{1}{(E_i + \omega_\nu - E_j)^2} (1 - e^{-i(E_i + \omega_\nu - E_j)t}) + \frac{it}{E_i + \omega_\nu - E_j} \right] \]  \hspace{1cm} (5.6)

Similarly, the off-diagonal elements of \( G_1(t) \) are:

\[ G_1(t)_{jk} = G_0(k, t) \sum_{i\nu} M_{ij\nu} M_{ik\nu}^* \left[ -\frac{1}{E_i + \omega_\nu - E_j} \frac{1}{E_i + \omega_\nu - E_k} (1 - e^{-i(E_i + \omega_\nu - E_k)t}) \right. \]

\[-\frac{1}{E_i + \omega_\nu - E_j} \frac{1}{E_k - E_j} (1 - e^{i(E_k - E_j)t}) \left. \right] \]  \hspace{1cm} (5.7)

In Eq. 5.4, we can make a decomposition into terms constant in time \( t \), terms proportional to \( t \), and terms oscillating in time \( e^{iEt} \).

\[ G_0^{-1} G_1 = G^a + G^b + G^c \]  \hspace{1cm} (5.8)

\[ G^a_{jk}(t) = \left\{ \begin{array}{ll}
\sum_{i\nu} M_{ij\nu} M_{ik\nu}^* & \left( -\frac{1}{\omega_\nu + E_i - E_j} \frac{1}{\omega_\nu + E_i - E_k} \right) & \text{if } j \neq k \\
-\sum_{i\nu} |M_{ij\nu}|^2 & \frac{it}{\omega_\nu + E_i - E_j} & \text{if } j = k 
\end{array} \right. \]  \hspace{1cm} (5.9)

\[ G^b_{jk}(t) = \delta_{jk} \sum_{i\nu} |M_{ij\nu}|^2 \frac{it}{\omega_\nu + E_i - E_j} \]  \hspace{1cm} (5.7)

\[ G^c_{jk}(t) = \left\{ \begin{array}{ll}
\sum_{i\nu} M_{ij\nu} M_{ik\nu}^* \left( \frac{1}{\omega_\nu + E_i - E_j} e^{-i(\omega_\nu + E_i - E_j)t} \right) + \frac{1}{\omega_\nu + E_i - E_k} e^{i(E_k - E_j)t} & \text{if } j \neq k \\
\sum_{i\nu} |M_{ij\nu}|^2 \frac{1}{\omega_\nu + E_i - E_j} e^{-i(\omega_\nu + E_i - E_j)t} & \text{if } j = k 
\end{array} \right. \]  \hspace{1cm} (5.9)

It turns out that even though the individual \( M_{ij\nu} \) may not be small, the off-diagonal terms \( (j \neq k) \) in Eq. 5.9 are negligible compared to the diagonal \( (j = k) \) terms. This is because of a cancellation of phases in the summations \( \sum_{i\nu} \). For instance, it was found that the off-diagonal terms in \( G^a \) were 20 times smaller than the diagonal terms, for the physical system analyzed in Sec. 5.3. The result of neglecting the off-diagonal terms in the first order cumulant approximation is

\[ G(j, t) = G_{jj}(t) \]

\[ = -i\theta(t)e^{-iE_j t} \exp \left( \sum_{i\nu} |M_{ij\nu}|^2 \left[ -\frac{1}{\omega_\nu + E_i - E_j} \frac{1}{(\omega_\nu + E_i - E_j)^2} + \frac{it}{\omega_\nu + E_i - E_j} \right] \right) \]  \hspace{1cm} (5.10)
The spectral function in the frequency domain is

\[
A(j, \omega) = -2i \text{Im} G(j, \omega) = 2\pi \sum_I \frac{1}{\tilde{I}!} e^{-\sum_{I} \lambda_{j,I}} \sum_{I_1 \ldots I_l} \lambda_{j,I_1} \ldots \lambda_{j,I_l} \delta(\omega - (E_j - \Delta_j) - (\Omega_{j,I_1} + \ldots + \Omega_{j,I_l})) \tag{5.11}
\]

Here, \( I = (i, \nu) \) represents a composite index labeling an electronic orbital \( i \) and phonon mode \( \nu \), and the sums over \( I \) are understood to run over unoccupied electronic orbitals and all phonon modes. In Eq. 5.11, the quantities

\[
\Delta_j = \sum_I \frac{|M_{j,I}|^2}{\Omega_{j,I}} \quad \lambda_{j,I} = \frac{|M_{j,I}|^2}{\Omega_{j,I}^2} \quad \Omega_{j,I} = \omega_\nu + E_i - E_j
\]

are calculated from the electronic orbital energies \( E_i \), the phonon frequencies \( \omega_\nu \), and the electron-phonon matrix elements \( M_{j,I} \), which can all be obtained from first-principles calculations.

With the spectral function Eq. 5.11, we can evaluate the LDOS within the diagonal approximation

\[
\text{LDOS}(r, E) \propto -2\text{Im} G(r, r; E) = -2\text{Im} \sum_{i,j} \psi_i^*(r) \psi_j(r) G_{ij}(E) \approx \sum_j |\psi_j(r)|^2 A(j, E) \tag{5.13}
\]

### 5.3 Application to a molecular lattice

We now apply the theory developed in Section 5.2 to a physical system. We consider a 2D molecular lattice of 1,3,5-tris(2,2-dicyanovinyl)benzene (CVB) molecules adsorbed on graphene. This system has been realized in the laboratory (28). We calculate structural properties within DFT, electronic excitations within the GW approximation Refs. (47; 48), and we use the 1st order cumulant approximation to obtain the electron spectral functions which are in good agreement experiment.

CVB self-assembles into a hexagonal lattice on graphene, with lattice constant 1.127 nm (Fig. 5.2). There are structural changes between CVB in gas phase and CVB on graphene. On graphene, the CVB molecule is planar, while the terminal nitrogen atoms are rotated out of plane in the gas phase. In the gas phase, the lowest unoccupied molecular orbital (LUMO) and the highest unoccupied molecular orbital (HOMO) of CVB are both two-fold
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Figure 5.2: Top view of equilibrium configuration of CVB lattice on graphene substrate (not shown). Outline of primitive unit cell is shown in black. Hydrogen, carbon, and nitrogen atoms are colored cyan, yellow, and lavender respectively.

degenerate, while LUMO+1 is non-degenerate. In this paper, we will focus on the electronic properties and the electron-phonon coupling of the LUMO and LUMO+1. Wavefunctions obtained from our DFT calculations show that the LUMO and LUMO+1 do not hybridize strongly with graphene. Both the LUMO and LUMO+1 have strong electron density near the hydrogen atoms of the molecule (Fig. 5.3d, 5.3e). In the CVB molecular lattice on graphene, the LUMO and LUMO+1 of adjacent molecules hybridize into energy bands of band width 70 meV and 80 meV respectively.

There are 5 phonon modes with frequencies from 193 meV to 196 meV that contain a strong C-H in-plane bending component, and a C-C stretching component (Fig. 5.3b, 5.3c), belonging to representations $A'_1$, $E'_1$, $E'_2$ of the $C_{3h}$ point group. Our DFT calculations show that the LUMO and LUMO+1 couple the most strongly to these modes (Fig. 5.4). There is also significant, but weaker, coupling to six C-N stretching modes with frequencies in the range 276 meV to 279 meV. Based on the electron distribution of the LUMO and LUMO+1 shown in Fig. 5.3d, 5.3e, the strong electron-phonon coupling to the C-H bending modes can be understood as a result of the large electron densities near the hydrogen atoms. Compared to the electron-phonon coupling within the states LUMO, LUMO+1, the coupling from LUMO, LUMO+1 to other unoccupied molecular orbitals or to states localized on graphene is negligibly small.

The evaluation of Eq. 5.11 can be simplified by letting the indices $i, j$ in Eqs. (5.11, 5.12) run over only a subset of all electronic states of the combined CVB+graphene system. Firstly, we neglect the dependence on the electron wavevector $k$, and the phonon wavevector $q$, based on the observation that the coupling between neighboring C molecules is weak. The electron (80 meV) and phonon bandwidths (0.4 meV) are both relatively small, and the electron-
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Figure 5.3: (a) Electronic structure of CVB molecule, referenced from the Fermi level, calculated within the GW approximation. Arrows label the LUMO and LUMO+1. (b) Phonon density of states of the CVB+graphene system. Arrow marks a C-H bending/C-C stretching mode shown in (c), where blue areas denote the range of motion of atoms (greatly exaggerated). (d), (e) Electron density of LUMO and LUMO+1, respectively.
Figure 5.4: Dimensionless electron-phonon coupling constants plotted as a function of phonon energy, for various electronic orbitals. The dimensionless electron-phonon coupling constants are defined in the text. Diagonal coupling of LUMO (top left), diagonal coupling of LUMO+1 (top right), off-diagonal coupling between the two degenerate LUMO orbitals (bottom left), off-diagonal coupling between LUMO and LUMO+1 (bottom right).
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phonon matrix elements do not change appreciably with electron and phonon wavevector. We include in Eqs. (5.11, 5.12) only the electronic states LUMO, LUMO+1 because of the aforementioned weak coupling to other unoccupied molecular orbitals and graphene states. Occupied states do not play a role in Eq. (5.11) because an electron occupying the LUMO is unable to hop onto occupied states at the measurement temperature of $T = 4K$.

DFT calculations on the CVB+graphene system were performed using the PBE-GGA exchange-correlation functional. Van der Waals forces were accounted for using a semi-empirical dispersion term (DFT-D) (49; 50). We used norm-conserving pseudopotentials with a 60 Ry plane wave kinetic energy cutoff, and a 4x4x1 Monkhorst-Pack grid for the determination of the self-consistent chage density. The unit cell of the CVB+graphene system, which contains a single CVB molecule and 21 unit cells of graphene, was fixed to have the experimental lattice constant of 1.127 nm. The positions of the CVB and graphene atoms were allowed to relax to their equilibrium positions, obtaining the structure shown in Fig. ???. The total energy, orbital energies, and other electronic properties of this structure are insensitive to the horizontal relative displacement between CVB and graphene. Frequencies of phonon modes and the electron-phonon matrix elements were calculated within the framework of density functional perturbation theory (DFPT) (51). In order to account for electron-correlation effects not captured by DFT, we apply the GW correction to the DFT orbital energies. 800 empty states were used in constructing the dielectric function and the electron self-energy, which was calculated in the plasmon-pole approximation. The GW-corrected orbital energies are used in the spectral functions Eq. 5.11.

We calculate the local density of states from the diagonal approximation spectral functions (Eq. 5.11), broadening the delta-functions by 80 meV, which is comparable to the LUMO and LUMO+1 bandwidths. The result of our calculation is shown in Fig. 5.5. The zero-phonon peak (located at bias = 1.85 eV) and two phonon satellites of the LUMO, and the zero-phonon peak (located at bias = 2.66 eV) and one phonon satellite of the LUMO+1 are visible in this energy range. The two phonon satellites spaced at multiples of 171 meV apart from the LUMO, can be understood as the emission of a single phonon and of two phonons from the LUMO, respectively. The dominant contribution to the phonon satellites comes from the emission of the 195 meV C-H phonons, which are the most strongly coupled to the LUMO. Weaker coupling to a multitude of lower frequency phonons lowers the satellite peak spacing from 195 meV to 171 meV. Similarly, the phonon satellite of the LUMO+1 can be understood primarily as the emission of C-H phonons from the LUMO+1. We have found that the sum over $l$ in Eq. 5.11 can be truncated at $l = 2$. Higher-order terms, which give rise to phonon satellites corresponding to emission of three or more phonons, do not noticeably affect the spectrum.

The relative positions of the LUMO+1 zero-phonon peak and the LUMO zero-phonon peak are renormalized by the electron-electron interaction and electron-phonon interaction. Within DFT, the energy difference between these two levels is $E_{\text{DFT\ LUMO+1}}^{\text{DFT}} - E_{\text{DFT\ LUMO}}^{\text{DFT}} = 0.37eV$. The GW correction changes this energy difference to $E_{\text{GW\ LUMO+1}}^{\text{GW}} - E_{\text{GW\ LUMO}}^{\text{GW}} = 0.37eV$. The electron-phonon interaction cause a further shift in the energy differences between these two levels ($\Delta_j$ terms in Eq. 5.11), resulting in a final energy difference of 0.78 eV between LUMO
Figure 5.5: Theory and experimental $\frac{dI}{dV}$ curves (in arbitrary units), as a function of bias voltage between STM tip and sample. Numbers in blue denote the number of vibrons emitted for each peak. (b) Theory and experimental $\frac{d^2 I}{dV^2}$ curves (in arbitrary units), as a function of bias voltage between STM tip and sample.
and LUMO+1.

We compare our results to an STM experiment on the CVB+graphene system. Experimental $\frac{dI}{dV}$ data taken at the position indicated in Fig. 5.3d is shown in Fig. 5.5a. Because the STM tip is placed in a region of high electron density (bright areas in Fig. 5.3d, 5.3e), the $\frac{dI}{dV}$ spectra taken at this position is expected to closely resemble the density of states. Since the orbital energies $E_j$ have only been calculated up to a constant energy shift, a constant energy shift is added to align the theory and experimental LUMO levels in Fig. 5.5. There is good agreement between theory and experiment for the relative positions of LUMO, LUMO+1, and the various phonon satellite peaks. The weights of the LUMO, LUMO+1, and the one-phonon satellite peak are well explained by our calculation. The LUMO peak, which would be twice as high as the LUMO+1 peak in the absence of electron-phonon interaction because of the two-fold orbital degeneracy, is strongly reduced in intensity in both the calculation and experiment. In Fig. 5.5b, we plot the second derivative as a function of bias voltage, showing good agreement between theory and experiment. For a comparison of dI/dV images, see Ref.(28).

The intensity of the two-phonon peak is underestimated in the calculation. It is possible that 2nd or higher order cumulant methods, where more terms are included in the expansion of Eq. 5.3, will increase the intensity of the two-phonon peak. "High-order coupling" theories, in which the phonon coordinate is take beyond linear order in the coupling Hamiltonian , have been successful in describing multiphonon relaxation in oxides (52), and may be able to describe the two-phonon peaks in the CVB+graphene system as well. Such theories are beyond the scope of the present chapter, and their application to systems of molecular adsorbates will be left to future study.
Chapter 6

Artificial lattices

6.1 Introduction

In the previous chapters, we have seen how the low-energy Dirac-like electronic structure of graphene gives rise to its unusual properties. It was proposed in (53) that a Dirac-like electronic structure can be created in a lattice of molecules arranged on a metal surface. The periodic potential of the molecules modifies the metallic surface state, changing the ordinary 2DEG-like parabolic dispersion into a graphene-like Dirac cone. Such systems have been called artificial graphene. Depending on the symmetry class and the strengths of the molecular potential, other unusual electronic structures, such as semi-Dirac points, can also be created. The general theory behind these artificial lattices is described in Section 6.2.

Artificial graphene has been constructed in the laboratory (54; 55). These systems are constructed by positioning small molecules in a regular array on the Cu(111) surface, using the tip of a scanning tunneling microscope (STM). Depending on the nature of the molecules used and the spacing between the molecules, these artificial graphenes display slightly different characteristics and have different effective graphene parameters. In Section 6.3, we examine and explain the properties of an experimentally realized artificial graphene system.

The advantage of artificial graphene over real graphene is the degree of microscopic control. Modified graphene structures, such as defects and edges, can be easily created in artificial graphene by positioning molecules appropriately on the metal surface. The corresponding structures in real graphene are often harder to create without introducing unwanted disorder. This topic is further examined in Section 6.4.

6.2 Optimal design of artificial lattices

Any artificial lattice with $p6m$ symmetry can support Dirac points at the $K$ point of the Brillouin zone. However, not all such Dirac points are easily observable in experiments. If the Dirac point is obscured by other energy bands at the same energy (Fig. 6.1), or if the energy scale of the Dirac cone is too small, these artificial lattices will not exhibit Dirac fermion
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Figure 6.1: Band structures of artificial graphene showing an easily observable Dirac cone at the K point of the Brillouin zone (left) and a Dirac cone that is obscured by band overlap (right).

physics. Similar considerations apply for artificial lattices supporting semi-Dirac points, which are band contact points with linear dispersion along one direction and quadratic dispersion along another. In this section, we examine how experimentally observable Dirac points and semi-Dirac points can be created in artificial lattices.

6.2.1 Dirac points

We model the artificial graphene electronic structure using a simple one-electron model. We assume that the host surface supports a 2DEG-like surface state, parametrized by an effective mass \( m \). The effect of the molecular potential on the surface state is described effectively by a periodic one-electron potential \( V(r) \).

\[
H = -\frac{\hbar^2}{2m} \nabla^2 + V(r) \tag{6.1}
\]

We are interested only in the low-energy bands of artificial graphene, because the energy scale of the characteristic features induced by the molecular potential are small for the higher bands of artificial graphene. We study the Dirac point at the contact point between bands \( n = 1 \) and \( n = 2 \), or between \( n = 2 \) and \( n = 3 \). This allows us to restrict the potential \( V(r) \) to have only a few non-zero fourier components, since fourier components of large wavevector \( G \) do not affect the low-energy bands significantly.

\[
V(r) = \sum_{|G| G_{\text{max}}} V_G e^{iG \cdot r} \tag{6.2}
\]

The space group and time-reversal symmetry further constrain the number of independent fourier components \( V_G \). In the following, we choose \( G_{\text{max}} \) such that the potential \( V(r) \) is described by 6 independent fourier components. We assume that the overall energy shift is set to zero: \( V_0 = \int dr V(r) = 0 \).
In order to quantify the effects of band overlap and the energy scale of the Dirac cone, we define the quantities \( \Delta^+ = E(n, k = M) - E(n, k = K) \) and \( \Delta^- = E(n - 1, k = K) - E(n - 1, k = M) \), which represent the energy differences between the van Hove singularities at the \( M \) point and the Dirac point at the \( K \) point (see Fig. 6.2). Here, \( E(n, k) \) is the energy of band \( n \) at \( k \)-point \( k \). The ideal situation for an easily observable Dirac point is when \( \Delta^+ \) and \( \Delta^- \) are both large and positive.

To investigate the relationship between the structural properties of artificial graphene (captured by \( V(r) \)) and its electronic properties (\( \Delta^+, \Delta^- \)), we generate \( 10^6 \) random realizations of \( V(r) \) and examine trends exhibited by their electronic properties. The different potentials are generated by uniform random sampling of the parameters \( \{V_G | G < G_{\text{max}} \} \), subject to the abovementioned symmetry constraints as well as a constraint on the maximum strength of the potential \(|V(r)| < V_{\text{max}}\). The latter constraint is motivated by the fact that physical realizations of artificial graphene cannot have arbitrarily large potential strengths. For molecules on metal surfaces, \( V_{\text{max}} \) should be of the order of a few eV. We consider artificial lattices with period 10, corresponding to molecular networks constructed out of small molecules.

For \( V_{\text{max}} = 1 \text{eV} \), we obtain the left panel of Fig. 6.3. The different potentials fall into two main groups: those with \( V_1 > 0 \) have varying \( \Delta^+ \) and a constant \( \Delta^- \) at around \( \approx 0.2\text{eV} \), while those with \( V_1 < 0 \) have varying \( \Delta^- \) and a constant \( \Delta^+ \) at around \( \approx -0.2\text{eV} \). Further increase of \( V_{\text{max}} \) does not change this picture significantly. Therefore, only those potentials with \( V_1 > 0 \) are suitable for observing Dirac physics at the low energy bands.

We search for potentials with \( V_1 > 0 \) that maximize \( \Delta = \min(\Delta^+, \Delta^-) \). To efficiently search the high-dimensional parameter space of artificial lattices, we have employed the
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Figure 6.3: $\Delta_+$ and $\Delta_-$ for different potentials. Left panel shows results for $V_{\text{max}} < 1.0 \text{eV}$ while the right panel shows results for $V_{\text{max}} < 3.0 \text{eV}$. Potentials for which the first Fourier component $V_1$ is positive (negative) are represented by red (blue) points.

Simulated annealing method. First, we initialize the potential to have random Fourier components. Next, we iteratively perturb these Fourier components randomly, respecting the $V_{\text{max}}$ constraint. The new potential is accepted with probability $\max(1, \exp[(\Delta_{i+1} - \Delta_i)/T])$, where $\Delta_{i+1}$ is the value of $\Delta$ for the current step and $\Delta_i$ is its value for the previous step. $T$ is the fictitious temperature parameter controlling the rate of annealing. This procedure is repeated while the temperature is reduced, until the potential converges. We have found that the potential converges within 100 iterations for all our simulated annealing runs. We have performed 100 simulated annealing runs, with all runs converging to the same potential.

The optimal value of $\Delta$, denoted as $\Delta_{\text{max}}$, increases with $V_{\text{max}}$, but with diminishing returns. Beyond $V_{\text{max}} \approx 2 \text{eV}$, $\Delta$ does not change more than 200 meV.

Next, we examine the characteristics of potentials that maximize the Dirac fermion energy scale. We select all potentials (realized in our random sampling) that result in $\Delta$ within 10% of $\Delta_{\text{max}}$. We find that the Fourier components of these potentials cluster around those of the optimal potential (Fig. 6.5). This shows that the optimal potential is unique, supporting the observations of our simulated annealing runs. The first Fourier component $V_1$ of the optimal potentials is positive and much bigger in magnitude than the higher Fourier components. In real space, this means that the optimal potential contains a single repulsive center as its main feature. The right panel of Fig. 6.5 confirms this picture. Such a potential is considerably similar to real graphene, where the repulsive regions correspond to the hexagonal "holes" of graphene, and the attractive regions to the $\pi$-bonds between carbon atoms.

6.2.2 Semi-Dirac points

The approach taken to maximize the energy scale of Dirac fermions in artificial lattices can be extended to other types of band structures. Here, we consider semi-dirac points, which are band contact points in two dimensions, with a linear dispersion in one direction,
Figure 6.4: The maximum Dirac fermion energy scale $\Delta_{\text{max}}$ over all potentials with maximum amplitude $V_{\text{max}}$.

Figure 6.5: Optimal potential which maximizes the Dirac fermion energy scale. Left panel shows the Fourier components of the optimal potential in red, and the Fourier components of potentials with almost-optimal potentials in blue. Right panel shows a real space representation of the optimal potential.
and a quadratic dispersion in another. An example is the proposed TiO$_2$/VO$_2$ superlattice (56; 57).

Here, we consider artificial lattices with $pmm$ symmetry. We find that with the right potential, a semi-Dirac point can be created at the $M$ point at the corner of the Brillouin zone. While the Dirac points discussed above were protected by the $p6m$ symmetry of the potential, these semi-Dirac points are not symmetry protected, but require fine-tuning of the potential parameters. The TiO$_2$/VO$_2$ superlattices discussed in (56) likewise require a certain number of superlattice layers to display the semi-Dirac physics.

In Fig. 6.6 we show such a semi-Dirac point in an artificial lattice. We maximize the semi-Dirac energy scale by considering the energy differences between the semi-Dirac point and van Hove singularities at other points in the Brillouin zone. In Fig. 6.7 we show the result of this optimization procedure. In real space, the optimal potential consists of a single oblong attractive center. Such a potential might be realized on a metallic surface by arranging molecules of the appropriate symmetry. Furthermore, the electronic structure of the molecule should facilitate charge transfer from the molecule to the surface, in order to create an attractive potential.

### 6.3 Realization of an artificial lattice on Cu(111)

Here we report a systematic study of three isostructural honeycomb supramolecular network architectures used to modulate the 2DEG on a Cu(111) surface. We compare model calculations with band structures resolved from Fourier-transformed scanning tunneling spectroscopy. We determine quantitatively how the band bottom, bandwidth, and band gap are tailored by the periodicity of the supramolecular networks and by the molecule-substrate interaction. Moreover, we found that two bands touch at the K points of the network Brillouin
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Figure 6.7: Real space representation of the optimal potential which maximizes the semi-Dirac fermion energy scale. A single unit cell is shown.

The supramolecular self-assembly method was used to construct the 2D architectures from 1,3,5-tris(pyridyl)benzene (M1), 1,3,5-tris(4-(pyridin-4-yl)phenyl)benzene (M2) and 1,3,5-tris(4-bromophenyl)benzene (M3) (insets of Fig. 6.8a-c). To simulate the 2DEG band structures, we first calculated the effective potentials of the supramolecular systems using density functional theory (DFT) calculations as depicted in Fig. 6.8d. These calculations were performed in a plane-wave basis set, using a 60 Ry kinetic energy cutoff, norm-conserving pseudopotentials, and a Perdew-Burke-Ernzerhof (PBE) exchange-correlation energy functional. Then we calculated the 2D band structures by solving Schrödinger’s equation of a single electron inside a 2D periodic potential using plane waves and Bloch’s theorem. The effective electron mass used is $0.4m_e$.

As shown in Fig. 6.8ab, the self-assembly of M1 or M2 resulted in large domains of network architectures with a honeycomb motif stabilized via pyridyl-Cu-pyridyl coordination bonds, and denoted S1 or S2, respectively. M3 molecules underwent debromination and formed a honeycomb organometallic structure (Fig. 6.8c) in which the neighboring molecules are linked by C-Cu-C bonds, denoted S3. The domain size of this structure is smaller than that of M1 or M2, presumably due to the fact that the stronger organometallic bonds restrict the development of large networks in the self-assembly process. Fig. 6.8d illustrates the common structural characters of the three honeycomb networks, where red three-arm stars represent the molecules and blue dots the Cu adatoms. The effective potential provided by the molecules and Cu atoms seen by a surface state electron, as shown in Fig. 6.8e, was
Figure 6.8: (a)-(c) STM topographic images (0.5 nA; 1.0 V) showing three isostructural supramolecular honeycomb networks. Insets: chemical structure of the molecule used to assemble the structures. (d) Structural model of the networks. (e) Effective potential seen by a surface state electron as calculated by DFT. (f) $dI/dV$ spectra recorded at the center of four different pores in S1 (top), S2 (middle), and S3 (bottom) structures.
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Fig. 6.8f shows the differential tunneling ($dI/dV$) spectra, which represent the local density of states (LDOS) of the 2DEG, with the tip located at the center of four randomly selected pores for each of the three structures. These spectra display a broad peak, indicating that the Cu(111) surface electrons are modulated by the supramolecular structures. The rather broad peak suggests in part imperfect confinement provided by the pore boundary (58). The peaks of the S2 spectra are at lower energy compared with those of S1, which can be associated with the larger area of the pore. Although S3 is of a same periodicity as S1, its spectra have a peak at relative higher energy, implying that M3 provides a different scattering potential. Interestingly, in all three cases, different pores exhibit peaks of different characteristics (e.g., relative peak intensities, peak shape, and peak positions).

FT-LDOS maps have been widely used to image the band dispersions of a variety of systems (59–62). Here we provide calculations showing that the FT-LDOS can be used to image the band dispersions in our supramolecular networks. The FT-LDOS is sensitive to scattering transitions of electrons within a constant energy contour (assuming elastic scattering). In this experiment, defects or impurities on the Cu(111) surface are the likely cause of the elastic scattering, because the Cu(111) surface band can be imaged under FT-LDOS, in the absence of the supramolecular networks. We assume that the scattering matrix elements are slowly varying in k-space, since they are likely to be caused by short-range scattering. The FT-LDOS can then be approximated by a joint density of states calculation ((59)) in Fig. 6.9), we show the results of such a calculation for a 2D electron gas, and for the S1 and S2 supramolecular structures using the DFT-estimated model potential.

We have constructed the energy dispersion in momentum space from the experimental FT-LDOS maps. For each energy within the measured energy range, we averaged the FT-LDOS signal over all wave vectors of equal magnitude (radial averaging of FT-DOS maps) to compile power spectra as a function of wave vector and energy. The results for S1 and S2 are shown in Figs. 6.10ab respectively. Both spectral functions display a dispersive band in the Brillouin zone of the honeycomb networks (NBZ; the white dashed lines define the K and M points of the NBZ). As a reference, the power spectral function of the clean Cu(111)

![Figure 6.9: FT-LDOS calculations for (a) a 2D electron gas, (b) the S1 network, and (c) the S2 network. All plots are along the $\Gamma - K$ direction](image-url)
Figure 6.10: (a)-(c) Power spectral functions of 2DEG of S1, S2 (the supramolecular lattice spots are subtracted for clarity), and clean Cu(111) from top to bottom. Black dotted lines, simulated first band; red dotted lines, dispersion of Cu(111) surface state. (d) Experimental (black curve) and simulated (DFT-estimated potential) TDOS of S1 (top), S2 (middle), and S3 (bottom). (e), (f) Experimental (left) and simulated (right) unit-cell-averaged LDOS maps of S2 (8 nm x 8 nm) and S3 (5 nm x 5 nm) at the given energies. The inserted model is a guide for the eye.
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The dispersion of the 2DEG of the clean Cu (111) is plotted as the red dotted parabolas in Figs. 6.10a and b. One can see that the band bottom of S1 is at 0.34 V, upwardly shifted by 60 meV compared with the clean Cu(111) 2DEG. The band bottom of S2 is at 0.37 V. The intensity of both bands is significantly reduced at the NBZ boundary. Similar measurements on clean Cu(111) do not show such intensity reductions, which excludes the possibility that the intensity reduction is due to low tunneling matrix elements. We attribute this feature to a finite bandwidth: S1 has a band from 0.34 to 0.22 eV, and S2 has a band from 0.37 to 0.28 eV. These experimental findings provide clear evidence that the periodical supramolecular architectures modulate the Cu(111) surface-state electrons to form different dispersive 2D bands. In our model calculations, we have used two different effective scattering potentials to model the molecules and Cu adatoms. The shape of the first potential, which has been estimated by the DFT total potential, is depicted in Fig. 6.8d. We have evaluated the DFT total potential (Fig. 6.82) on a plane at a distance of 3 from the molecules. For S1 and S2, the model molecular potential (red region with width 4.9) is set as $V_m = 0.3\text{eV}$, and the Cu potential (blue region with diameter 3.5) $V_{\text{Cu}} = 0.1\text{eV}$, since Cu is slightly positively charged in the coordination bond. For S3, we set $V_m = V_{\text{Cu}} = 0.9\text{eV}$, accounting for the covalent nature of the organometallic bond, which is expected to change the nature of the molecule-surface interaction and thus the effective potential. We compare the results of using this effective potential with a second effective potential, where the molecules and Cu adatoms are represented by muffin-tin potentials of diameter 4.9 and 3.5, with the same values of potential depth as above, respectively. The simulated first band along $\Gamma K$ direction of S1 and S2 are shown as black dotted curves in Figs. 6.10a and b. Both methods reproduce the experimentally resolved band dispersions fairly well for both S1 and S2 within the first NBZ. We also evaluated the total density of states (TDOS) of the three structures. Experimental TDOS were obtained through integrating the $dI/dV$ spectra of the entire area. As shown in black curves in Fig. 6.10d, the TDOS of S1 displays a broad peak at 0.3 eV and two shoulders at 0.2 and 0.05 eV; The TDOS of S2 has three peaks at 0.3, 0.2, and 0.1 eV and two dips at 0.25 and 0.15 eV; The TDOS of S3 has two peaks (0.1 and 0.52 eV), two shoulders (0.05 and 0.45 eV), and a dip (0.15 eV). The red curves in Fig. 6.10d are simulated TDOS using the DFT-estimated potential (with a 25 mV broadening) of the three structures, showing fair agreement with the experimental TDOS. Upon comparison to the band structure, the TDOS peaks are associated with the first, the second, and the higher order bands; the dips are associated with the band gaps.

To better understand the band characteristics, we examine the LDOS maps averaged over the unit cells in a given sample. Fig. 6.10e left panels are the unit-cell-averaged LDOS maps of S2 at the energies that are marked by the red arrow in Fig. 6.10d. The 330 meV map shows a domelike feature at the pore center, which corresponds to the states of the first band. Upon increasing energy to 200 meV, a hexagon with a dip at the center appears, which can be assigned to the states of the second band. At 50 meV, a protrusion in the center and six bright spots in the hexagonal corner appear, which can be assigned to the states of the higher bands. Fig. 6.10f left panels show the unit-cell-averaged LDOS maps...
of the S3 structure at two energies corresponding to the red arrows in Fig. 6.10d. The domelike and the hexagon feature at 70 and 300 meV can be assigned to the states of the first and the second bands, respectively. The simulated LDOS intensity maps, calculated from the DFT-estimated potential, are shown in the right panels in Figs. 6.10e and f, which reproduce the general features of the experimental results. We have found that the LDOS calculated from both model potentials give good agreement with experimental results at low energies, while the DFT-estimated potential is more accurate than the muffin-tin potential at higher energies because of the importance of higher Fourier components in that energy range.

The full band structures of the three structures calculated with the DFT-estimated potentials are plotted in Figs. 6.11a to c. The interplay of the artificial supramolecular architectures with the surface-state electrons tunes the band structure in three aspects: shifting the band bottom and varying the band width and the band gap size. We now discuss the general trends exhibited by the band characteristics depending on the unit cell length of the supramolecular lattice and the effective potential. In the 2DEG model, the extent to which the periodic potential affects the surface state can be quantified by a dimensionless parameter \( \zeta = \frac{m}{(2\pi \hbar)^2} V_1 L^2 \), where \( L \) characterizes the unit cell length and \( V_1 \) the first Fourier component of the potential (63). For the band bottom, it is offset from the Cu(111) surface state band bottom by the average value of the potential in the unit cell. We thus expect that S3, which has a larger band bottom offset than S1, provides a higher potential. We also expect that S1, which has a greater proportion of the unit cell occupied by the molecules, has a larger band bottom offset than S2. Both of these expectations are verified by our experiments. The parameter \( \zeta \) also explains why S3, which has an identical configuration as S1, has a larger band gap. For a given potential, it was reported that the band gap is enlarged as the network pore size is reduced (58). However, we find that when the unit cell size is below a critical value, the trend can be reversed. A similar trend for band gap as a function of potential strength was reported in (64). In Fig. 6.11d, the calculated band gaps of 14 supramolecular network structures with increasing size are plotted (the molecular model is shown in the inset). The critical unit cell length is \( \sim 4 \) nm for the weak potential \( (V_m = 0.3 \text{ eV}) \) and \( \sim 2.5 \) nm for the strong potential \( (V_m = 0.9 \text{ eV}) \). The effective potential in the limit of \( L \rightarrow 0 \) is almost homogeneous because the molecular backbone (see inset of Fig. 6.10d) occupies an increasingly large proportion of the unit cell, and the pores become vanishingly small as \( L \) approaches zero. Consequently, the band dispersion should be free electron-like and gapless in this limit. For the smallest molecule in our calculations, the pores occupy only 19% of the unit cell area; the first and second bands overlap, and the band gap disappears.

The circled region in Fig. 6.11c, where the second and the third bands meet at \( K \) points, is magnified in the inset in Fig. 6.11e. For a small nonzero momentum deviation, \( q \), away from the \( K \) points, a linear dispersion emerges, and the two bands form Dirac cones at the \( K \) points (63). We can define \( E(K + q) = E_D + \frac{h^2 q^2}{2m^*} + h q v_D \), where \( E_D \) is the energy level of the Dirac point and \( v_D \) the carrier velocity. Note this type of massless quasi-particle is different from those in graphene, considering other states are present at the same energy.
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Figure 6.11: (a)-(c) Calculated (DFT-estimated potential) band gaps as a function of the unit cell size ($L$) of 14 supramolecular networks. Different values of $L$ correspond to different numbers ($n$) of benzene rings in the arms of the network. (d) Calculated band gaps and (e) Dirac point energy and carrier velocity of 14 supramolecular networks. The black (red) squares denote the weak (strong) potential. The inset in the upper panel shows the magnified view of the red circle in S3. The dashed line in the low panel indicates the result obtained from $k.p$ theory.
6.4 Defect structures of artificial graphene

In this section, we demonstrate the artificial graphene behaves similar to real graphene not just in the bulk, but also where edges and other defect structures are concerned. The physical system addressed here is a artificial lattice of coronene molecules arranged by low-temperature STM manipulation on a Cu(111) surface.

Subjected to the repulsive potential provided by the coronene molecules, the two-dimensional electron gas (2DEG) provided by the Cu(111) surface states electrons are confined in the channels of a honeycomb network (Fig. 6.12a). The center of the triangle formed by three neighboring molecules can be viewed as the atomic site of the honeycomb structure, whereas the middle bridges between two adjacent molecules corresponds to the "bonds" of the honeycomb structure. Fig. 6.12b shows a tunneling spectrum averaged over the artificial graphene, which corresponds to the density of states (DOS). The V-shape DOS is a manifestation of massless Dirac Fermions (53; 54; 65). The down of the V, Dirac point, is at 0.23 V below the Fermi level, and is 0.17 V above the onset of the Cu(111) surface state-state band that forms the 2DEG. Fig. 6.12c shows the power functions in $K$ (left) and $M$ (right) directions, resolved using Fourier-transformed scanning tunneling spectroscopy (2D FT-LDOS). At -0.23 eV, the band structure can be described by a Dirac cone at the $K$ and $K'$ points of the Brillouin zone. Scattering between these Dirac cones give rise to characteristic features in the FT-LDOS spectrum along the $K$ and $M$ directions. We have calculated the band structure by treating the system as a non-interacting 2DEG in a triangular array of repulsive potential disks as illustrated in the down inset of Fig. 6.12a (55). The potential is set as 1.0 eV, the muffin-tin radius is 0.53 nm, and the effective mass of the Cu surface-state band is $0.4m_e$. The calculated DOS and FT-LDOS are plotted in Fig. 6.12b and d, respectively. The experiments and theory agree very well.

6.4.1 1-Dimensional defects

Termination of infinite graphene sheet results in edge(s). Ideal graphene nanoribbons (GNRs) should have two parallel edges. We have studied artificial GNRs of specific configurations. The left part of Fig. 6.13a shows a section of a 6-ZGNR where the dashed lines are guides for the eye. Since the 2DEG outside the GNR region is depleted by the close-packed
Figure 6.12: (a) STM image of an artificial pristine graphene structure of a triangular array consisting of 300 coronene molecules. Top inset: chemical structure of coronene; down inset: simulation model (the red discs are 1.0 eV potentials). Scale bar: 5 nm (b) Experimental $dI/dV$ (solid) and simulated DOS spectrum (dashed). (c) Power function along $K$ (left) and $M$ (right) directions resolved by 2D-FT-LDOS. Dashed curves are simulated band dispersions along the defined directions. (d) Simulated FT-LDOS.
Figure 6.13: (a-d) An artificial 6-ZGNR. (a) STM image (left part) and simulation model (right part). (b) STS map acquired at -0.26 V (left part) and simulated LDOS map at -0.24 V (right part). (c) Experimental row-averaged dI/dV spectra and calculated LDOS. Black dashed line indicates Dirac point. (d) The amplitude of the edge state as a function of row index. Experimental (calculated) results are shown in solid (open) symbols. (e-g) An artificial 7-AGNR. (e) STM image (left part) and simulation model (right part). (f) STS map acquired at -0.23 V. (g) Experimental row-averaged dI/dV spectra and calculated LDOS. Scale bars: 5 nm.
molecules, this structure can be viewed as a ZGNR. We define that the down edge is of sublattice A and the top edge is of sublattices B, and different rows are numbered from 1 to 6. Row-averaged DOS acquired at the defined rows are plotted in Fig. 6.13c. Both edge rows (A1 and B6) have a pronounced peak emerging at Dirac point as marked by the dashed line. The amplitude decays in the interior of the ribbon (Fig. 2d.), indicating the state is localized at the two edges. Interestingly, the two sublattices behave independently and each one can be fitted by an exponential function $e^{-L/\xi}$ with a decay constant $\xi = 1.1a_0$ ($1.6a_0$) for A (B) sublattice, where $a_0$ is the artificial bond length. The localization of the state is apparent in the DOS map, as shown in the left part of Fig. 6.13b, which was acquired at the energy of the edge states (-0.26 V). One can see that the high intensity spots are at the lattice sites of the two edges (A1 or B6). All these features are consistent with the predictions (66–68).

We simulated a 6-ZGNR shown in the right part of Fig. 6.13a. The simulated row-averaged DOS, as shown in Fig. 6.13c, manifest states (marked by the dashed line) at -0.24 V whose intensity is maximum at the two edges and decays in the interior. The decay trend is plotted in Fig. 6.13d, which can be fitted by an exponential function with a decay constant of 1.6 $a_0$. The simulated real-space DOS map at -0.24 V shown in the right part of Fig. 6.13b further reveals the spatial localization of these states along the two edges. In our measurements, we do not observe any splitting of the edge states arising from magnetic effects (68); we neglect such effects in our simulations. Overall the simulation nicely reproduces the characteristics of the experimentally-resolved edge states. The single-sublattice behavior of the zero-energy (relative to the Dirac point) edge states of the ZGNRs can be understood by considering the appropriate boundary conditions in $k.p$ perturbation theory (69). On a single zigzag edge, the terminal honeycomb sites all belong to a single (B) sublattice. The wavefunction should vanish on the A sites exterior to the ribbon that are adjacent to these terminal B sites. Furthermore, for the zero energy states, the $k.p$ wavefunction should vanish on all interior A sites as well (69). The 558 line defect and single vacancy structures we have constructed further illustrate this principle.

For comparison, we constructed a system not expected to show such single-sublattice behavior: an artificial 7-AGNR as shown in the left part of Fig. 6.13e. Row-averaged DOS acquired at the defined rows are displayed in Fig. 6.13g. In clear contrast to the ZGNRs, the AGNR does not have any edge states near the Dirac point energy. Fig. 6.13f shows a DOS map at -0.24 V, which reveals that the states are distributed in the entire ribbon. We simulated the artificial 7-AGNR (right part of Fig. 6.13f (the calculated quasiparticle band structure is shown in Supplementary Materials). As shown in Fig. 6.13g, the simulated DOS exhibit comparable features as the experimental ones - a dip at -0.24 V and the absence of any localized edge state. In conclusion, both experimental observations and theoretical simulations confirm that the artificial AGNR does not have the edge states.

Now we turn our focus to line defect. A widely-studied topological line defect consists of repeating paired pentagons fused with octagons (70), named as 558 line defect. Recently, Lahiri et al. (71) reported on experimental observation of this type of line defect when growing graphene on a Ni substrate. The DFT calculation predicted the existence of metallic states that are localized at the line defect and such lines are expected to provide a metal-
Figure 6.14: (a) STM image (up part) and simulation model (down part) of an artificial 558 defect line. (b) STS map acquired at -0.23 V (up part) and simulated LDOS map at -0.21 V (right part). (c) Experimental column-averaged dI/dV spectra and calculated LDOS. (d) Calculated LDOS intensity (up panel) measured LDOS amplitude (down panel) at -0.22 V as a function of column index. Scale bars: 5 nm.
lic channel (71). An artificial structure analogous to 558 line defect has been constructed by shifting the molecules of the two neighboring columns in a way that four neighboring molecules were pushed together while the molecules in the upper and lower rows were separated apart. This process was repeated along the entire column. Fig. 6.14a up panel shows a section of the artificial defect line (the full length is four times larger), where a structural model of the 558 line defect is sketched. We define the center of the two columns as the defect line (DL) and different columns as ALn, BLn, ARn, BRn, respectively, where A(B) stands for a sublattice, L(R) for a column to the left (right) of the DL and n the distance index. Column-averaged DOS acquired at the defined columns are plotted in Fig. 6.14c. One can see that the V-shape dip disappears at the DL. Interestingly, the spectra at BL1 and BR1 show a peak at -0.23 V, which indicates that there are new states emerging at Dirac point at the B sublattice. In contrast, the new states are absent at A sublattice. Fig. 6.14d down panel displays the measured DOS amplitude at -0.23 V as a function of column index, manifesting (1) the new states are absent in the DL or the A sublattice, (2) in the B sublattice, the amplitude decays away from the DL. In Fig. 6.14b up panel, a DOS map acquired at -0.23 V reveals that the new states are confined within four lattice sites in the vicinity of the DL. We simulated the artificial 558 line defect (Fig. 6.14a down panel). The calculated column-averaged LDOS spectra is shown in Fig. 6.14c. Similar as the experimental observation, at -0.21 V, a new state emerges at B sublattice only but are absent at A sublattice. As shown in Fig. 6.14d up panel, away from the DL, the amplitudes of the new state at B sublattice decays exponentially. A DOS map of -0.21 V is shown in Fig. 6.14b down panel, which reproduces the localization characteristics observed in the experiment. These results confirm that the 558 line defect exhibit states near Dirac point along the line and in particular, the state is only present at the sublattice which borders the line defect.

6.4.2 0-Dimensional defects

We now present the results of two basic types of intrinsic point defects - single vacancies and Stone-Wales defects. It was shown theoretically that vacancies induce quasi-localized states at the Fermi level if the intrinsic electronic structure shows electron-hole symmetry (72). Experimentally, STM revealed that single vacancies on a graphite surface can introduce a sharp electronic resonance at the Fermi energy around each single graphite vacancy (73; 74). Artificial vacancy structures were created by inserting an extra coronene molecule at the center of three adjacent coronene molecules in a regular array. As shown in Fig. 6.15a, the extra molecule occupies a lattice site in the honeycomb structure. Since this molecule provides a repulsive potential, this site becomes a barrier for the 2D surface electrons, so this structure can be viewed as an artificial missing-atom defect. The local DOS at the sites that are in specific distance to the defect are denoted as An or Bn, where A(B) stands for A(B) sublattice (Note the vacancy is at sublattice B) and n the distance index (n=1 defines the three nearest sites). As shown in the left panel of Fig. 6.15b, the two sublattices exhibit very different characters: a measured peak (-0.23 V) appears near Dirac point only at A sites, while the B sites show a V-shape dip. In accordance with the breaking of the A-B sublattice
symmetry, the measured dI/dV map (upper panel of Fig. 6.15c) taken at -0.23 V shows that
the new state appears at the A sublattice sites only. The dI/dV map further reveals that the
new state is localized around the vacancy. To resolve the spatial localization quantitatively,
we averaged the spectra of the equivalent sites of An and Bn in all radial directions originated
from the defect. The results are summarized in Fig. 6.15d. One can find two interesting
features: (1) the intensity of the new states at A sites decays exponentially, which can be
fitted by an exponential function with a decay constant of 1.2 $a_0$; (2) the intensity is low
at B sites and increases slightly away from the vacancy. The symmetry-breaking becomes
insignificant beyond tenth lattice site. All these features are explained and quantitatively
reproduced by theory as seen in Fig. 6.15.

Stone-Wales (S-W) defect represents the simplest example of topological defects, in which
four hexagons are transformed into two pentagons and two heptagons by rotating a C-C
bond by $90^\circ$ (75–78). We study an artificial S-W defect made by re-locating four adjacent
coronene molecules that are in orthogonal positions as shown in Fig. 6.15e. We found that
this structure also exhibits a pronounced peak near Dirac point (-0.23 V), as revealed by the
site-specific dI/dV acquired at one of the pentagons as shown in the upper panel of Fig. 6.15f.
For reference, the dI/dV acquired at the black dot in Fig. 6.15e is also plotted, showing a
normal V-shape dip. Fig. 6.15g (left panel) is a -0.23 V dI/dV map which manifests that
the new states are spatially localized at the two pentagons. We observe an emergence of
localized states near the Dirac point. We simulated the artificial single vacancy and the SW
defects and have obtained good agreement with experiment (Fig. 6.15). The defect state
decays exponentially with a decay length of 2.0 $a_0$. The discrepancies of the simulation and
the experiment presumably are caused by the simplicity of the muffin-tin type potential
used in the simulation. The error caused by this approximation affects the energies of the
defect states but not their topological properties, as can be seen by the dI/dV simulations
(Fig. 6.15c,g).
Figure 6.15: (a-d). An artificial single vacancy. (a) STM image. (b) Experimental (left) and simulated (right) $dI/dV$ spectra acquired at sites A1 and B1 (marked as the black and red dots in (a)). (c) Experimental (up) and simulated (down) $dI/dV$ maps at -0.23 V. (d) Experimental (solid) and simulated (empty) -0.23 V LDOS amplitude as a function of sites. (e-g). An artificial Stone-Wales defect. (e) STM image. (f) Experimental (left) and simulated (right) $dI/dV$ spectra (Red: acquired with the tip located at the red dot marked in (e); Black: from the un-modified sites). (g) Experimental (left) and simulated (right) $dI/dV$ maps at -0.23 V. Scale bars: 5 nm.
Chapter 7

Graphene superlattices

In Chapter 6, we examined the consequences of subjecting a 2-dimensional electron gas (2DEG) to a long wavelength external potential. Here, we consider the effect of external potentials on graphene. It turns out that quasiparticles in graphene superlattices (GSs) behave very differently from quasiparticles in 2DEG superlattices. For simplicity, we will focus on one-dimensional (1D) GSs, where the external potential is periodic in one direction and constant in the perpendicular direction.

7.1 Graphene under an external periodic scalar potential

The unusual transport properties of graphene superlattices have been intensively studied in the literature. The superposition effect \( (79; 80) \) is a consequence of the changes in the low-energy band structure brought about by the presence of an external scalar potential \( (81) \). In a one-dimensional GS, the charge carriers are supercollimated along the periodic direction, with almost no dispersion in the perpendicular direction (hereafter called the constant direction) \( (79; 82–84) \).

There are several ways of realizing external periodic scalar potentials on graphene. These structures can be constructed by the positioning of adatoms and ad-molecules via scanning tunnelling electron microscopy \( (85) \) or self assembly \( (86–88) \), or by applying a local top-gate voltage to graphene \( (89–91) \). Another approach is to place graphene on a substrate with nanometer scale periodicity. Several choices of substrates are Ru and Ir surfaces \( (92) \), hexagonal boron nitride \( (93) \), silicon carbide \( (94) \), and nanotrenches \( (95) \). These experiments have observed modification of the band structure caused by the periodic potential.

In this section, through analytical calculations, we show that when a 1D periodic scalar potential is applied to graphene: (i) the group velocity of the massless Dirac fermions is anisotropically renormalized in momentum space in an unexpected fashion, and (ii) new massless Dirac fermions are generated at the supercell Brillouin zone boundaries \( (81) \).

We consider a situation where the spatial variation of the external periodic potential is much slower than the inter-carbon distance so that inter-valley scattering between the \( K \) and \( K' \) points in the Brillouin zone may be neglected \( (96) \). We shall further limit our discussion
7.1. GRAPHENE UNDER AN EXTERNAL PERIODIC SCALAR POTENTIAL

Figure 7.1: (a) Graphene superlattice. The periodic direction is the $x$ direction. (b) A schematic drawing of the band structure near the Dirac point. Due to the presence of the superlattice, the Dirac cone is distorted. An optical transition between the first valence band and first conduction band is indicated by the arrow.
7.1. **Graphene under an external periodic scalar potential**

To the low-energy electronic states of graphene which have wavevector $k + K$ close to the $K$ point.

There are two carbon atoms per unit cell in graphene, forming two different sublattices. Hence the eigenstate of charge carriers in graphene can be represented by a two component basis vector. The Hamiltonian of the low-energy quasiparticles in pristine graphene in a pseudospin basis, $\begin{pmatrix} 1 \\ 0 \end{pmatrix} e^{ik.r}$ and $\begin{pmatrix} 0 \\ 1 \end{pmatrix} e^{ik.r}$, which symbolically represent Bloch sums of $\pi$-orbitals with wavevector $k$ on the sublattices A and B, is given by (Chapter 2)

$$H_0 = \hbar v_0 (-i\sigma_x \partial_x - i\sigma_y \partial_y)$$

(7.1)

where $v_0$ is the band velocity and the $\sigma$ matrices are the Pauli matrices. The eigenstates and the energy eigenvalues are given by

$$\psi_{s,k}^0(r) = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ se^{i\theta_k} \end{pmatrix} e^{ik.r}$$

(7.2)

and

$$E_s^0(k) = s\hbar v_0 k$$

(7.3)

respectively, where $s = \pm1$ is the band index and $\theta_k$ is the angle between $k$ and the $+k_x$ direction.

We now assume that a 1D scalar potential $V(x)$, periodic along the $x$ direction with period $L$, is applied to graphene (Fig. 7.1). The Hamiltonian is then

$$H = H_0 + V(x)$$

(7.4)

Next we perform a similarity transform, $H' = U_1^\dagger H U_1$, using the unitary matrix

$$U_1 = \frac{1}{\sqrt{2}} \begin{pmatrix} e^{-i\alpha(x)/2} & -e^{i\alpha(x)/2} \\ e^{-i\alpha(x)/2} & e^{i\alpha(x)/2} \end{pmatrix}$$

(7.5)

where $\alpha(x)$ is given by

$$\alpha(x) = 2 \int_0^x V(x')dx'/\hbar v_0$$

(7.6)

Here, without losing generality, we shall assume that an appropriate constant has been subtracted from $V(x)$ and that $V(x)$ has been shifted along the x-direction so that the averages of both $V(x)$ and $\alpha(x)$ are zero. The transformed Hamiltonian $H'$ takes the form

$$H' = \hbar v_0 \begin{pmatrix} -i\partial_x & -e^{i\alpha(x)} \partial_y \\ e^{-i\alpha(x)} \partial_y & i\partial_x \end{pmatrix}$$

(7.7)

We are interested in the low-energy quasiparticle states whose wavevector $k = p + G_m/2$ where $G_m = m(2\pi/L)\hat{x}$ is a reciprocal vector) is such that $|p| \ll G$ In this case, we could
treat the terms containing $\partial_y$ in Eq. 7.7 as a perturbation. Also, to a good approximation, $H'$ may be reduced to a 2x2 matrix using the following two states as basis functions

\[ (1\ 0) e^{i(p+G_m/2).r} \text{ and } (0\ 1) e^{i(p-G_m/2).r} \] (7.8)

Here, we should note that the spinors $(1\ 0)'$ and $(0\ 1)'$ now have a different meaning from $(1\ 0)$ and $(0\ 1)$. In order to calculate these matrix elements, we perform a Fourier $e^{i\alpha(x)}$.

\[ e^{i\alpha(x)} = \sum_{l=-\infty}^{\infty} f_l[V] e^{ilGx} \] (7.9)

where the Fourier components $f_l[V]$'s are determined by the periodic potential $V(x)$. We should note that in general $|f_l| < 1$ which can directly be deduced from Eq. 7.9. The physics simplifies when the external potential $V(x)$ is an even function and hence $\alpha(x)$ in Eq. 7.6 is an odd function. If we take the complex conjugate of Eq. 7.9 and change $x$ to $-x$, it is evident that $f_l[V]$'s are real. General cases other than even potentials are discussed in (81). For states with wavevector $k$ very close to $G_m/2$, the 2x2 matrix $M$ whose elements are calculated from the Hamiltonian $H'$ with the basis given by Eq. 7.8 can be written as

\[ M = \hbar v_0 (p_x \sigma_z + f_m p_y \sigma_y) + \hbar v_0 mG/2 \] (7.10)

After performing yet another similarity transform $M' = U_2^T M U_2$

\[ U_2 = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 & 1 \\ -1 & 1 \end{pmatrix} \] (7.11)

we obtain the final result:

\[ M' = \hbar v_0 (p_x \sigma_x + f_m p_y \sigma_y) + \hbar v_0 mG/2 \] (7.12)

The energy eigenvalue of the matrix $M'$ is

\[ E_s(p) = s \hbar v_0 \sqrt{p_x^2 + |f_m|^2 p_y^2 + \hbar^2 v_0 mG/2} \] (7.13)

which holds in general and not only for cases where the potential $V(x)$ is even (81). The only difference between this energy spectrum and $E^0_s$, other than a constant energy term, is that the group velocity of quasiparticles moving along the y-direction has been changed from $v_0$ to $|f_m|v_0$. Thus, the electronic states near $k = G_m/2$ are also those of massless Dirac fermions but having a group velocity varying anisotropically depending on the propagation direction. The group velocity along the x-direction is unchanged independent of the potential.
Moreover, the group velocity along the y-direction is always lower than $v_0$ regardless of the form or magnitude of the periodic potential $V(x)$ as schematically depicted in Fig. 7.1a.

We have thus shown that other than the original Dirac points, new massless Dirac fermions are generated around the supercell Brillouin zone boundaries, i.e., the case with non-zero $m$ values in Eq. 7.13. It has also been shown that these newly generated massless Dirac points are the only available states in a certain energy window if graphene is subjected to a 2D repulsive periodic scalar potential having triangular symmetry (81).

## 7.2 Optical dichroism of graphene superlattices

In this section, we extend our study of Dirac fermions in periodic potentials by considering the optical absorption spectrum of one-dimensional GSs. While the unusual transport properties of GSs can be understood as a consequence of the highly anisotropic low energy band structure, the optical properties of GSs are the result of an interplay between van Hove singularities in the band structure and anisotropic matrix element effects. In pristine graphene, the low-frequency constant absorbance (97; 98) of $A_0 = \pi \alpha \approx 2.3\%$ is a signature of massless Dirac fermions. We have found that this behavior is changed considerably in GSs. At low frequencies (99) and weak external potentials, the absorbance of GS is enhanced for polarizations along the periodic direction of the GS, and is suppressed for polarizations along the constant direction. At higher frequencies, the absorption spectrum is dominated by features due to van Hove singularities for polarizations in the constant direction, while the traces of the van Hove singularities are completely absent for polarizations in the periodic direction. There are many examples of optical dichroism - different absorbance for different linear polarizations of light - in condensed matter systems (100) In the context of our paper, optical dichroism provides an experimental signature of the GS discernible above isotropic backgrounds.

We first derive an analytic result to illustrate how the absorbance at low frequencies changes as a function of polarization and modulation strength before presenting numerical calculations which cover a larger range of frequencies.

We assume that the frequencies are high enough so that the effects of Drude scattering can be ignored. For graphene on a SiO$_2$/Si substrate at 45 K, intraband scattering effects are typically negligible at frequencies higher than 100 meV (101), and we confine our attention to frequencies in this range. We work with the two-component Dirac Hamiltonian. This is justified because the length scale of the external modulating potential is usually larger than 10 nm, much larger than the intercarbon distance, so that intervalley scattering may be ignored. Furthermore, trigonal warping effects do not play a significant role here - only the first few supercell Brillouin zones (SBZs) are important at low frequencies, and these SBZs come from a region of the original Brillouin zone with virtually no trigonal warping. We consider light at normal incidence, as in Fig.7.1b. The external potential is constant along the y-direction and periodic along the x-direction. We assume that the graphene is undoped and the effect of plasmons (102) can be neglected. Using the effective Hamiltonian of this
system (Eq. 7.12), for an even potential function $V(x)$, the eigenstates can be written in a simple representation in the basis of Eq. 7.12

$$\psi_{s,k}(r) = \frac{1}{\sqrt{2}} \left( \frac{1}{s} e^{i\phi_p} \right) e^{ikr}$$  \hspace{1cm} (7.14)

where $\phi_p = \tan^{-1} \left( \frac{|f_k|}{k} \right)$. With the eigenenergies (Eq. 7.13), the absorbance due to vertical interband transitions (Fig. 7.1b) can be calculated using the standard formula

$$A(\omega) \propto \frac{1}{\omega} \sum_{c,v} \int_{SBZ} |M|^2 \delta(E_c - E_v - \hbar\omega)$$  \hspace{1cm} (7.15)

where $E_c$ and $E_v$ refer to the energies of the conduction and valance bands respectively. For simplicity, we restrict our attention to transitions between the first valence and first conduction band.

$$|M_x|^2 = |\langle \psi_c | \sigma_x | \psi_v \rangle|^2 = \sin^2 \phi_p$$  \hspace{1cm} (7.16)

is the matrix element when the incident light is $x$-polarized, and

$$|M_y|^2 = |\langle \psi_c | \sigma_y | \psi_v \rangle|^2 = (\text{Im} f)^2 + (\text{Re} f)^2 \cos^2 \phi_p$$  \hspace{1cm} (7.17)

is the matrix element when the incident light is $y$-polarized. We have used the minimal coupling scheme for the Dirac Hamiltonian, along with the radiation gauge. $\sigma_x$ and $\sigma_y$ in the above equations are expressed in the basis of Eq. 7.1, not in the new basis of Eq. 7.12. The absorbance for the $x$ and $y$ polarizations can be written in terms of the absorbance of pristine graphene $A_0$ as

$$A_x = \frac{A_0}{f}$$

$$A_y = A_0 f$$  \hspace{1cm} (7.18)

The absorbance of light polarized in the periodic direction is enhanced due to the increased density of states in the deformed-cone band structure of Eq. 7.13. On the other hand, for the light polarized in the constant direction, a reduction in $|M_y|^2$ (Eq. 7.17) overcomes the increase in density of states to result in a net decrease in absorbance.

The preferential absorbance in one direction will result in a change in polarization direction of the transmitted and reflected light. The polarization axis would be rotated towards the $x$ axis upon passing through or reflecting off a sheet of graphene. Because of the high transparency of graphene, this rotation will be small for small modulating potentials and will increase as the modulating potential is increased.

It should be noted that the above analysis is only accurate when either $k_y$ is small or when $V(x)$ is small in comparison with $\hbar v_0 / L$, where $L$ is the spatial period of a GS, because the wavefunctions (Eq. 7.14) are exact in these limits, as long as $f \neq 0$. Eq. 7.18 describes the
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low energy limit of the absorbance exactly even for finite , because the integral in Eq. 7.15 only involves small \( k_y \) in this limit. For higher energies, the Eqs. 7.18 become more accurate as \( V(x) \) becomes smaller.

We have performed numerical calculations based on diagonalizing the Hamiltonian in Eq. 7.4, and using the resulting eigenvalues and eigenfunctions in evaluating the absorption spectrum, Eq. 7.15. In this calculation the length of one period of the superlattice was chosen to be \( L = 15 \) nm. The external potential used was one of the square-wave type: \( V(x) = V_0 \text{sgn}(\sin(2\pi x/L)) \). In Fig. 7.2 we show the absorbance for the frequency range 0.075 eV to 0.4 eV, for both polarizations, and for a range of potential heights \( V_0 \). For this potential shape, the condition \( f = 0 \) corresponds to \( V_0 = 0.59 \) eV. We used an arbitrary broadening of 5 meV in the numerical evaluation of Eq. 7.15.

The dashed lines in Fig. 7.2 indicate the prediction for the low frequency absorbance based on the analytic result developed above (i.e. using Eq. 7.18). The figures show good agreement in the frequency absorbance between the analytic result and the numerical calculations.

The presence of the dip in the absorbance of light polarized in the periodic direction is explained in Fig. 7.3, which shows the contribution to the total absorbance of different interband transitions. The dip occurs at 0.29 eV, the energy difference between the 1\textsuperscript{st} conduction band and the 1\textsuperscript{st} valence band at the SBZ boundary. Above this energy, the contribution due to this transition diminishes, while the contribution due to the 1\textsuperscript{st} valence band - 2\textsuperscript{nd} conduction band transition and the 2\textsuperscript{nd} valence band - 1\textsuperscript{st} conduction band transition becomes important.

The absorbance of the light polarized in the constant direction shows the opposite behaviour of a peak located at 0.25 eV to 0.28 eV. This peak arises from a transition between saddle point van Hove singularities of the 1\textsuperscript{st} valence band and the 1\textsuperscript{st} conduction band (indicated by the arrow in Fig.7.4a). The reason van Hove singularities affect light polarized in the constant direction but not the periodic direction is the highly anisotropic oscillator strengths (Figs. 7.4bc). There is significant oscillator strength in the vicinity of the van Hove singularities for the former but not the latter. The frequency of this peak decreases with increasing \( V_0 \), eventually affecting the absorbance at low frequency, as can be seen from Fig. 7.2b. As with light polarized in the periodic direction, the analytic result of Eq. 7.18 becomes more accurate as \( V_0 \) is decreased.

It is useful to contrast this behaviour to the optical absorption spectrum of a 2DEG in a Kronig-Penney type potential within the dipole approximation. For a strictly one-dimensional potential, the absorbance is dominated by van Hove singularities for polarization along the periodic direction while the absorbance is zero for polarization along the constant direction. The optical matrix element \( \langle \psi_i | A_y p_y | \psi_j \rangle \) for polarization in the constant direction vanishes because the wavefunctions are eigenstates of \( p_y \), the momentum in the constant direction. Compared to the 2DEG case, the periodic and constant directions follow different trends in the GS because of the chiral nature of electrons in graphene.
Figure 7.2: The absorbance of a graphene superlattice, expressed in units of the absorbance in pristine graphene, $A_0$. (a) the absorbance for light polarized in the periodic direction and (b) the absorbance for light polarized in the constant direction. The dashed lines indicate the predictions for the absorbance at low frequencies according to our simple analytic result Eq. 7.18.
Figure 7.3: The absorbance of a graphene superlattice, in units of the absorbance in pristine graphene, for light polarized in the periodic direction (a) and for light polarized in the constant direction (b). The contribution from the individual interband transitions is shown. For example v1→c2 indicates the contribution coming from transition from the 1st valence band to the 2nd conduction band, which is the same as that coming from the 2nd valence band to the 1st conduction band. In these figures, the external potential has magnitude \( V_0 = 280 \) meV.
Figure 7.4: (a) The band structure of the graphene superlattice, with an external potential of magnitude $V_0 = 280$ meV. The position of saddle point van Hove singularities are marked by arrows. (b) The oscillator strength of the 1st valence band - 1st conduction band transition in a graphene superlattice with the same external potential, for polarization in the periodic direction. The range of $k_x$ shown is the entire span of the supercell Brillouin zone in the $k_x$ direction. Positions of the $\Gamma$ and $M$ points, and van Hove singularities are marked in red. (c) The oscillator strength of the 1st valence band - 1st conduction band transition in a graphene superlattice with the same external potential, for polarization in the constant direction.
7.3 Graphene under an external periodic vector potential

The electrostatic graphene superlattices (EGSs) studied in the previous sections have very different properties than magnetic graphene superlattices (MGSs), which are spatially varying vector potential profiles on graphene. Nevertheless, we demonstrate here that systems of 1D electric and magnetic profiles in graphene are closely related via a transformation of the Dirac equation. This transformation simplifies the analysis of and bring new physical insights into the electronic behavior of field-induced nanoscopic and mesoscopic structures in graphene. We have made use of this transformation, together with known results for the 1D EGS, to solve for the electronic structure of a 1D MGS in the case when the average magnetic flux vanishes, \( \langle B \rangle = 0 \). In this case, the group velocity of the charge carriers is isotropically reduced as the strength of the magnetic field is increased (Fig. 7.5), a surprising result given that the external periodic magnetic field is anisotropic. The band structure for the case where \( \langle B \rangle \neq 0 \) is calculated using both exact numerical and perturbative methods. It is found that, in the limit of large \( \langle B \rangle \), the bandwidth of the Landau bands decreases as \( \frac{1}{\sqrt{B}} \), unlike the analogous system of a 2DEG in a periodic magnetic field where the bandwidth approaches a constant as \( \langle B \rangle \) is increased (103). We have also shown through our transformation, the relationship between the transmission probability through electrostatic and magnetic barriers in graphene.

7.3.1 The transformation

We focus on low energy excitations near the \( K \) point, and neglect Zeeman interactions and intrinsic spin-orbit couplings, which have respective energy scales of \( \mu_B B \approx 5 \times 10^{-4} \text{ eV} \) (at \( B = 5 \text{ T} \)) and \( 1.7 \times 10^{-5} \text{ eV} \) (3). In contrast, the energy scale of an MGS is \( \hbar v_0/\sqrt{\hbar c/(eB)} \), which is at least two orders of magnitude larger than either of these two energy scales when \( 0.005 \text{T} \leq B \leq 10 \text{T} \).

We first treat the general case of electric and magnetic modulations where the field strengths vary in the \( x \) direction and are constant in the \( y \) direction. The electronic states of the system can be described by the Dirac equation:

\[
i\hbar \frac{d\psi}{dt} = \{v_0 \vec{\sigma} \cdot (-i\hbar \nabla + \frac{e}{c} \vec{A}(x)) + V(x)\} \psi
\]

(7.19)

where the wavefunction \( \psi \) is a two component spinor function, \( A(x) \) and \( V(x) \) are vector and scalar potentials, respectively, which do not necessarily have to be periodic. We shall use the Landau gauge, and the magnetic field is taken to be perpendicular to the graphene layer. Writing the wavefunction as \( \psi(x, y; t) = e^{i k_y y} e^{-iEt/\hbar} \varphi(x) \), the Dirac equation becomes:

\[
E \varphi(x) = \{-i\hbar v_0 \sigma_x \partial_x + v_0 \sigma_y (\hbar k_y + \frac{e}{c} A(x)) + V(x)\} \varphi(x)
\]

(7.20)

Relating the electric and magnetic graphene systems is a two step process: first, we show that a complex Lorentz boost changes the Dirac equation with real magnetic (electric) fields into a Dirac equation with imaginary electric (magnetic) fields. Next, we perform an analytic
Figure 7.5: (a) Structure of pristine graphene. (b) Band dispersion of pristine graphene near the point. (c) Structure of a 1D MGS, with the darker regions denoting a magnetic field pointing along the $-z$ direction and lighter regions denoting a magnetic field pointing along the $+z$ direction. This structure repeats itself in both the $x$ and $y$ directions. (d) The isotropically renormalized band structure of a 1D MGS of the kind shown in (c).
continuation to relate the Dirac equation with imaginary electric (magnetic) fields to a Dirac equation with real electric (magnetic fields).

Starting from Eq. 7.20, we multiply throughout by $\sigma_y$ and make the unitary transformation $\psi'(x) = U \psi(x)$ with

$$U = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 & 1 \\ 1 & -1 \end{pmatrix} \quad (7.21)$$

Also we transform Eq. 7.20 to new energy and momentum variables:

$$E = -i \hbar v_0 k_y'$$

$$k_y = \frac{iE'}{\hbar v_0} \quad (7.22)$$

The result of these operations is to transform the original Dirac equation Eq. 7.20 into

$$E' \psi'(x) = \left\{ -i \hbar v_0 \sigma_x \partial_x + \sigma_y (\hbar v_0 k_y' - iV(x)) + \frac{eV_0}{c} iA(x) \right\} \psi'(x) \quad (7.23)$$

This transformation interchanges the role of the $x$-dependent electric and magnetic fields. The transformation is actually a complex Lorentz boost with an imaginary rapidity: if a general Lorentz boost that mixes a spatial coordinate with time is represented by

$$\begin{pmatrix} t' \\ y' \end{pmatrix} = \begin{pmatrix} \cosh \theta & -\sinh \theta \\ -\sinh \theta & \cosh \theta \end{pmatrix} \begin{pmatrix} t \\ y \end{pmatrix} \quad (7.24)$$

then Eqs. 7.22 correspond to a Lorentz boost with rapidity $\theta = \frac{i\pi}{2}$, followed by a mirror reflection $y' = -y$. It should be noted that other choices for the rapidity are possible, these will result in the mixing of the electric and magnetic profiles (104).

Now, an analytic continuation is used to relate the solutions of the Dirac equation with imaginary fields (Eq. 7.23) to a Dirac equation with real fields. Suppose that a Dirac equation with real electric potentials (for simplicity let us assume no magnetic fields, although this can be easily added in) has been solved and the eigenenergies are known to be given by an equation $g(E, k_y, V) = 0$, where $E, k_y, V$ are all real. We argue that the Dirac equation with an imaginary electric potential of the same shape (i.e., writing $V = V_0 w(x)$ with $V_0$ now an imaginary number) has imaginary eigenenergies given by the same equation, but now with $E, k_y, V$ all imaginary.

The above argument is true since the eigenfunctions $\psi(x, y; k_y, V)$ of the original Dirac equation with real electric potential can be analytically continued to imaginary values of $k_y, V_0$. This is because the Dirac operator in Eq. 7.19 consists of differentiation and matrix operations, which act on the eigenfunction in the same way regardless of where $k_y$ and $V_0$ lie in the complex plane. Therefore, the analytic continuation of the eigenfunctions to imaginary $k_y$ and $V_0$ values are eigenfunctions of the Dirac equation with $k_y$ and $V_0$ imaginary. This implies that the imaginary eigenenergies are given by the same equation $g(E, k_y, V) = 0$, with $E, k_y, V$ imaginary.
Type of system & Dirac equation and wavefunction \\
--- & --- \\
Real magnetic (RM) & $E \varphi^{RM}(x) = \left\{-i\hbar v_0 \sigma_x \partial_x + v_0 \sigma_y (\hbar k_y + \frac{e}{c} A(x))\right\} \varphi^{RM}(x)$ \\
$E, k_y, A$ real & $\psi^{RM}(x,y,t) = \varphi^{RM}(x) e^{i k_y y} e^{-i E t / \hbar}$ \\
Imaginary electric (IE) & $E \varphi^{IE}(x) = \left\{-i\hbar v_0 \sigma_x \partial_x + v_0 \sigma_y \hbar k_y + V(x)\right\} \varphi^{IE}(x)$ \\
$E, k_y, V$ imaginary & $\psi^{IE}(x,y,t) = \varphi^{IE}(x) e^{i k_y y} e^{-i E t / \hbar}$ \\
Real electric (RE) & $E \varphi^{RE}(x) = \left\{-i\hbar v_0 \sigma_x \partial_x + v_0 \sigma_y \hbar k_y + V(x)\right\} \varphi^{RE}(x)$ \\
$E, k_y, V$ real & $\psi^{RE}(x,y,t) = \varphi^{RE}(x) e^{i k_y y} e^{-i E t / \hbar}$ \\

Table 7.1: Various stages of the transformation taking a magnetic structure to an electrostatic structure on graphene. The form of the wavefunctions and the corresponding Dirac equation are shown for each stage. To obtain $\varphi^{IE}$ from $\varphi^{RE}$, perform an analytic continuation in $E, k_y, V_0$. To obtain $\varphi^{RM}$ from $\varphi^{IE}$, replace the imaginary $V$ with real $A$ and make a unitary transformation as described in Eqs. 7.21, 7.22.

The system with imaginary electric fields is solved if the system with real electric fields is solved. And, by the above results, the system with real magnetic fields is solved if the system with imaginary electric fields is solved. We can thus relate the solutions of graphene under electric field profiles to those of graphene under magnetic field profiles. The two steps of this transformation are summarized in Table 7.1. This procedure is quite general as it is applicable to inhomogeneous fields of 1D profiles of both finite and infinite extent, as well as to states with finite lifetimes (imaginary eigenenergies).

An important consideration in applying this method in practice is the fixing of boundary conditions. It is possible that after the analytic continuation, a wavefunction displays unphysical behaviour at the boundaries. Such solutions must be excluded and domain of validity of the energy dispersion relations restricted accordingly. These considerations however do not appear in the examples considered in the next section.

It should be noted that the imaginary values of energy and momentum in the intermediate stages of the transformation bear no physical significance - they are purely mathematical crutches and should not be interpreted as indicators of finite lifetimes or confined states.

### 7.3.2 Magnetic graphene superlattices

We now apply this method to the system of a $\langle B \rangle = 0$ 1D MGS, where $V(x) = 0$ and $A_y = A(x)$ in the Landau gauge is periodic and assumed to average to zero in one unit cell of the superlattice. Both $k_x$ and $k_y$ are good quantum numbers. The transformed system is that of a 1D EGS, (i.e. $A'(x) = 0$ and $V'(x)$ is periodic and imaginary) with $\langle E' \rangle = 0$. We are interested in the imaginary ($E', k_y'$) solutions of the latter system, which we find by making use of the real ($E, k_y$) solutions of the 1D EGS with $V(x)$ real. The 1D EGS with a real potential has been solved in the previous sections, and the energies to lowest order in $k$ are given by Eq. 7.13.

Using the imaginary energy eigenvalues of the 1D EGS with $k_y$ and $V_0$ imaginary via
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Eq. 7.22, the energy bands in the MGS are found, to lowest order in \( k \), to be:

\[
E(k_x, k_y) = \pm \frac{\hbar v_0 \sqrt{k_x^2 + k_y^2}}{\int_{\text{unit cell}} \exp(-2 \int_0^{eA(x')} dx'/\hbar c) dx} \tag{7.25}
\]

Remarkably, the dispersion relation near the \( K \) point is isotropic, and there is no energy gap between the valence and conduction bands, regardless of the magnetic field strength. Furthermore, the group velocity near the \( K \) point is always renormalized to be less than \( v_0 \), and it decreases monotonically as the strength of the magnetic field is increased. The group velocity is monotonically reduced because the derivative of the denominator of Eq. 7.25 with respect to \( A_0 \) (writing \( A(x) = A_0 h(x) \)) is non-negative, due to the assumption that \( \alpha(x) \) (Eq. 7.6) averages to zero over one unit cell.

These results are also applicable to states around a single valley in \( k \)-space in an effective gauge field treatment of corrugated graphene (105), where a gauge field is introduced with opposite signs at each valley in order to simulate the effects of ripples in graphene. For example, applying Eq. 7.25 to the effective magnetic field generated by the corrugation in Fig. 2 of (105) gives a velocity renomalization that is in good agreement with the results in that figure. It should be noted that the regime considered in corrugated graphene is different from that considered here: ripples of reasonable size tend to reduce the velocity to almost zero, whereas MGSs do not.

Interestingly, carbon nanotubes under a constant, transverse magnetic field (106; 107) can be considered approximately to be a special case of Eq. 7.25 here, for the specific value of \( k_x = 0 \) and \( k_x = \pm 2\pi/(3L) \), corresponding to metallic and semiconducting carbon nanotubes with circumference \( L \), respectively. In addition to corroborating the predictions of velocity reduction in metallic carbon nanotubes and gap reduction in semiconducting nanotubes in (106; 107), Eq. 7.25 provides a description of velocities in arbitrary directions as well.

For concreteness, let us focus on the specific cases of two magnetic Kronig-Penney superlattices: i) \( A(x) = A_0 \text{sgn}(\sin(2\pi x/l_0)) \) which corresponds to a periodic 1D \( \delta \)-function magnetic field of alternating signs, and ii) a periodic piecewise constant magnetic field of alternating sign: \( B(x) = \frac{4A_0}{l_0} \text{sgn}(2\pi x/l_0) \). These magnetic superlattices have period \( l_0 \).

Evaluating Eq. 7.25 for the \( \delta \)-function magnetic field Kronig-Penney superlattice gives

\[
E(k_x, k_y) = \hbar v_0 \sqrt{k_x^2 + k_y^2} \text{sech}(eA_0l_0/(4\hbar c)) \tag{7.26}
\]

This result, together with a similar formula for the piecewise constant magnetic field, is shown in Fig. 7.6, and the results are identical to those of numerical solutions to the Dirac equation, also shown in Fig. 7.6, obtained using a plane-wave basis (60 plane waves were used in the expansion of the wavefunction). In contrast, the analogous system of a 2DEG in a magnetic superlattice (108; 109) has an anisotropic energy spectrum near the \( k = 0 \) point, which is expected considering the anisotropic nature of the superlattice potential.

One use of the transformation presented above is in identifying features of the EGS with features of the MGS. A simple application of Eq. 7.22, shows that the isotropic velocity
Figure 7.6: The ratio of the Fermi velocity $v_g$ in the presence of a periodic magnetic field to the Fermi velocity $v_0$ of pristine graphene near the $K$ point is plotted as a function of the vector potential magnitude $A_p$, for both a $\delta$-function magnetic field and a piecewise constant magnetic field Kronig-Penney superlattices. The analytical (lines) and numerical (symbols) results are in agreement. $l_0$ is the superlattice period and $B = \hbar c/(el_0^2)$ is the characteristic magnetic field strength associated with $l_0$. The group velocity is identical in all directions. For $l_0 = 100$ nm and a magnetic field of 1.8 T, $v_0$ is renormalized by a factor of 1/2.
reduction in an MGS can be predicted from the constant (superlattice potential independent) group velocity in the $k_x$ direction in an EGS. On an intuitive level, one can think of isotropic velocity reduction as the magnetic analogue of Klein tunnelling, with both features arising from the Dirac nature (pseudospin physics) of the quasiparticles.

For the case of an 1D MGS where $\langle B \rangle \neq 0$, we may write the vector potential in the Landau gauge as $A_y(x) = A_p(x) + B_0x$, where $A_p(x)$ gives the periodic magnetic modulation and $B_0$ is the uniform background magnetic field. In this system, $k_x$ is no longer a good quantum number; we are interested in the $E$ vs. $k_y$ dispersion relation. Let us first consider the low $B_0$ semiclassical limit. We start with the energy spectrum of the 1D $\langle B \rangle = 0$ MGS found above and treat the background magnetic field as a perturbation. In this limit, the quasiparticles circulate along constant energy contours in momentum space. The quantization of these orbits leads to the formation of Landau levels. The Landau levels for pristine graphene in a uniform perpendicular magnetic field $B$ is $E_n = \text{sgn}(n)\sqrt{2e\hbar v_0^2 |n| B}$ where $n \in \mathbb{Z}$ (Chapt. 2). Since the introduction of a periodic modulating magnetic field leaves the conic energy spectrum intact and only renormalizes the group velocity, the Landau levels for the 1D $\langle B \rangle = 0$ MGS is given by the same formula as the Landau levels for pristine graphene, except for the renormalization of $v_0$. This is in agreement with the numerical solution of Eq. 7.19 in the low $B_0$ regime (Fig. 7.7a). Since we have not assumed any range of values of $A_p$, this regime includes (at least when all the magnetic fields are small) the experimentally convenient situation of constructing the superlattice using strips of ferromagnetic material arranged in a regular spacing, which corresponds to $B_0 \approx B_p$, where $B_p$ is the periodic magnetic field. A measurement of the Landau level spacings would be one means to directly verify the isotropic velocity reduction discussed above.

The higher Landau levels are not flat (as a function of $k_y$), but show broadening in the form of oscillations as a function of $k_y$ (Fig. 7.7a). This behavior can be understood by considering $k_y$ as the parameter that controls the position of the wavefunctions along the $x$ direction under the gauge we adopted (3). Changing $k_y$ changes the local environment felt by the wavefunction, and thus changes its energy. From this argument, the period of oscillations is $l_0/l_B^2$, where $l_0$ is the size of the unit cell and $l_B = \sqrt{\hbar c/(e\langle B \rangle)}$ is the magnetic length associated with the average background magnetic field strength. As can be seen in Fig. 7.8a, this period agrees with the results of numerical calculations (by diagonalizing the Hamiltonian in a plane-wave basis).

The lower-energy Landau levels are not affected because these states (Fig. 7.8b) have few nodes, and the distance between nodes is typically much larger than $l_0$ (in the limit of low $B$), so that those states effectively perform an "averaging" of the local magnetic field and their energies are not greatly affected by their position. On the other hand, higher-energy states might have a node-to-node distance comparable to $l_0$. It would then be possible to position such a state so that the peaks coincide with regions of high (or low) magnetic field, and thus affect the magnetic field strength "felt" by those states and hence their energies. This criterion for the onset of energy bands has been verified for the states in Fig. 7.7a.

As the strength of the background magnetic field is increased from zero, the bandwidth of the Landau level energy bands first increases monotonically from zero (not shown for the
7.3. GRAPHENE UNDER AN EXTERNAL PERIODIC VECTOR POTENTIAL

Figure 7.7: (a) The first 10 energy bands of a piecewise constant magnetic field pattern with magnetic field strength \( B_p / B_l = 1.4 \), immersed in a uniform background field of \( B_0 / B_l = 0.6 \), where \( B_l = \hbar c / (e l_0^2) \). (b) The bandwidths \( \Delta E \) of the first three bands, as a function of \( B_0 \), of a piecewise constant magnetic field with magnetic field strength \( B_p / B_l = 2 \), immersed in a uniform background field of strength \( B_0 \).
Figure 7.8: (a) A comparison of the period of oscillation of the Landau bands in $k_y$ as obtained from the numerical calculations with the analytic prediction that this period is equal to $l_0/l_B^2$, where $l_0$ is the size of the unit cell, and $l_B = \sqrt{\hbar c/(e\langle B \rangle)}$. (b) Three representative wavefunctions for the system with $\langle B \rangle \neq 0$. The same parameters are used as in Fig. 7.7a: a piecewise constant magnetic field pattern with magnetic field strength $B_p/B_t = 1.4$, immersed in a uniform background field of $B_0/B_t = 0.6$, where $B_t = \hbar c/(e l_0^2)$. The index $n$ in this figure refers to the $n^{th}$ Landau level as defined in Fig. 7.7a.
range of magnetic fields plotted in Fig. 7.7b), and then fluctuates, similar to the analogous system of a 2DEG in a 1D periodic magnetic modulation \(^\text{(103)}\). However, in the limit of large \(B/B_l\) with \(B_l\) defined as \(\hbar c/(e\ell_0)^2\), (i.e. in the limit the magnetic length becomes significantly smaller than the period \(\ell_0\) of the superlattice), a qualitative difference between the two systems arises, in that the bandwidth approaches a constant in the case of the 2DEG, while it vanishes in the limit of large magnetic fields in the case of graphene. To obtain a physical understanding of this limit, we take the unperturbed system to be graphene in a uniform background magnetic field, while the perturbation \(\Delta H = (ev_0/c)A_p(x)\sigma_y\) is the periodic modulating magnetic field. Using the zeroth order wavefunctions

\[
\varphi_n(x) = (|n-1\rangle/|n\rangle)
\]

the first order correction to the energy is found to be

\[
\Delta E = \sum_G \frac{ev_0}{c} A_G e^{-iGk_B l_0^2} (n-1)|e^{iGk_B(a+a^\dagger)}/\sqrt{2}|n\rangle
\approx \sum_G \frac{ev_0}{c} A_G e^{-iGk_B l_0^2} iG_B \sqrt{n/2}
\]

in the limit \(l_B/l_0 \ll 1\). Here, \(n\) is the Landau level index, \(|n\rangle\) the quantum harmonic oscillator eigenstates, \(a^\dagger\) and \(a\) the creation and annihilation operators, and \(A_G\) are the Fourier components of the periodic vector potential \(A_p(x)\). The bandwidth falls off as \(1/\sqrt{B}\) as \(B \to \infty\), and the bandwidths of successive bands increases as \(\sqrt{n}\). The numerical results of our calculations shown in Fig. 7.7 are in good agreement with these asymptotic results.

This peculiarity can be understood as a consequence of the linear dispersion relation of graphene and the fact that the energy levels of graphene in a uniform magnetic field grow as \(\sqrt{B}\) rather than linearly in \(B\) as in the case for a 2DEG. In the limit of large \(B\), the wavefunctions are well localized, and one can consider the difference in energies between two states of the same Landau band localized at different positions in a saw-tooth type of MGS vector potential. Each of these two states is in a local environment of an (approximately) uniform magnetic field with strengths \(B+B_1\) and \(B+B_2\) \((B_1, B_2 \ll B)\), and so the difference in their energies is approximately \(\sqrt{2n(B+B_1)} - \sqrt{2n(B+B_2)} \approx (B_1-B_2)\sqrt{n/(2B)}\), which is in agreement with the result from perturbation theory.

### 7.3.3 Finite magnetic barriers

Now, we consider the transmission of electrons through finite magnetic barriers in graphene. We relate the transmission probability through single magnetic barriers in graphene to the transmission probability though electrostatic barriers in graphene. This is done using the complex Lorentz transformation developed in previous sections. For simplicity, we consider here square electrostatic or vector potential barriers, as shown in Fig. 7.9.

The transmission coefficient for a vector potential barrier such as in Fig. 7.9a is given by Eq. 6 of \((110)\). This equation gives the transmission coefficient \(t\) in terms of the angles
Figure 7.9: Vector potential (a) and electrostatic (b) barriers in graphene, and the transmission probabilities through the vector potential (c) and electrostatic (d) barriers, as a function of incident angle.
of propagation inside ($\theta$) and outside ($\phi$) the vector potential barrier. The variables $\theta$ and $\phi$ are easily expressed as functions of $k_y, E, A_0$ (the transverse momentum, the energy of the propagating wave, and the vector potential height, respectively). Once this is done, the transmission coefficient $t(k_y, E, A_0)$ will be a function of the vector potential amplitude, the transverse momentum, and the energy. To relate this to the electrostatic barrier, Eq. 7.22 as well as $V' = i(v_0e/c)A_0$ are used. The last equation $V' = i(v_0e/c)A_0$ comes from a comparison of Eqs. 7.20 and 7.23.

If these substitutions are made in $t(k_y, E, A_0)$, an expression $t'(k'_y, E', V')$ is obtained, which is the transmission coefficient through an electrostatic barrier in graphene. It can be checked with (111) that this is indeed the correct expression for the transmission coefficient. Fig. 7.9c,d show representative transmission probabilities (as a function of the incident angle $\phi$) for both types of barriers.

7.3.4 Disorder

An experimental realization of a magnetic (or electrostatic) superlattice will not be perfectly periodic due to variations in both the period of the superlattice and the strength of the local magnetic fields. We have simulated such randomness using a supercell approach, where we have solved for the bandstructure of a simulation cell consisting of 30 smaller unit cells. Each unit cell has a period which follows a normal distribution with a randomness parameter $r = \sigma/\mu$, where $\sigma$ and $\mu$ are the standard deviation and mean of the normal distribution, respectively. Similarly, the strength of the magnetic field in each unit cell is also normally distributed. We have performed calculations using values of $r$ up to 0.1. An ensemble average of 20 independent random magnetic configurations was taken in the calculations. A broadening of 0.2, in the energy units of Fig. 7.10, was used in the density of states calculation.

The density of states (after ensemble averaging) is shown in Fig. 7.10. In pristine graphene, the density of states is linear in the energy from the Dirac point energy. In the presence of a perfect magnetic superlattice, the density of states is still linear, but increased from the pristine graphene case, due to the velocity reduction effect described above. Fig. 7.10 shows that this observation remains true even if the magnetic superlattice is disordered. The density of states for the disordered magnetic superlattice is approximately linear, with nearly the same slope as that of the perfect magnetic superlattice. This provides evidence that the presence of low level disorder should not change significantly the magnitude of the velocity reduction effect described above.

At low energies ($E < 0.2$ in Fig. 7.10), which correspond to approximately 1/10th of the bandwidth of a perfect superlattice in the limit of no magnetic field, the density of states of the disordered magnetic superlattice is not linear, but instead approaches a finite value as the energy decreases to zero. For a superlattice of period $L = 100$ nm, this energy range is $E < 2$ meV.
Figure 7.10: The ensemble-averaged density of states of a random magnetic superlattice, with randomness parameters $r = 0.05$ and $r = 0.1$ (see text), compared with a perfectly periodic superlattice ($r = 0$). The density of states of pristine graphene is also shown ($r = 0$, $B$ field off). The velocity reduction factor that corresponds to this change in density of states is $v/v_0 = 0.58$. The energy range in this plot is 1/2 the bandwidth of a empty-lattice graphene superlattice.
7.4 Bilayer graphene superlattices

We now consider the effect of periodically modulated electrostatic potentials on bilayer graphene. It has been shown (112; 113) that the effect of a series of δ-function potentials on bilayer graphene is to either open an energy gap or to generate new zero energy modes in the electronic structure, depending on the strength and periodicity of the δ-functions. In this section, we demonstrate that this behavior is robust against charge screening effects, as well as being present for a wide range of shapes of the external potential. We show that, unlike the case of monolayer graphene, a strong external potential is not needed for the generation of new Dirac points. In fact, these new zero-energy modes can be generated at arbitrarily weak periodic external potentials. The transition from this new semi-metallic state with Dirac points to the previously found semiconducting state (113) occurs at a critical value of the external potential. Finally, further increase of the external potential closes the band gap and a semi-metallic band-structure is restored, albeit with Dirac points in different locations in reciprocal space than before.

We note that similar physics arises in twisted graphene bilayers (114; 115) where a new pair of Dirac points is generated at each valley. Unlike the case considered in this paper, the Dirac points in the twisted graphene bilayers are topologically protected against breaking of the inter-layer symmetry, as a result of the low energy Hamiltonian belonging to a different universality class than the one considered in this paper (115).

We begin our analysis of bilayer graphene superlattices (with the two layers in the Bernal stacking) with a two-band continuum model for the lowest energy electron and hole states in a bilayer system, given by the Hamiltonian

\[
H = -\frac{1}{2m} \begin{pmatrix} 0 & (p_x - ip_y)^2 \\ (p_x + ip_y)^2 & 0 \end{pmatrix} + V(x) \tag{7.29}
\]

where \(\vec{p} = -i\hbar \vec{\nabla}, \) \(m = \gamma_1/(2v_0^2)\) is the effective mass in bilayer graphene, \(\gamma_1\) is the interlayer tunneling amplitude and \(v_0\) is the Fermi velocity of graphene. The one-dimensional external periodic potential \(V(x)\) is assumed to average to zero and has periodicity large compared to the inter-atomic distance. The potential on both graphene layers is taken to be the same at a given point \((x, y)\). (Later, we discuss the case where this symmetry is broken). Analyzing the effect of \(V(x)\) on the low energy carriers in this manner is justified if its period is much larger than the lattice constant \(a = 0.246\text{nm}\) in graphene (Fig. 7.11). Inter-valley scattering is then negligible and Eq. 7.29 describes a single, independent valley. In this initial analysis, for simplicity, the external periodic potential is taken to be of the form \(V(x) = V_{ext}\sin(2\pi x/L)\). Use of a two-band model in the form of Eq. 7.29 neglects the effect of trigonal warping. As will be seen from our tight-binding calculations below, such effects do not change the nature of our results.

We have performed a numerical diagonalization of Eq. 7.29, using as a basis the eigen-
states of pristine bilayer graphene (i.e., with $V(x) = 0$ in Eq. 7.29):

$$|\psi(0)\rangle(\vec{k}) = \frac{1}{\sqrt{2}} \left( \pm e^{2i\theta_k} \right) e^{i\vec{k} \cdot \vec{r}}$$

(7.30)

where $\vec{k}$ and $\vec{r}$ are two-dimensional vectors and $\tan \theta_k = k_y/k_x$ and the + and - signs refer to the conduction and valence bands, respectively. At low values of $V^{\text{ext}}$, a pair of zero energy modes are generated along the $k_y = 0$ line (Fig. 7.12) symmetrically at different values of $k_x$ depending on the strength of $V^{\text{ext}}$. At these values of $V^{\text{ext}}$, these are the only zero energy modes, as seen in Fig. 7.12a. The band structure close to these zero energy modes is Dirac-cone like, with an $k$-space anisotropy that is dependent on the value of $V^{\text{ext}}$. As $V^{\text{ext}}$ is increased from zero, this pair of zero energy modes are initially generated near the $\vec{k} = 0$ point of the superlattice Brillouin zone (i.e., the $K$ or $K'$ point of the original Brillouin zone of bilayer graphene), and they move in opposite directions away from the $\vec{k} = 0$ point as $V^{\text{ext}}$ is increased (Fig. 7.12b-d) but always keeping $k_y = 0$. At a certain value of $V^{\text{ext}}$, both zero energy modes reach the edge of the supercell Brillouin zone. Further increase in opens a direct band gap at $(k_x = \pm \pi/L, k_y = 0)$, where $L$ is the superlattice period (Fig. 7.12e). In general, the critical value at which the gap opens depends on $L$ in the following manner:

$$V^* = CE_L$$

(7.31)
where $E_L - \hbar^2/(2mL^2)$ and $C$ is a numerical constant determined by the shape of the external potential, as we show later (see Eq. ??).

The band gap opened at $V^{\text{ext}} = V^*$ continues to increase with increasing $V$ until it reaches a maximum value. Thereafter, the band gap decreases with increasing $V$ and it eventually vanishes. The closing of the band gap corresponds to generation of new Dirac points along the $k_x = 0$ line, as illustrated by Figs. 7.13c-e. At the higher value of $V^{\text{ext}}$, the system remains in a semi-metallic state as $V^{\text{ext}}$ increases because some of the new Dirac points persist with increasing $V^{\text{ext}}$ (Fig. 7.13e).

The generation of new Dirac points in the limit of low $V^{\text{ext}}$ (Fig. 7.12) can be understood as a consequence of the specific pseudospin structure of the eigenstates of bilayer graphene. Within second order perturbation theory (the first order term vanishes), the effect of the superlattice potential is to cause a shift of the conduction band by an amount

$$E^{(2)}_c(\vec{k}) = \sum_{\vec{G},i} \frac{|\Delta V^{c,i}_{\vec{k},\vec{k}+\vec{G}}|^2}{E^{(0)}_c(\vec{k}) - E^{(0)}_i(\vec{k} + \vec{G})}$$  \hspace{1cm} (7.32)

where $E^{(0)}_i(\vec{k})$ are the band energies of the conduction or valence band of pristine bilayer graphene, $\vec{G}$ are the superlattice reciprocal lattice vectors, and $V^{c,i}_{\vec{k},\vec{k}+\vec{G}}$ is a matrix element of $V(x)$ using the unperturbed states $|\psi^{(0)}(\vec{k})\rangle$ and $|\psi^{(0)}(\vec{k} + \vec{G})\rangle$ given by Eq. 7.30. Consider $E^{(2)}_c(\vec{k})$ for a point on the $k_y = 0$ line. Due to the spinor structure of the electronic wavefunctions (the pseudospin factor in Eq. 7.30), the matrix element in Eq. 7.32 is non-zero only between those states from the same band (i.e. $V^{c,v}_{\vec{k},\vec{k}+\vec{G}} = 0$, but $V^{c,c}_{\vec{k},\vec{k}+\vec{G}} \neq 0$). From Eq. 7.30, it follows that the energy of the conduction band is reduced and the energy of the valence band increased, leading to their overlap and the formation of Dirac points. When $V^{\text{ext}} > V^*$, the lowest conduction subband and the highest valence subband of the superlattice are shifted to the extent that the former lies below the latter in energy and a band gap is opened as a result.

While the two-band continuum Hamiltonian (Eq. 7.29) provides a simple explanation for the generation of new Dirac points at low values of $V^{\text{ext}}$ and the opening of the band gap at $V^{\text{ext}} = V^*$ and above, it is not sufficient for more quantitative predictions due to the neglect of the effects of the higher bands and of electronic screening. To address this issue, we have performed a tight binding calculation, which takes into account the effect of the four bands arising from the $p_z$ orbitals of the four carbon atoms in the Bernal bilayer unit cell. We have included the charge transfer and screening effects via a self-consistent Hartree potential. The tight-binding Hamiltonian is of the form

$$H = \sum_{\langle i,j \rangle} t_{ij}(c_i^\dagger c_j + c_j^\dagger c_i) + \sum_i (V^{\text{ext}}_i + V^{\text{Hartree}}_i)c_i^\dagger c_i$$  \hspace{1cm} (7.33)

where $c_i, c_i^\dagger$ are the electron annihilation and creation operators for site $i$, $t_{ij}$ the hopping parameter between sites $i$ and $j$, $V^{\text{ext}}_i$ and $V^{\text{Hartree}}_i$ the external and Hartree potentials,
Figure 7.12: The band structure of bilayer graphene superlattice for the case of \( V(x) = V_{\text{ext}} \sin(2\pi x/L) \) with \( V_{\text{ext}} < V^* \) (see text) calculated within the two-band continuum model. A pair of Dirac points is shown in (a), where the lowest valence and conduction bands are plotted in the first Brillouin zone of the superlattice and the magnitude of the external potential is \( V_{\text{ext}} = 5E_L \) where \( E_L = \frac{\hbar^2}{2m^*} \). (b)-(e) show cuts of the band structure along the \( k_y = 0 \) plane, for various magnitudes of the external potential \( V_{\text{ext}} \). The band structure of pristine bilayer graphene is shown in (b).
Figure 7.13: The band structure of bilayer graphene superlattice for selected $V^{\text{ext}} > V^*$ calculated for $V(x) = V^{\text{ext}} \sin(2\pi x/L)$ within the two-band continuum model. Two pairs of new Dirac points are shown in (a), where the lowest valence and conduction bands are plotted in the first Brillouin zone of the superlattice and the magnitude of the external potential is $V^{\text{ext}} = 70E_L$ where $E_L = \frac{k^2}{2mL}$. (b)-(e) show cuts of the band structure along the $k_x = 0$ plane, for various magnitudes of the external potential $V^{\text{ext}}$. 
respectively. For the intra-layer nearest-neighbor hopping amplitude, the value \( \gamma_0 = t_{AB} = 2.6 \text{ eV} \) is used, while the interlayer tunneling amplitudes \( \gamma_1 = t_{\tilde{A}B} \) and \( \gamma_3 = t_{A\tilde{B}} \) are set at 0.34 eV and 0.3 eV respectively. Here \( A \) and \( B \) (\( \tilde{A} \) and \( \tilde{B} \)) denote the two atoms in the unit cell on the lower (upper) layer. See (116) for a definition of the notation and a justification of these numerical values. A sinusoidal form \( V_{\text{ext}}^i = V_{\text{ext}} \sin(2\pi x_i/L) \) is used for the external potential, where \( x_i \) denotes the \( x \) coordinate of the \( i \)th atomic site. For results discussed below, we have used a value of \( L = 15 \text{ nm} \). The Hartree potential is given by

\[
V_i^{\text{Hartree}} = \sum_{\alpha l} \int_{A_\alpha} d^2r \frac{e n_{\alpha l}}{|\vec{r} - \vec{r}_i|} \tag{7.34}
\]

where the index \( \alpha \) refers to a specific unit cell of a single graphene layer, \( l = 1 \) or 2 is the layer index, \( A_\alpha \) is the area of the unit cell (which is the same for all \( \alpha \)), and is the net charge density (induced by the superlattice potential) in this particular unit cell that is approximated to be uniform within the cell. The excess electron density depends on the wavefunctions as

\[
n_{\alpha l} A_\alpha = 2 \sum_{i \in A_{\alpha l} \text{ occ.}} \sum_{j \in \text{occ.}} \int_{BZ} \frac{d^2k}{4\pi^2} |\psi_{i,j}(\vec{k})|^2 - N_{\alpha l} \tag{7.35}
\]

Here, \( \psi_{i,j}(\vec{k}) \) is the amplitude of an eigenstate of Eq. 7.33 at site \( i \), of the energy band \( j \), and with wavevector \( \vec{k} \). The sum over \( i \) in Eq. 7.35 runs over both sites in the single-layer unit cell \( A_{\alpha l} \) and the sum over \( j \) runs over all occupied energy bands. \( N_{\alpha l} \) is the number of \( \pi \) electrons in a unit cell of a single layer, i.e., \( N_{\alpha l} = 2 \). The factor of 2 in Eq. 7.35 arises from spin degeneracy. We solve Eqs. 7.33-7.35 self-consistently to find the tight-binding energy bands in the presence of the superlattice potential. The energy eigenvalues are converged to within 1 meV with respect to the \( k \)-grid sampling for the two-dimensional momentum space integration.

The results of the self-consistent tight-binding calculation show that the basic picture presented above for the two-band continuum Hamiltonian remains unchanged, except for some quantitative changes. We plot the band gap as a function of \( V_{\text{ext}} \) in Fig. 7.14 for a superlattice period of \( L = 15 \text{ nm} \). There is no band gap for low \( V_{\text{ext}} \), up to a value of \( V^* \approx 0.8 \text{ eV} \). (With \( L = 15 \text{ nm} \), the value for \( E_L \) is 5 meV.) An examination of the low energy band structure (not shown in Fig. 7.14) shows that for this range of \( V_{\text{ext}} \), a pair of new Dirac points is generated for each \( K \) and \( K' \) valley, consistent with the calculations based on the two-band continuum Hamiltonian. Similarly, the opening of a band gap for intermediate \( V_{\text{ext}} \) (0.8eV \( \leq \) \( V_{\text{ext}} \) \( \leq \) 4eV in Fig. 7.14) and its subsequent closure at higher \( V_{\text{ext}} \) are features in agreement with the two-band continuum Hamiltonian.

We have found that the effect of Hartree-level screening can be well described by a dielectric constant. For \( L = 15 \text{ nm} \), the in-plane dielectric constant (describing screening
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Figure 7.14: The band gap of bilayer graphene superlattice as a function of the magnitude of the external potential \( V(x) = V^{\text{ext}} \sin(2\pi x/L) \) obtained from self-consistent tight binding calculations for \( L = 15 \) nm. The results for systems with and without a bias potential between the two graphene layers are plotted in red dashed and blue solid lines, respectively.
along the graphene layers rather than between)

\[ \varepsilon = \frac{V^{\text{ext}}}{V^{\text{ext}} + V^{\text{Hartree}}} \approx 11 \]  

is approximately constant for the range of \( V^{\text{ext}} \) shown in Fig. 7.14. Screening is the main reason for the increase in the value of \( V^{\text{ext*}} \) from the two-band model value of 45 meV to the self-consistent tight-binding value of 0.8 eV. For comparison, the value of \( V^{\text{ext*}} \) obtained in a tight-binding calculation without self-consistent Hartree level screening was 70 meV.

It is of experimental interest to determine the robustness of our results to small changes in the form of \( V^{\text{ext}} \). We consider the effect of a small bias voltage \( V^{\text{bias}} = 10 \) meV between the two graphene layers:

\[ V^{\text{ext}}_i = V^{\text{ext}} \sin \left( \frac{2\pi x_i}{L} \right) \pm \frac{V^{\text{bias}}}{2} \]  

where the \( \pm \) sign refers to the two different layers. Our self-consistent tight-binding results with Eqs. 7.34, 7.35 appropriately reflecting the different charges on the two layers (Fig. 7.14) indicate that apart from the opening of a small band gap at \( V^{\text{ext}} < 1 \) eV and at \( V^{\text{ext}} > 3.9 \) eV, the results are very similar to the case where \( V^{\text{bias}} = 0 \). The opening of the small band gap is consistent with the behavior of bilayer graphene (without any lateral external periodic potential) under the influence of a transverse electric field (117), where a gap opening occurs because of the symmetry breaking effect of the applied electric field.

The generation of new Dirac points and the opening of the band gap for \( V^{\text{ext}} > V^{\text{ext*}} \) is likewise not a consequence of any special symmetries of the external periodic potential. Even though the potential \( V^{\text{ext}}_i = V^{\text{ext}} \sin(2\pi x_i/L) \) has the special symmetries \( V(x) = -V(-x) \) and \( V(L/2 + x) = V(L/2 - x) \), we find that the breaking of either of these symmetries does not affect our results significantly. Using a potential of the form

\[ V^{\text{ext}}_i = V^{\text{ext}} \sin(2\pi x_i/L) + V^{\text{SB}}_i \]  

where \( a \) is a variable length less than \( L/4 \) and \( V^{\text{SB}}_i < V^{\text{ext}}/10 \) is the magnitude of the symmetry breaking potential, we obtain from tight-binding calculations that the two main features, 1) Dirac point generation for \( V^{\text{ext}} < V^{\text{ext*}} \) and 2) opening of a band gap for \( V^{\text{ext}} > V^{\text{ext*}} \) persist. We thus expect these to be salient features of a large class of superlattice potentials on Bernal bilayer graphene.

A modification of the perturbation theory argument following Eq. 7.32 can be used to show that deviations from uniformity of \( V(x) \) along the \( y \) direction do not affect the presence of Dirac points for \( V < V^* \), as long as these deviations have a length scale much larger than \( L \). Consider a sinusoidal superlattice potential with a perturbation of the form
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$\Delta V \sin(2\pi x/L)f(y)$. By analogy with Eq. 7.32, this results in a second order change to the energy of the conduction band of

$$E_c^{(2)}(\vec{k}) = \sum_{\vec{p},i} \frac{|\Delta V_{c,i}^{c,v}|^2}{E_c^{(0)}(\vec{k}) - E_i^{(0)}(\vec{k} + \vec{p})}$$

(7.39)

The sum is over all wavevectors $\vec{p}$ which are linear combinations of $\vec{G}_0 = (2\pi/L)\hat{x}$ the superlattice reciprocal lattice vector, and $p_y\hat{y}$, the various Fourier components of $f(y)$. If $f(y)$ is slowly varying compared to the superlattice potential, then the relevant wavevectors in the Fourier transform of $f(y)$ are $p_y \ll 2\pi/L$. This implies that $V_{c,v}^{c,v}_{\vec{k},\vec{k} + \vec{p}} \approx 0$ and $V_{c,c}^{c,c}_{\vec{k},\vec{k} + \vec{p}} \neq 0$ in Eq. 7.39. $E_c^{(2)}(\vec{k})$ is therefore negative and $E_v^{(2)}(\vec{k})$ positive, as before, leading to the formation of Dirac points.

Thus far, we have considered a fixed $L$, and investigated the effect of varying $V^{\text{ext}}$. We have found that a combined variation of both $L$ as well as $V^{\text{ext}}$ does not introduce any new features other than those already discussed. From the point of view of the 2-band Hamiltonian (Eq. 7.29), this system is invariant under the scaling

$$L \rightarrow \alpha L$$

$$V \rightarrow \frac{V}{\alpha^2}$$

(7.40)

and can be well described by the single parameter $VL^2$. This is different from the case of monolayer graphene superlattices, where the analogous parameter is $VL$. In the bilayer system, the effect of increasing $L$ is to decrease the value of $V^*$ and the value of the band gap. At the self-consistent Hartree level, this observation is still true, although the scaling behavior of Eq. 7.40 no longer holds exactly. In spite of the breakdown of exact scaling behavior, we find that the general trend of decreasing bandgap and $V^{\text{ext}}$ with increasing $L$ remains true.
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