ULTRAFAST LASER-INDUCED KINETICS IN TWO-DIMENSIONAL MATERIALS

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In this dissertation, we theorize the fundamentals of an ultrafast and ultrastrong optical field interacting with graphene and graphene-like nanocrystals as a prototype of two-dimensional class of materials. Graphene exhibits dramatically different characteristics from both insulators and metals. Field-induced, Zener-type electron transfer from the valence band to the conduction band is deeply irreversible (nonadiabatic) in graphene. Correspondingly, an ultrashort electronic current can be induced on a femtosecond timescale. The ultrafast optically-induced current and charge transfer in graphene may provide a fundamental basis for detection and calibration of ultrashort intense laser pulses and are promising for petahertz information processing.

We further studied and proposed techniques to manifest the topological properties of graphene using the few-cycle circularly polarized pulse. Our findings hold application in spectroscopy, imaging, laser technology, transmitting and processing information with speed and accuracy far beyond the capabilities of conventional optics and electronics.

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ULTRAFAST LASER-INDUCED KINETICS IN TWO-DIMENSIONAL MATERIALS

by

HAMED KOOCHAKI KELARDEH

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ULTRAFAST LASER-INDUCED KINETICS IN TWO-DIMENSIONAL MATERIALS

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May 2017
DEDICATED

Dedicated to my family
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1 CHAPTER ONE: INTRODUCTION

In this dissertation and during my PhD duration, I theoretically studied the dynamics of electrons in graphene and other two-dimensional nanocrystals under the interaction of ultrafast and strong electric field of the optical pulses. My study is, in fact, the emergence of two important and growing branches of fundamental science: ultrafast optics and two-dimensional graphene-like nanomaterials.

Ultrafast optics or more specifically, attosecond physics, is the science and technology developed to study the quantum mechanical dynamics of electrons, both collective and individual, on atomic and molecular scales and in high-density mesoscopic systems. Until recently, a wide range of electron dynamics such as collective motion and coherence phenomena, carrier transport and screening effects, population dynamics and charge transfer have been elusive because their speed has exceeded the resolution of the fastest metrologies available. Recent advances in attosecond metrology and generation of ultrashort optical pulses with just a few oscillations of electric field in the optical regime has provided real-time access to the motion of electrons on atomic and sub-atomic scales and opened a unique possibility for the coherent control of electron dynamics at sub-femtosecond time scale. The tools and techniques of attosecond science enable detailed investigations of a relatively unexplored regime of nondestructive strong-field effects. Such extremely nonlinear effects can be utilized to steer electron motion with precisely controlled optical fields and switch electric currents at a rate that is far beyond the capabilities of conventional electronics.

Graphene has indeed redefined the limits of what a material can do. Graphene and related materials pertain to a larger family that encompasses all kinds of two-dimensional materials,
from boron nitride lattices to transition-metal dichalcogenides (MoS$_2$, WS$_2$, ...), to the silicon analog of graphene, silicene, a recently discovered zero-gap semiconductor. What most interesting about graphene is the unconventional physics behind its electronic properties. Indeed, the electron motion in graphene is governed by the Dirac equation with vanishing effective mass. This has been shown to give rise to various unprecedented electronic phenomena, such as Ballistic transport, half-integer quantum Hall effect, Klein tunneling due to the absence of backscattering, and Berry’s phase.

Interestingly, low-energy excitations in two-dimensional graphene, known as massless Dirac fermions, also develop at the surface of topological insulators (such as BiSe$_2$, Bi$_2$Te$_3$, etc.), which are bulk insulators. Topological insulators thus display connections with graphene and exhibit other features such as spin-momentum locking that offer different and groundbreaking perspectives for spintronics. Therefore, we believe that our research and exploration of the ultrafast dynamics of electrons in graphene and graphene-like materials under the illumination of few-cycle optical field should prove useful to a growing community of scientists and hold promises for future technology especially high-speed memories, ultrafast imaging and petahertz signal processing (about 1000 time faster than current processors).

The dissertation starts with an introduction to the electronic structures and basic physical, electronics and topological concepts of graphene in chapter 2 and then proceeds to the findings of our theoretical studies. In chapter 3, we study the physics of graphene in strong stationary electric fields. We report on the properties of the so-called Wannier-Stark states of monolayer graphene and calculate the coupling operator for states in the conduction and valence band and analyze the anticrossing points and the corresponding anticrossing gaps of graphene. The results
of this chapter are predominantly used in description of the interaction of strong optical field with electrons in graphene, that is the subject of chapter 4.

In chapter 5 we employ the theory described in chapter 4 and extend it to other two – dimensional graphene-like materials with Buckled structure, namely, Silicene and Germanine. These are novel materials which find numerous potential applications, in particular to build ultrafast Field effect transistor technologies (FET). Chapter 6 and 7 associate with the manifestation of topological properties of graphene. Taking circularly polarized field, we proposed a self-referenced interferometry in reciprocal space which reveals the geometric phase of the Dirac points known as Berry phase. The interference fringes of electron population carry rich information of the electronic spectra and interband dynamics near the Dirac points and the chirality of the pulse. This dynamics of the interferogram formation provides an attosecond “clock” that may be useful in studying the fastest electron dynamics in nature, which takes place in graphene subjected to strong optical fields. The predicted attosecond kinetics in the reciprocal space can be visualized using Time- and Angle-resolved Photoemission Spectroscopy (Tr-ARPES).
CHAPTER TWO: ELECTRONIC PROPERTIES OF GRAPHENE AND GRAPHENE-LIKE MATERIALS

The objective of this chapter is to describe the physical and electronic structure of graphene. The electronic band structure of graphene is of primary importance because (i) it is the starting point for the understanding of graphene’s solid-state properties and analysis of graphene devices and (ii) it is also crucial for the understanding and derivation of the band structure of buckled graphene-like materials such as silicene and germanine which I study in detail successively.

2.1 Introduction

Graphene is a planar allotrope of carbon where all the carbon atoms form covalent bonds in a single plane. In graphene, the 2s orbital interacts with the 2px and 2py orbitals to form three sp2 hybrid orbitals with the electron arrangement shown in Figure 2.1. The sp2 interactions result in three bonds called σ-bonds, which are the strongest types of covalent bonds. The σ-bonds have the electrons localized along the plane connecting carbon atoms and are responsible for the great strength and mechanical properties of graphene. The 2pz electrons form covalent bonds called π-bonds, where the electron cloud is distributed normal to the plane connecting carbon atoms. The 2pz electrons are weakly bound to the nuclei and, hence, are relatively delocalized. These delocalized electrons are the ones responsible for the electronic properties of graphene and graphene-like materials.
Figure 2.1 valence orbitals of graphene: three σ orbitals and π orbital perpendicular to the sheet.

The σ bonds in the carbon hexagonal structure strongly connect the carbon atoms and are responsible for the binding energy and the structural properties of the graphene sheet. The π bonds are perpendicular to the surface of the sheet. The corresponding bonding and antibonding σ bonds are separated by a large energy gap of \( \sim 12 \text{ eV} \); consequently, the σ bonds are safely neglected for prediction of the electronic properties of graphene around the Fermi energy.

In the following Section, we use the tight-binding approximation to treat the covalent π energy bands for graphene, which determines the solid-state properties of graphene, reflecting the strong coupling of the in-plane carbon atoms.

2.2 **Crystal Structure of Monolayer Graphene**

The fundamental crystal structure that constitutes the basis for \( sp^2 \) carbon nano-structures is graphene, which is a two-dimensional (2D) planar structure based on a unit cell containing two carbon atoms A and B, as shown by the unit vectors \( a_1 \) and \( a_2 \) in Figure 2.2(a). The carbon atoms in monolayer graphene are located at the vertices of the hexagons where \( a_1 \) and \( a_2 \) are basis vectors.
Figure 2.2 Direct space and reciprocal space configuration of graphene
(a) The basis vectors $\mathbf{a}_1$ and $\mathbf{a}_2$ in the hexagonal network of graphene. This network is a triangular Bravais lattice with a two-atom basis: A (full dots) and B (empty dots). (b) The reciprocal lattice points corresponding to the triangular Bravais lattice (full dots) as well as the associated basis vectors $\mathbf{b}_1$ and $\mathbf{b}_2$. The unit cell/Brillouin zone are shown shaded gray in (a) and (b) respectively. Highly symmetric points labeled with $\Gamma$, $K_+$, $K_-$, and $M$ are marked.

As shown in Figure 2.2(a), Carbon atoms in a graphene plane are located at the vertices of a hexagonal lattice. This graphene network can be regarded as a triangular Bravais lattice with two atoms per unit cell (A and B) and basis vectors $(\mathbf{a}_1, \mathbf{a}_2)$:

$$\mathbf{a}_1 = a \begin{pmatrix} \sqrt{3}/2 \\ 1/2 \end{pmatrix}, \quad \mathbf{a}_2 = a \begin{pmatrix} \sqrt{3}/2 \\ -1/2 \end{pmatrix}$$

with $a = |\mathbf{a}_1| = |\mathbf{a}_2| = \sqrt{3} a_{c-c}$ where $a_{c-c} = 1.42 \text{ Å}$ is the carbon–carbon distance in graphene.

From this figure, we see that three atoms of the opposite type surround each A- or B-type atom. Using the condition $\mathbf{a}_i \cdot \mathbf{b}_j = 2\pi \delta_{ij}$, the reciprocal lattice vectors $(\mathbf{b}_1, \mathbf{b}_2)$ can be obtained,

$$\mathbf{b}_1 = b \begin{pmatrix} 1/2 \\ \sqrt{3}/2 \end{pmatrix}, \quad \mathbf{b}_2 = b \begin{pmatrix} 1/2 \\ -\sqrt{3}/2 \end{pmatrix}$$

with $b = |\mathbf{b}_1| = |\mathbf{b}_2| = 4\pi / \sqrt{3}$. The first Brillouin zone, which is a central idea in describing the electronic bands of solids, is illustrated as the shaded hexagon in Figure 2.2(b). This hexagonal-shaped Brillouin zone is built as the Wigner–Seitz cell of the reciprocal lattice. Out of its six
corners, two of them are inequivalent (the others can be written as one of these two plus a reciprocal lattice vectors). These two special points are denoted with \( \mathbf{K} \) and \( \mathbf{K}^+ \) with coordinate:

\[
\mathbf{K}_+ = \frac{2\pi}{3a} \begin{pmatrix} \sqrt{3} \\ -1 \end{pmatrix}, \quad \mathbf{K}_- = \frac{2\pi}{3a} \begin{pmatrix} \sqrt{3} \\ 1 \end{pmatrix}
\]  

(3)

It should be noted that in the following chapters we often use alternative labeling as \( \mathbf{K} \) and \( \mathbf{K}' \) instead. We also sometimes use the terminology \( k \)-space to refer to the reciprocal space and the vector that locates any point within the Brillouin zone is the wave vector \( \mathbf{k} \).

2.3 Graphene Two-Band Model

In this section, we overview the derivation of the electronic \( \pi \)-bands of graphene based on the tight-binding model which is used here to provide an approximate description of the \( \pi \)-bands of monolayer graphene. For a more detailed development of the tight-binding model applied to graphene and other \( sp^2 \) carbon systems, see [1] [2].

Within the nearest neighbor tight-binding (NNTB) model, the unperturbed eigenvectors are represented by atomic orbitals, and the crystalline potential is treated as a perturbation, thus forming the crystalline electronic states which are represented by the Bloch theorem. Since there are two atoms in the unit cell, there are two-component Bloch functions. Then taking the Schrödinger equation, one obtain a \( 2 \times 2 \) eigenvalue problem with the matrix elements of Hamiltonian as below:

\[
H_{AA}(\mathbf{k}) = H_{BB}(\mathbf{k}) = \varepsilon_{2p}
\]

\[
H_{AB}(\mathbf{k}) = H_{BA}^*(\mathbf{k}) = \gamma \left[ e^{i\mathbf{k} \cdot \mathbf{r}_1} + e^{i\mathbf{k} \cdot \mathbf{r}_2} + e^{i\mathbf{k} \cdot \mathbf{r}_3} \right] = \gamma f(\mathbf{k})
\]

(4)

where \( \gamma \) is the hopping (or transfer) energy between nearest neighbor \( \pi \) orbitals (with typical value \( \sim -3 \) eV).

The nearest neighbor vectors \( \mathbf{r}_i \) (\( i = 1, 2, 3 \)) in Cartesian coordinate are given by
\[ r_1 = \frac{a}{2} \left( \begin{array}{c} 1 \sqrt{3} \\ 1 \end{array} \right), \quad r_2 = \frac{a}{2} \left( \begin{array}{c} 1 \sqrt{3} \\ -1 \end{array} \right), \quad r_3 = a \left( \begin{array}{c} -1 \\ 0 \end{array} \right) \] (5)

and the function \( f(k) \) is therefore found to be:

\[
f(k) = e^{-ik,a/\sqrt{3}} + 2e^{-ik,a/(2\sqrt{3})} \cos(k_xa/2)
\]

(6)

Setting \( \varepsilon_{2p} = 0 \) (as the energy reference), the explicit form of Hamiltonian can be written as:

\[
H(k) = \begin{pmatrix}
0 & \gamma f(k) \\
\gamma f^*(k) & 0
\end{pmatrix}
\]

(7)

This 2 × 2 Hamiltonian can be written in terms of Pauli matrices as in [3], thereby emphasizing the analogy with a spin Hamiltonian\(^1\).

The energy dispersion relations are obtained from the diagonalization of \( H(k) \) as:

\[
E(k) = \pm \gamma \left| f(k) \right|
= \pm \gamma \sqrt{1 + 4\cos(k_xa/2) \cos(\sqrt{3}k_ya/2) + \cos(k_ya/2)}
\]

(8)

Correspondingly, the eigenstates (wave functions) for the graphene are equal to:

\[
\Psi_k(r) = \frac{e^{ik \cdot r}}{\sqrt{2}} \left( \begin{array}{c} \pm 1 \\ e^{i\psi_k} \end{array} \right)
\]

(9)

where \( f(k) = |f(k)|e^{i\psi_k} \). The + and - signs correspond to the Valence band (or bonding \( \pi \) energy band), and Conduction band (antibonding \( \pi^* \) band), respectively. The wavevectors \( k = (k_x, k_y) \) are chosen within the first hexagonal Brillouin zone (BZ).

\(^1\) Writing the Hamiltonian in terms of Pauli matrices allows us also to classify the terms according to their symmetries. A particularly important one is electron–hole symmetry. The Hamiltonian is said to have electron–hole symmetry if there is a transformation \( \mathcal{P} \), such that \( \mathcal{P} \mathcal{H} \mathcal{P} = -\mathcal{H} \). This guarantees that if \( \Psi \) is an eigenstate of \( \mathcal{H} \) with a positive energy \( E \) (electron), then \( \mathcal{P}\Psi \) is also an eigenstate with energy \( -E \) (hole) and the spectrum is symmetric with respect to the Fermi energy.
In Figure 2.3, the electronic energy dispersion relations for the \( \pi \)-bands of monolayer graphene are shown throughout the two-dimensional first Brillouin zone. Graphene displays a metallic (zero-gap) character. As a result, the term \textit{semi-metal} or zero-gap semiconductor is usually used to categorize graphene.

![Energy dispersion of graphene](image)

The existence of a zero gap at the K (K') points comes from the symmetry requirement that the two carbon sites A and B in the hexagonal lattice are distinct but equivalent to each other by symmetry. If the A and B sites had different atoms, such as Boron (B) and Nitrogen (N), then the site energy \( E_{2p} \) would be different for B and N, and therefore the calculated energy dispersion would show an energy gap between the \( \pi \) and \( \pi^* \) - bands (\( E_g = 3.5 \text{ eV} = \varepsilon_{2p}^B - \varepsilon_{2p}^N \) for BN).

\section*{2.4 Description Close to the Dirac Point: Massless Dirac Fermions}

By expanding Hamiltonian Eq. (7) around \( K \) and \( K' \) (the two inequivalent corners of the Brillouin zone) further properties of graphene can be derived. Putting \( \mathbf{k} = \mathbf{K} + \mathbf{q} \) where \( |\mathbf{q}| \ll |\mathbf{K}| \) (\( \mathbf{q} \) measures the deviations from K points) one obtain:
\[ H(\mathbf{q}) = \hbar v_F \begin{pmatrix} 0 & q_x - iq_y \\ q_x + iq_y & 0 \end{pmatrix} = v_F p_x \sigma_x + p_y \sigma_y, \]  

(10)

where \( v_F = \sqrt{3}(\gamma a / 2\hbar) \) is the electronic group velocity (Fermi velocity) of graphene (\( \sim c / 300 \), with \( c \) as the speed of light). Also \( p_{x(y)} = \hbar q_{x(y)} \) and the Pauli matrices are defined as usual:

\[
\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}.
\]

(11)

The effective Hamiltonian can also be written in the more compact form:

\[ H_K = v_F \hat{\sigma} \cdot \mathbf{p}, \]

(12)

where \( \hat{\sigma} = (\sigma_x, \sigma_y, \sigma_z) \) and momentum operator \( \hat{\mathbf{p}} = -i\hbar \hat{\nabla} \). For the inequivalent \( K' \) point Hamiltonian is transposed: \( H_{K'} = H_K^\dagger \).

Eq. (12) is equivalent to the Dirac–Weyl Hamiltonian in two dimensions which is used to describe the relativistic particles with zero effective mass. Therefore, the low-energy excitations mimic those of massless Dirac particles of spin 1/2 (such as a massless neutrino), with the velocity of light \( c \), and inherent chirality as explained below. However, in contrast to relativistic Dirac particles, low-energy excitations of graphene have a Fermi velocity \( v_F \) about 300 times smaller than the light velocity, whereas the Pauli matrices appearing in the low-energy effective description operate on the sublattice degrees of freedom instead of spin, hence the term pseudospin is used to describe the orbital wave functions sitting in two different sublattices of the honeycomb lattice. In other words, the low energy spectrum of graphene near the charge neutrality point (i.e., Dirac point), where the linear carrier dispersion mimics the “quasi-relativistic” dispersion relation, pseudospin replaces the role of real spin in the usual relativistic...
fermion energy spectrum. The low-energy quasiparticles in graphene are often referred to as Massless Dirac Fermions (MDF).

2.5 Pseudospin and Chirality of Graphene

Chirality is the key concept to identify and describe the electronic band structure of graphene. The term chirality is derived from the Greek term for hand, and it is used to describe the reflection symmetry between an object and its mirror image. Formally, a chiral object is an object that is not superimposable on its mirror image; and conversely, an achiral object is an object that is superimposable on its mirror image. For example, consider the left hand; its mirror image is the right hand. We see that it is not possible to superimpose the two hands or images such that all the features coincide precisely, as illustrated in Figure 2.4. Therefore, the human hand is a chiral object. Now, consider a circle as another example; its mirror image is also an identical circle, which superimposes precisely on top of the original image. Therefore, a circle is an achiral object. In a general usage, chirality is invoked to highlight the presence or lack of mirror symmetry that provides intuition about understanding phenomena.

![Figure 2.4 Example of a chiral object. (a) The left hand and its mirror image (right hand). (b) It is not possible to superimpose the left hand on the right hand; therefore, the human hand is chiral.](image-url)
One of the most interesting properties of the Dirac–Weyl equation is its helical or chiral nature which is a direct consequence of the Hamiltonian being proportional to the helicity operator, which here for the case of the Hamiltonian in Eq. (12) is defined as:

\[ \hat{h} = \hbar \hat{\sigma} \cdot \frac{\mathbf{k}}{|\mathbf{k}|}. \]  

(13)

The helicity (or chirality) operator \( \hat{h} \) is essentially the projection of the sublattice pseudospin operator \( \hat{\sigma} \) on the momentum direction. Interestingly, since \( \hat{h} \) commutes with the Hamiltonian, the projection of the pseudospin is a well-defined conserved quantity which can be either positive or negative, corresponding to pseudospin and momentum being parallel or antiparallel to each other (see Figure 2.5). If we apply a similar analysis at \( K_+ \) point instead of \( K_+ \), then the Hamiltonian will be proportional to \( \hat{\sigma} \cdot \mathbf{k} \), where \( \hat{\sigma} \) are the complex conjugate of the Pauli matrices \( \hat{\sigma} \) and are known to describe left-handed massless particles in contrast to \( \hat{\sigma} \) which are the right-handed Pauli matrices at \( K_- \). Therefore, one says that chirality is inverted when passing from \( K_+ \) to \( K_- \) as represented in Figure 2.5.

To explore this in more detail, let us rewrite the Hamiltonian as:

\[ \mathcal{H}_\xi(k) = \hbar v_F \left| k \right| e^{i \xi \varphi_k} \begin{pmatrix} 0 & e^{-i \xi \varphi_k} \\ e^{i \xi \varphi_k} & 0 \end{pmatrix}, \]  

(14)

where \( \mathbf{k} = |\mathbf{k}| e^{i \varphi_k} \), \( \varphi_k = \tan^{-1}(ky/kx) \) and \( \xi \) can take the values \( \xi = +1 \) which corresponds to \( K_+ \) and \( \xi = -1 \) to \( K_- \). The eigenstates of Eq. (14) can be written as:

\[ |\Psi_{\xi,s}\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ se^{+i \xi \varphi_k} \end{pmatrix}. \]  

(15)

The index \( s = \pm 1 \) is the band index (\( s = +1 \) for the conduction band and \( s = -1 \) for the valence band) and \( \xi \) the valley index as stated before (\( \xi = +1 \) (\( K_+ \)), \( \xi = -1 \) (\( K_- \))). Using this explicit form
of the eigenstates, we can directly verify that they are also eigenstates of the helicity operator (also called chirality operator) with eigenvalues $\pm 1$.

![Diagram](image)

Figure 2.5 The two inequivalent Dirac cones at $K_+$ and $K_-$ points of the first Brillouin zone. As well as the direction of the pseudospin parallel or antiparallel to the momentum $p$ of selected energies in conduction and valence bands.

Around $K_+$ ($\xi = +1$), the pseudospin of eigenstates in the conduction band is parallel to the momentum and antiparallel for eigenstates in the valence band. The chirality, in this case, is simply the band index. The property around $K_-$ ($\xi = -1$) is reversed as illustrated in Figure 2.5. This peculiarity has a strong influence in many of the most intriguing properties of graphene. For example, for an electron to backscatter (i.e. changing $k$ to $-k$) it needs to reverse its pseudospin. But as the pseudospin direction is locked to that of momentum, backscattering is not possible if the Hamiltonian is not perturbed by a term which flips the pseudospin (this is also termed absence of backscattering [4]).

Although we are dealing all the time with both valleys separately, it is important to keep in mind that a four-component spinor wavefunction describes the full structure of the eigenstates, $\Psi_{K_+,A}, \Psi_{K_+,A'}, \Psi_{K_+,B}, \Psi_{K_-,B}$. The full Hamiltonian of ideal graphene is given by,
\[
\hat{H} = v_F \begin{pmatrix}
0 & \pi^* & 0 & 0 \\
\pi & 0 & 0 & 0 \\
0 & 0 & 0 & \pi \\
0 & 0 & \pi^* & 0
\end{pmatrix},
\]

With \( \pi = p_x + ip_y \) and \( \pi^* = p_x - ip_y \).

### 2.6 Phase Uncertainty and Berry Phase

Graphene is highly peculiar for its linear energy–momentum relation and electron–hole symmetry. The electronic properties in the vicinity of the corners of the 2D Brillouin zone mimic those of massless Dirac fermions forming “Dirac cones” as illustrated in Figure 2.3. The six points where the Dirac cones touch are referred to as the Dirac points.

The existence of an inherent phase ambiguity of the electron wavefunction is well illustrated through the Bloch theorem. It states that the eigenstates of a given Hamiltonian \( H \) can generally be written as \( |\Psi_k\rangle = e^{ikr} |\psi_k\rangle \), with \( |\psi_k\rangle \) defined inside the unit cell (invariant under any transformation such as \( |\psi_k\rangle \rightarrow e^{i\phi} |\psi_k\rangle \), with \( e^{i\phi} \) an arbitrary phase function in \( k \)-space). To leave the phase ambiguity and capture the phase interferences in physical observables, one has to define the so-called Berry connection (equivalent to a vector potential) as \( \hat{A} = i \langle \psi_k | \hat{V}_k | \psi_k \rangle \). All physical quantities will be invariant under any gauge transformation \( \mathcal{A} \rightarrow \mathcal{A} + \hat{V}_k \varphi_k \), while the Berry phase defined as a gauge-invariant quantity

\[
\gamma_c = \oint \mathcal{A} \cdot d\mathbf{k},
\]

measures the total phase accumulated upon transformation (rotation) of the wavefunction in \( k \)-space along a closed loop. The Berry curvature \( \mathbf{F} = \hat{V}_k \cdot \mathbf{A} \) is analogous to the magnetic field, while \( \gamma_c = \iint \mathbf{F} d^2k \) gives the Berry flux. The existence of a nontrivial Berry phase has been
demonstrated to have many profound consequences in quantum physics [5] [6]. In graphene and graphene-like materials, in particular, it attributes unconventional phenomena such as the absence of backscattering in nanotubes and graphene, Klein tunneling, weak antilocalization, and zero-energy Landau level.

Under $2\pi$ rotation of the electron wavefunction in reciprocal space, the eigenstates of the Dirac excitations get a $\pi$ phase factor. Using the rotation operator $\mathcal{R}(\theta) = e^{-i\theta S/\hbar}$ with $S = \hbar/2\hat{\sigma}_z$ for spin-1/2 particles, it is shown that $\mathcal{R}(\theta = 2\pi)\left|\Psi_{K, s}(s = \pm 1)\right\rangle = e^{i\pi\hat{\sigma}_z}\left|\Psi_{\xi, s}\right\rangle = -\left|\Psi_{\xi, s}\right\rangle$ (using $e^{-i(n\cdot\hat{\sigma})/\hbar} = \cos\theta + i(n\cdot\hat{\sigma})\sin\theta$).

One can also directly compute the Berry phase from the general definition as

$$A = i\langle\psi_k|\hat{\nabla}_k|\psi_k\rangle = -\frac{i}{2}(1 - e^{-i\theta})\begin{pmatrix} 0 \\ i\nabla_k\theta e^{i\theta} \end{pmatrix} = \frac{\mathbf{e}_\theta}{2|\mathbf{k}|}.$$  \hspace{1cm} (18)

($\mathbf{e}_\theta$ is a unit vector perpendicular to wave vector $\mathbf{k}$) while

$$\gamma_c = \oint \mathbf{A} \cdot d\mathbf{k} = \int_0^{2\pi} d\theta \frac{\mathbf{e}_\theta}{2|\mathbf{k}|} = \pi.$$  \hspace{1cm} (19)

Figure 2.6 Intensity maps of graphene at Fermi energy with $x$- and $y$-polarized light. White arrows denote intensity maxima, and the electronic band structure of single-layer graphene is shown in the sketch. $E_F$ is 0.4 eV above the Dirac point energy [7].
The observation of a Dirac cone and the existence of pseudospin-related quantum phases has been confirmed, in particular through polarization-dependent angle-resolved photoemission spectroscopy (ARPES) [7, 8]. Figure 2.6 shows the experimental photoelectron intensity maps at the Fermi level $E_F$ versus the two-dimensional wave vector $k$ for single-layer graphene for the two polarization geometries. The main feature in the intensity maps of both geometries is an almost circular Fermi surface centered at the $K$-point. Additionally, the angular intensity distribution is seen to be polarization-dependent in the sense that the minimum intensity position is in the first Brillouin zone for $X$-polarization, while the maximum intensity position is in the first Brillouin zone for $Y$-polarization, suggesting a $\pi$ rotation of the maximum intensity in the $k_x - k_y$ plane around the K point upon rotating the light polarization by $\pi/2$, from $X$ to $Y$.

We can deduce the $\pi$ Berry phase differently by simple analogy of pseudospin degree of freedom of electron in graphene and rotation property of a spin 1/2 angular momentum. Given that the pseudospin direction is locked to the direction of momentum when $p$ (or similarly wave vector $k$) is forced to rotate in a full circle ($2\pi$), so does the pseudospin. We know from quantum mechanics that rotating a spin 1/2 state along the z direction by an angle of $\varphi$ can be done with the operator $e^{-i\varphi S_z/\hbar} = e^{-i\varphi z/2}$. When $\varphi$ is $2\pi$, the rotation operator brings a minus sign to the electron wavefunction, which can be viewed as multiplied by $e^{i\pi}$, hence the extra phase of $\pi$ is acquired.
3 CHAPTER THREE: GRAPHENE IN EXTERNAL STRONG ELECTRIC FIELD

3.1 Introduction

The dynamics of an electron in periodic potential and external electric field is characterized by Bloch oscillations [9], which are a feature of the intraband electron dynamics, and Zener tunneling [10], which is related to interband coupling. The Bloch oscillations occur due to the acceleration of an electron by the electric field, which is described by the “acceleration theorem” in the reciprocal space [11], and subsequent Bragg reflections from the periodic lattice potential at the boundaries of the first Brillouin zone. The interference of the electron wave packet, following such periodic dynamics in the reciprocal space, results in Wannier-Stark (WS) localization of an electron in the coordinate space [11]. The Bloch oscillation frequency separates these WS states within a given band forming an equidistant WS ladder. The Bloch oscillations and the corresponding WS states have been observed experimentally in semiconductor superlattices [12-15]. Recently, the Bloch oscillations were reported to play a significant role in the high harmonic generation (HHG) by intense infrared [16] and terahertz [17] pulses in crystalline solids.

The external electric field not only modifies the intraband electron dynamics, which results in the formation of the WS states but also introduces interband coupling of the states of different bands. Such coupling can be described in terms of the Zener tunneling resulting in finite widths of the WS levels (resonances) of individual bands [18, 19], or in terms of the eigenstates of coupled Hamiltonian, which results in a mixture of the corresponding WS states of different bands. The strongest mixing occurs at the resonance when the energies of the WS levels of
different bands are equal. As a function of electric field, at these points, the levels exhibit anticrossing behavior. In a time-dependent electric field, e.g., in the electric field of an optical pulse, passing of these anticrossings defines time-dependent electron dynamics. This can be described as an adiabatic formation of WS states of different bands with subsequent passage of the anticrossing points. Depending on the relation between the anticrossing gap and the rate of change of electric field, the dynamics of this passage can be adiabatic or diabatic [20]. Such a description of electron dynamics in the time-dependent electric field was successfully used for interpretation of experimental results on the interaction of ultrashort intense optical pulses with dielectrics [21, 22].

Description of the interaction of time-dependent electric field, e.g., optical pulse, with a solid in terms of the dynamics of the passage of anticrossing points requires knowledge of both the positions of the anticrossing points and the magnitudes of the corresponding anticrossing gaps. These parameters depend on the band structure of the solid and the strength of the interband coupling. In this chapter, we study the properties of the WS states of monolayer graphene with potential application to the description of the interaction of strong optical field with electrons in graphene.

As we explained in the previous chapter, graphene monolayer has a honeycomb two-dimensional crystal structure with a unique energy dispersion relation. Namely, the low-energy excitations are gapless and are described by the Dirac relativistic massless equation with two Dirac cones. Another important feature of this relativistic energy dispersion is the singularity of the interband dipole matrix element between the valence and conduction bands at the Dirac points. In this case, the corresponding interband coupling, introduced by an electric field, is strong near the discrete Dirac points.
In this chapter, we show that due to this property, the stationary Schrödinger equation in a constant electric field can be solved exactly within the nearest neighbor tight-binding model of graphene for the electric field in the rational crystallographic directions. Previously, the WS energy spectra of electrons on a honeycomb lattice were studied in Ref. [26] in the tight-binding approximation for both rational and irrational directions of the electric field. It was shown that for an electric field in a rational direction, there was the WS localization of the electron wave functions in the field directions while in the normal direction, they were delocalized.

3.2 Main Equations

The WS states of an electron in graphene are defined as electron states in periodic lattice potential of graphene and constant external electric field. These can be found as solutions of the Schrödinger equation

\[ \mathcal{H}\Psi = E\Psi , \]  

where \( \mathcal{H} \) is a single-particle Hamiltonian, which has the form

\[ \mathcal{H} = \mathcal{H}_0 + e\mathbf{F} \cdot \mathbf{r} , \]  

Here, \( \mathcal{H}_0 \) is a single-electron Hamiltonian of graphene, which determines the electron dynamics in periodic lattice potential of graphene, \( \mathbf{r} = (x,y) \) is a two-dimensional vector, \( e \) is unit charge, and \( \mathbf{F} = [F\cos\theta , F\sin\theta ] \) is the external constant electric field with the magnitude \( F \) and the direction, determined by angle \( \theta \) relative to the \( x \)-axis [see Figure 3.1(b)].

We describe the electron states in graphene within the nearest neighbor tight-binding model [1, 2, 27, 28] with the tight-binding coupling between the sites of two sublattices A and B of the graphene crystal structure [see Figure 3.1(a)]. Such a model describes both the conduction
and valence bands of graphene and captures the properties of the Dirac points. In the reciprocal space, the tight-binding Hamiltonian $H_0$ can be represented by $2 \times 2$ matrix of the form

$$H_0 = \begin{pmatrix} 0 & \gamma f(k) \\ \gamma f^*(k) & 0 \end{pmatrix}$$

(3)

where $\gamma = -3.03$ eV is the hopping integral and

$$f(k) = \exp\left(i \frac{ak_x}{\sqrt{3}}\right) + 2 \exp\left(-i \frac{ak_x}{2\sqrt{3}}\right) \cos\left(\frac{ak_y}{2}\right)$$

(4)

Here, $a = 2.46$ Å is the lattice constant. The energy spectrum of Hamiltonian $H_0$ consists of CB ($\pi^*$ or antibonding band) and VB ($\pi$ or bonding band) with the energy dispersion $E_c(k) = -\gamma |k|$ (CB) and $E_v(k) = \gamma |k|$ (VB). This energy dispersion is shown in Figure 3.1(c). It consists of two inequivalent sets of three Dirac points (and cones) $K$ and $K'$. The corresponding wave functions of the conduction and valence bands are, respectively,

$$\Psi_k^{(c)}(r) = \frac{e^{ikr}}{\sqrt{2}} \left( \begin{array}{c} 1 \\ e^{i\varphi_k} \end{array} \right)$$

(5)

$$\Psi_k^{(v)}(r) = \frac{e^{ikr}}{\sqrt{2}} \left( \begin{array}{c} -1 \\ e^{i\varphi_k} \end{array} \right)$$

(6)

where we denote $f(k) = |f(k)| e^{i\varphi_k}$. The wave functions $\Psi_k^{(c)}$ and $\Psi_k^{(v)}$ have two components corresponding to two sublattices A and B.
Figure 3.1 Honeycomb lattice structure, the first Brillouin zone, and energy spectrum of graphene (a) Honeycomb lattice structure of two-dimensional (2D) graphene, which consists of two sublattices with atoms labeled by A (open circles) and B (filled circles), respectively. The nearest neighbor coupling with hopping integral $\gamma$ is also shown. (b) The first Brillouin zone of graphene. Points $K$ and $K'$ are two inequivalent Dirac points, which correspond to two valleys of low-energy spectrum of graphene. The direction of electric field is shown by the blue line and is characterized by an angle $\theta$ relative to the $x$-axis. (c) Energy dispersion of graphene within the nearest neighbor tight-binding model. The $K$ and $K'$ Dirac points are labeled. The conduction and the valence bands correspond to positive and negative energies, respectively.

Taking the eigenfunctions $\psi_k^{(e)}$ and $\psi_k^{(v)}$ of Hamiltonian $H_0$ as the basis, we express the general solution of the Schrödinger equation (1) in the form

$$\Psi(\mathbf{r}) = \sum_k \left[ \phi_v(k) \psi_k^{(v)}(\mathbf{r}) + \phi_c(k) \psi_k^{(c)}(\mathbf{r}) \right]$$

(7)

Expansion coefficients $\phi_v(k)$ and $\phi_c(k)$ satisfy the following eigenvalue equations (see the Appendix A):

$$E\phi_v(k) = E_v(k)\phi_v(k) + ie\mathbf{F} \frac{\partial \phi_v(k)}{\partial \mathbf{k}} + \mathbf{F} \mathbf{D}(k) \phi_v(k)$$

(8)

$$E\phi_c(k) = E_c(k)\phi_v(k) + ie\mathbf{F} \frac{\partial \phi_c(k)}{\partial \mathbf{k}} + \mathbf{F} \mathbf{D}(k) \phi_c(k)$$

(9)

where $\mathbf{D}(k) = [D_v(k), D_c(k)]$ is the dipole matrix element between the conduction and valence band states with the wave vector $\mathbf{k}$, i.e.,

$$\mathbf{D}(k) = \langle \psi_k^{(c)} | e \mathbf{r} | \psi_k^{(v)} \rangle = \frac{e}{2} \frac{\partial \phi_k}{\partial \mathbf{k}}$$

(10)
Substituting conduction and valence band wave functions (5) and (6) into Eq. (10), we obtain the following expressions for the interband dipole matrix elements

\[ D_x(k) = \frac{ea}{2\sqrt{3}} \frac{1 + \cos \left(\frac{ak_x}{2}\right)}{1 + 4\cos \left(\frac{ak_x}{2}\right)} \left[ \cos \left(\frac{3ak_x}{2\sqrt{3}}\right) - 2\cos \left(\frac{ak_x}{2}\right) \right] \]

and

\[ D_y(k) = \frac{ea}{2} \frac{\sin \left(\frac{ak_x}{2}\right) \sin \left(\frac{3ak_x}{2\sqrt{3}}\right)}{1 + 4\cos \left(\frac{ak_x}{2}\right)} \left[ \cos \left(\frac{3ak_x}{2\sqrt{3}}\right) + \cos \left(\frac{ak_x}{2}\right) \right] \]

A solution \( \phi_v(k) \) and \( \phi_c(k) \) of Eqs. (8) and (9) should satisfy the periodic boundary condition in the reciprocal space with the periodicity of the reciprocal lattice. From this condition, we obtain the WS energy spectrum.

Equations (8) and (9) constitute a system of the first-order differential equations, where a constant electric field introduces both interband and intraband coupling of the electron states. The interband coupling is realized only between the states with the same wave vector, while the intraband coupling occurs only between the states laying in the reciprocal space along a trajectory determined by the direction of electric field. These trajectories can be identified by considering electron dynamics in a reciprocal space in a constant electric field. If an electron is initially at some point \( k \) of the reciprocal space and a constant electric field is applied, then this electron will drift along the direction of the electric field following the acceleration theorem \( \hbar d\mathbf{k}/dt = e\mathbf{F} \), experiencing Bragg scattering at the boundaries of the Brillouin zone. Then, the corresponding electron trajectory in the reciprocal space determines the line of coupled states.

The intraband-coupled states can be described by considering the states either in the first Brillouin zone only or in the entire reciprocal space. In either case, the equivalence of the points connected by a vector of reciprocal lattice should be taken into account. Such equivalence
determines the periodic boundary conditions in the reciprocal space, from which the energy spectrum can be obtained.

First, we assume that the electric field is parallel to the x-axis. In this case, the lines of coupled states are also parallel to the x-axis and are parametrized by the y-component of the wave vector \( k_y \). In Figure 3.2, the states coupled by this electric field are shown in the first Brillouin zone [Figure 3.2(a)] and in the extended reciprocal space [Figure 3.2(b)]. In the first Brillouin zone, we need to take into account equivalence of the points connected by a vector of the reciprocal lattice, e.g., points \( A_1 \) and \( A_2 \) are equivalent. In Figure 3.2, two sets of coupled states (lines) corresponding to different values of \( k_y \) are shown. If \( k_y < 2\pi/a \), then solid blue line shows the typical line of coupled states in Figure 3.2. The solid blue points at the ends of the line are coupled by a vector of reciprocal lattice, which determines the periodic boundary conditions for the wave functions \( \phi_v(k) \) and \( \phi_c(k) \), i.e., \( \phi_v(-2\pi/a\sqrt{3},k_y) = \phi_v(-2\pi/a\sqrt{3},k_y) \) and \( \phi_c(-2\pi/a\sqrt{3},k_y) = \phi_c(-2\pi/a\sqrt{3},k_y) \). From these conditions, the energy spectrum is obtained.

If \( k_y > 2\pi/3a \), then the line of coupled states in the first Brillouin zone consists of two line segments, which are shown by solid red lines in Figure 3.2(a). These line segments have two sets of equivalent points: solid red points and open red points. The points in each set are connected by the corresponding vector of the reciprocal lattice.
Figure 3.2 Lines of coupled states in the reciprocal space.
The electron states of the reciprocal space, which are coupled by a constant electric field parallel to the x-axis, are shown by solid lines of two different colors (red and blue), where different colors correspond to two different values of $k_y$. (a) The coupled states are shown in the first Brillouin zone. The equivalent points (at the edges of the Brillouin zone) are shown by the same type of points, i.e., solid red points or open red points. A vector of reciprocal lattice connects the equivalent points. (b) The coupled states are shown in the whole reciprocal space. The first Brillouin zones, localized at different points of the reciprocal lattice, are also shown. The same type of points shows the equivalent points, which are connected by a vector of reciprocal lattice, e.g., two red points are equal.

In the extended reciprocal space, a part of which is shown in Figure 3.2(b), the lines, which describe the coupled states, are straight lines for both $k_y < 2\pi/3a$ and $k_y > 2\pi/3a$. For the case $k_y > 2\pi/3a$, the line of coupled states is located in two Brillouin zones [see Figure 3.2(b)]. For both the red and blue lines, the end points are connected by the same vector of reciprocal lattice $G = (4\pi/a\sqrt{3},0)$, which makes the end points equivalent and introduces periodic boundary conditions for the system of equations (8) and (9).

3.3 Results and Discussion

3.3.1 Wannier-Stark levels of a single band

Without interband coupling, i.e., for $D = 0$, Eqs. (8) and (9) become decoupled. For a single band, e.g., valence band, Eq. (8) becomes
where the electric field is parallel to the $x$-axis. Solution of the first-order differential equation (13) has the form
\[ \phi_{v}^{(0)}(k) = \frac{1}{\sqrt{2k_0}} \exp \left[ -i \frac{eF}{E} \left( E(k_x + k_0) - \int_{-k_0}^{k_0} E_v(k', k_y) dk' \right) \right] \]

(14)

where we introduced a notation $k_0 = 2\pi/(a\sqrt{3})$. From the periodicity of the wave function $\phi_v(-k_0, k_y) = \phi_v(k_0, k_y)$, we obtain the WS energy spectrum as
\[ E_{v,n}^{WS} = E_{v,0}(k_y) + \hbar \omega_B n \]

(15)

where $n$ is an integer, and the band offset $E_{v,0}(k_y)$ is
\[ E_{v,0}(k_y) = \frac{1}{2k_0} \int_{-k_0}^{k_0} E_v(k', k_y) dk' \]

(16)

The Bloch frequency $\omega_B$ in Eq. (15) is defined as
\[ \omega_B = \frac{\pi eF}{\hbar k_0} \]

(17)

The energy spectrum of Eq. (15) forms the WS ladder with equisidistant energy levels.

For the CB, the energy spectrum has a similar form
\[ E_{c,n}^{WS} = E_{c,0}(k_y) + \hbar \omega_B n \]

(18)

with the corresponding band offset
\[ E_{c,0}(k_y) = \frac{1}{2k_0} \int_{-k_0}^{k_0} E_c(k', k_y) dk' \]

(19)

For the tight-binding model, introduced above, there is a relation $E_{c,0}(k_y) = -E_{v,0}(k_y)$. The wave functions of the WS levels of the conduction band are
\[ \phi_c^{(0)}(\mathbf{k}) = \frac{1}{\sqrt{2k_0}} \exp \left[ -\frac{i}{eF} \left( E(k_x + k_0) - \int_{-k_0}^{k_0} E_c(k', k_y) dk' \right) \right] \]  

(20)

In the coordinate space, the WS levels are localized and the integer index \( n \) determines the center of localization.

### 3.3.2 Wannier-Stark states of two-band model: Analytical results

#### 3.3.2.1 Energy spectrum

The interband coupling, defined by dipole matrix elements \( \mathbf{D}(k) \), has a strong dependence on wave vector \( \mathbf{k} \). Near the Dirac points, the dipole matrix elements have sharp peaks. Dependence of the dipole matrix element \( D_x \) on the wave vector \( k_x \) for different values of \( k_y \) is shown in Figure 3.3. The K Dirac point is at \( \mathbf{k} = \mathbf{K} \equiv (K_x, K_y) = (2\pi/a)(1/\sqrt{3}, 1/3) \), i.e., it corresponds to \( k_x = K_x = (2\pi/a\sqrt{3}) - k_0 \) and \( k_y = K_y = (1/3)(2\pi/a) = k_0/\sqrt{3} \). Away from the Dirac point, i.e., when \( |k_y| \ll K_y \) [see Figure 3.3(a)], the dipole matrix element \( |D_x| \) has a broad maximum near \( k_x = k_0 \). With increasing \( k_y \), the maximum becomes more pronounced. Near the Dirac point [see e.g., the case of \( k_y = 0.33(2\pi/a) \) in Figure 3.3(b)], the dipole matrix element \( |D_x| \) has a sharp peak at \( k_x = K_x = k_0 \). Near this peak, the dipole matrix element \( D_x(k_x, k_y) \) behaves as

\[ D_x(k_x, k_y) \approx \frac{3ea}{4\pi} \left[ -\frac{1}{\delta_y} + \frac{3}{\delta_y^3} \delta^2_x \right] \]

(21)

where \( \delta_y = (k_y - K_y)/K_y \) and \( \delta_x = (k_x - K_x)/K_x \). Thus, for a given \( k_y \), the maximum value of the dipole matrix element is \( (3ea/4\pi)[K_y/(k_y - K_y)] \), diverging at \( k_y \to K_y \).
Although the shape of $D_x(k_x, k_y)$ as a function of $k_x$ depends on the value of the y-component of the wave vector $k_y$, the net interband coupling, which can be characterized by the integral

$$
\frac{1}{e} D_x^{(net)}(k_x) = \frac{1}{e} \int_{-k_0}^{k_0} D_x(k_x, k_y) dk_x = \frac{\varphi_k}{2} \left| \begin{array}{c} k_x = k_0 \\ k_x = -k_0 \end{array} \right| = -\frac{\pi}{3},
$$

(22)

which does not depend on $k_y$. The interband transitional dipole $D_x^{(net)}(k_y)$ is determined by the Pancharatnam-Berry phase $(\varphi_k / 2) |_{k_x = k_0}^{k_x = -k_0}$ [29, 30], as characteristic of dielectric responses of crystalline solids [6, 31, 32]. This also suggests that Eq. (22), as defined by the symmetry of the system, is more general than the tight-binding model, in which the specific calculations are made.

A strong dependence of the dipole matrix element on $k_x$ near the Dirac point, which is illustrated in Figure 3.3 and is supported by Eq. (21), can be approximated by the $\delta$ function, i.e.,

$$
D_x(k_x, k_y) = e \Lambda_0 \delta(k_x - k_0)
$$

(23)

Here, $\Lambda_0$, the strength of the $\delta$-function is determined by the condition that the net dipole coupling in Eqs. (22) and (23) is the same, which yields $\Lambda_0 = -\pi / 3$.

![Figure 3.3](image.png)  
**Figure 3.3** Dipole matrix element $D_x$ as a function of $k_x$ for different $k_x$. 
The wave vector $k_x$ is measured in units of $2k_0$, where $k_0 = \frac{2\pi}{a\sqrt{3}}$. The Dirac point is at $k_x = k_0$ and $k_y = k_0 / \sqrt{3} = (1/3)(2\pi/a)$. The numbers near the lines are the values of $k_y$ in units of $(2\pi/a)$. Panel (a) and (b) differ in the vertical scale.

For the $\delta$-function profile of the dipole matrix elements, the system of equations (8) and (9) can be solved analytically. Such solution can be obtained as follows. We are looking for a solution of the system of equations (8) and (9) within a line segment $0 \leq k_x < 2k_0$ with the periodic boundary conditions at the ends. (Here, it is convenient to consider interval $0 \leq k_x < 2k_0$ and not range $k_0 \leq k_x < k_0$ introduced before.) The dipole matrix element is nonzero only at $k_x = k_0$. Then, for $0 \leq k_x < k_0$ and $k_0 < k_x < 2k_0$, there is no interband coupling between the valence and conduction bands. Within these intervals, the general solution of the system (8) and (9) acquires the form for $0 \leq k_x < k_0$:

$$
\phi_v(k) = A_1 \exp \left[ -\frac{i}{eF} \left( Ek_x - \int_0^{k_x} E_v(k',k_x)dk' \right) \right]
$$

$$
\phi_c(k) = A_2 \exp \left[ -\frac{i}{eF} \left( Ek_x - \int_0^{k_x} E_c(k',k_y)dk' \right) \right]
$$

and the same form with different coefficients for $k_0 < k_x < 2k_0$:

$$
\phi_v(k) = B_1 \exp \left[ -\frac{i}{eF} \left( Ek_x - \int_0^{k_x} E_v(k',k_y)dk' \right) \right]
$$

$$
\phi_c(k) = B_2 \exp \left[ -\frac{i}{eF} \left( Ek_x - \int_0^{k_x} E_c(k',k_y)dk' \right) \right]
$$

where $A_1$, $A_2$, $B_1$, and $B_2$ are constants.

At point $k_x = k_0$, the $\delta$-function dependence of dipole matrix element (23) introduces the following relation between the values of the wave function at $k_x = k_0 - \Lambda$ and $k_x = k_0 + \Lambda$:

$$
\phi_v|_{k_0+0} = -i\phi_c|_{k_0-0} \sin \Lambda_0 + \phi_v|_{k_0-0} \cos \Lambda_0
$$
\[ \phi_c|_{k_0+0} = \phi_c|_{k_0-0} \cos \Lambda_0 - i \phi_v|_{k_0-0} \sin \Lambda_0 \] (29)

Thus, the \(\delta\)-function coupling results in rotation of a pseudospin, which is associated with two components of the wave function, by a finite angle \(\Lambda_0\).

Substituting expressions (24)–(27) into relations (28) and (29) and taking into account the periodic boundary conditions, we obtain an equation for the energy spectrum of the WS states

\[ \cos \left( \frac{2k_0}{eF} E \right) = \cos(\Lambda_0) \cos \left( \frac{2k_0}{eF} E_{c,0}(k_y) \right) \] (30)

where we took into account relation \(E_{c,0} = -E_{v,0}\), which is valid within the tight-binding model introduced above. The solution of Eq. (30) is parameterized by an integer number \(n\); it describes the WS-state energies and has the form

\[ E_n^{(\pm)} = \pm \frac{eF}{2k_0} \left\{ \cos^{-1} \left[ \cos \Lambda_0 \cos \left( \frac{2k_0}{eF} E_{c,0}(k_y) \right) \right] + 2\pi n \right\} \] (31)

Here, the \(\pm\) signs correspond to the conduction (c) and valence (v) bands, respectively.

It is convenient to rewrite Eq. (31) in dimensionless energy variables normalized to the Bloch frequency \(\varepsilon_n^{(\pm)} = E_n^{(\pm)} / \hbar \omega_B = E_n^{(\pm)} / [k_0 / (\pi eF)]\) and \(\varepsilon_{c,0} = E_{c,0}(k_y) / \hbar \omega_B = E_{c,0}(k_0 / (\pi eF))\) as

\[ \varepsilon_n^{(\pm)} = \pm (2\pi)^{-1} \cos^{-1} [\cos \Lambda_0 \cos(2\pi \varepsilon_{c,0})] + n \] (32)

The corresponding dimensionless energy spectrum is shown in Figure 3.4(a). The anticrossing points of the energy levels can be clearly identified. These points are the anticrossings of the WS ladders of the conduction and valence bands [see Figure 3.4(b)] corresponding to the interband Zener tunneling. This interband coupling (Zener tunneling) makes the initial WS states of isolated bands nonstationary (metastable) but causes the formation of new, stationary states of the coupled bands that we consider in this paper.
Figure 3.4 The energies of the WS states, as a function of parameter $\varepsilon_{c,0}$ and Bloch frequency

(a) Parameter $\Lambda_0$ is $\Lambda_0 = 0.6$. Different types of anticrossing points are labeled by integer parameter $l$. With increasing electric field, the last anticrossing point corresponds to $l = 1$ and occurs at $\varepsilon_{c,0} = \pi$. (b) The energies of the WS states as a function of Bloch frequency, which is proportional to the electric field. The anticrossing points, corresponding to $l = 1$ and 2, are marked by red lines. The parameter $\Lambda_0 = 0.6$, and $E_{c,0} = 1$ eV.

The anticrossing points can be labeled by an integer number $l = 1, 2, \ldots$, which has the meaning of the number of unit cells through which the Zener tunneling occurs. In dimensionless variables, the positions of the anticrossing points are

$$\varepsilon_{c,0}^{(l)} = l/2$$

or, in terms of the electric field, the anticrossing points are at

$$F^{(l)} = \frac{2k_0}{e\pi l} E_{c,0}$$

The positions of the anticrossing points can be also estimated from the expressions (15) and (18) for the energies of the WS states of uncoupled conduction and valence bands. For uncoupled bands, the anticrossing points are determined by an equation $E_{c,n_{c}}^{WS} = E_{v,n_{v}}^{WS}$ from which one can derive the positions of the anticrossing points at
\[ F_{\text{uncoupled}}^{(l)} = \frac{2k_0}{\pi e l} E_{c,0} \] (35)

where \( l = n_c - n_v \). Comparing exact expression (34) with approximation (35), we can conclude that the interband coupling for \( k_y \) in the vicinity of the Dirac point eliminates field-induced renormalization of an anticrossing position

\[ F^{(l)} = F_{\text{uncoupled}}^{(l)} \] (36)

At the same time, for \( k_y \) far from the Dirac point, the interband coupling shifts the anticrossing points to the higher values of electric field similar to ordinary solids [16] (see also Sec.3.3.3).

In the dimensionless units, the anticrossing gaps are the same for all anticrossing points [cf. Figure 3.4(a)]. The value of the dimensionless gap \( \Delta_g / \hbar \omega_B \) can be found as the difference between the corresponding energy levels \( \Delta_g / \hbar \omega_B = \varepsilon_1^{(-)} - \varepsilon_0^{(+)} \), calculated at a point \( \varepsilon_{c,0} = 1/2 \).

This way, we find

\[ \Delta_g / \hbar \omega_B = \Lambda_0 / \pi \] (37)

In the original units, the anticrossing gap corresponding to the anticrossing point with index \( l \) [see Eq. (33)] takes the form

\[ \Delta_g^{(l)} = \frac{2\Lambda_0}{l\pi} E_{c,0} \] (38)

Such weak dependence of the anticrossing gap on index \( l \) is a unique feature of graphene’s unique relativistic like low-energy dispersion relation. This behavior is quite different from that of conventional solids, e.g., dielectrics, for which the anticrossing gaps are exponentially decreasing with \( l \).
The physical meaning of $l$ is that the value of $al$ is the distance between the localized WS states of the conduction and valence bands. Then, the anticrossing gap with index $l$ is determined by a coupling of the WS states of the conduction and valence bands separated by spatial distance $al$ and is equal to the rate of Zener tunneling between these bands through $l$ unit cells in space. For graphene, such coupling has a long range in the direct space due to the strongly localized $\delta$-function profile of the dipole matrix elements in the reciprocal space. Such a long-range tunneling results in a weak dependence of the anticrossing gap on distance $l$.

The $\delta$-function profile of the dipole matrix elements in graphene is an approximation, used above to obtain an analytical solution of the problem. The exact dipole matrix element $D(k)$ has a small finite width $w_D$ in the reciprocal space (see Figure 3.4), where $w_D$ depends on $k_y$. Such a finite width introduces a cutoff both in the long-range coupling of the WS states of different bands and in the weak dependence of the anticrossing gap on $l$. Namely, the anticrossing gap $\Delta^{(l)}_s$ has the weak $l^{-1}$ dependence on $l$ for $l \leq l_c = (w_D a)^{-1}$; for $l \gg l_c$, the anticrossing gap becomes exponentially small with $l$.

Since the dimensionless parameter $\varepsilon_{c,0}$ is inversely proportional to the electric field, then in the energy spectrum, considered as a function of electric field, the anticrossing point with index $l = 1$ is the last anticrossing point [see Figure 3.4(a)]. In Figure 3.4(b), the energy spectrum calculated from Eq. (31), is shown as a function of electric field. The anticrossing points with indexes $l = 1$ and 2 are marked. The corresponding anticrossing gaps are given by Eq. (38). The last anticrossing points with index $l = 1$ have the largest anticrossing gap $\Delta^{(l)}_s = 2\Lambda_0 E_{c,0} / \pi$.

For graphene, within the tight-binding model introduced above, parameter $\Lambda_0$, calculated at $k_x = k_{x,0} = 2\pi / 3a$, is $|\Lambda_0| = \pi / 3 \approx 1.05$. For this value of $k_x = k_{x,0}$, the energy dispersion is
\[ E_c(k_x,k_{y,0}) = -2\gamma \cos \left( \frac{\sqrt{3}ak_x}{4} \right) \]  

(39)

Then, the band offset of the conduction band, defined by Eq. (19), is

\[ E_{c,0}(k_{y,0}) = \frac{4\gamma}{\pi} \approx 3.86 \text{ eV} \]  

(40)

For these values of \( \Lambda_0 \) and \( E_{c,0} \), we obtain from Eqs. (34) and (38) the positions of the anticrossing points and the corresponding anticrossing gaps

\[ F^{(l)} = \frac{8k_0|\gamma|}{e\pi^2l} \approx \frac{3.59}{l} \text{ V/Å} \]  

(41)

\[ \Delta_g^{(l)} = \frac{8|\gamma|}{3\pi l} \approx \frac{2.54}{l} \text{ eV} \]  

(42)

The anticrossing at \( l = 1 \) is the last one occurring at the maximum electric field of 3.59 V/Å. The anticrossing gap at this point is 2.54 eV.

### 3.3.2.2 Wave functions

The wave functions of the WS states of the two-band graphene model have two components \( \phi_v(k) \) and \( \phi_c(k) \), which give the amplitudes for an electron to be in the valence and conduction bands, respectively. Functions \( \phi_v(k) \) and \( \phi_c(k) \) are determined by Eqs. (24)–(27) where the unknown coefficients \( A_1, A_2, B_1, \) and \( B_2 \) can be found from the boundary conditions (28) and (29). At a given energy of the WS state \( E \), they have the following form:

\[ A_2 = A_1 \exp \left\{ -i \int_0^{2k_0} \left[ E_c(k',k_y) - E \right] dk' \right\} \]  

(43)

\[ B_1 = i \frac{A_2 - A_1 \cos(\Lambda_0)}{\sin(\Lambda_0)} \]  

(44)

\[ B_2 = B_1 \cos(\Lambda_0) - i A_1 \sin(\Lambda_0) \]  

(45)
Here, coefficient $A_1$ can be found from the normalization condition. The wave functions $\varphi_v(k)$, $\varphi_c(k)$ determine the electron amplitudes in the reciprocal space. A Fourier transform determines the corresponding wave functions in the direct coordinate space

$$\tilde{\varphi}_v(x,k_y) = \int dx \varphi_v(k_x,k_y)e^{ik_x x}$$

$$\tilde{\varphi}_c(x,k_y) = \int dx \varphi_c(k_x,k_y)e^{ik_x x}$$

(46) (47)

where we consider the spatial dependence of the wave function along x-axis only, i.e., along the direction of the electric field. In this case, the y component of the wave vector $k_y$ should be considered as a parameter.

Without interband coupling, i.e., for $\Lambda_0 = 0$, and for $k_y = k_{y,0}$, the WS wave functions for a given band, e.g., conduction band, can be expressed in terms of the Bessel functions

$$\tilde{\varphi}_c(x,k_y) \propto J_n \left( \frac{y}{\sqrt{|\omega - \frac{E}{eF}|}} \right) \left( \frac{y}{\hbar \pi \omega_B} \right)$$

(48)

where $J_n(z)$ is the Bessel function of order $n$, and the Bloch frequency is given by Eq. (17). Such analytical expression is obtained for energy dispersion (39). Wavefunction (48) is localized in the x space at a coordinate point $x = E/eF$, which is proportional to the energy of the WS state.

The interband coupling $\Lambda_0$ results in mixing of the wave functions of different (conduction and valence) bands. The mixing is strongest at the anticrossing points, and the resulting WS wave functions are also localized similar to single band approximation (48). Such wave functions are given by Eqs. (43)–(47).
Figure 3.5 Electron densities in the conduction and valence bands of a given WS state. The electric field is (a) \( F = 1.8 \text{ V/Å} \), (b) \( F = 2.4 \text{ V/Å} \), (c) \( F = 3.6 \text{ V/Å} \). The fields 1.8 and 3.6 V/Å corresponds to \( l = 2 \) and 1 anticrossing points. The y-component of the wave vector is \( k_y = k_{y,0} \). 

To illustrate the interband mixing introduced by an electric field, we show in Figure 3.5 the conduction and valence band probability densities for the WS wave functions, i.e., 

\[
\rho_v(x) = \left| \phi_v(x, k_y) \right|^2 \quad \text{and} \quad \rho_c(x) = \left| \phi_c(x, k_y) \right|^2.
\]

The results are shown for one of the WS energy levels for a given electric field. The electric field \( F = 1.8 \text{ and } 3.6 \text{ V/Å} \) are near \( l = 2 \) and 1 anticrossing points, respectively. In these cases, the interband mixing is strong, and the electron densities in the CB and VB are equivalent [see Figure 3.5(a) and (c)]. The spatial separation between the maxima of \( \rho_v(x) \) and \( \rho_c(x) \) is \( \approx la \). Thus, for \( F = 1.8 \text{ V/Å} \), i.e., \( l = 2 \), the distance between the maxima of \( \rho_v \) and \( \rho_c \) is \( \approx 2a \approx 4.8 \text{ Å} \), while for \( F = 3.6 \text{ V/Å} \), i.e., \( l = 1 \), the distance is \( \approx a \approx 2.4 \text{ Å} \). For electric field \( F = 2.4 \text{ V/Å} \), which is between \( l = 1 \) and 2 anticrossing points, the interband mixing is weak. In this case, only one component (in our case only the VB component \( \rho_v \)) is strong [see Figure 3.5(b)].
Figure 3.6 Total electron density \( \rho(x) = \rho_v(x) + \rho_c(x) \) of three WS states. The electric field is \( F = 3.6 \text{ V/Å} \), corresponding to the \( l = 1 \) anticrossing point. The y-component of the wave vector is \( k_y = k_{y,0} \). The curves are displaced vertically for clarity.

In both cases, i.e., at the anticrossing points and away from them, the wave functions are localized in the \( x \) space. The localization length depends on the electric field. The points, at which the WS wave functions are localized, depend on the energy of the WS states. In Figure 3.6, the total electron density, defined as \( \rho(x) = \rho_v(x) + \rho_c(x) \), is shown for different WS states at electric field \( F = 3.6 \text{ V/Å} \), which correspond to \( l = 1 \) anticrossing point. With changing the energy of the WS state, the electron density distribution is shifted as a whole along the \( x \)-axis.

### 3.3.3 Wannier-Stark states of two-band model: Numerical results

In the previous section, analytical results for the WS spectra of the tight-binding model were obtained in the case of the \( \delta \)-function dipole matrix elements. Such strong dependence of the dipole matrix element on the wave vector occurs near the Dirac points. Away from the Dirac points, the dipole matrix element \( |D_x| \) as a function of the wave vector has a broad peak. In such a case, the WS energy spectra can be obtained numerically.
It is convenient to solve the system of the eigenvalue equations (8) and (9) by expanding functions \( \phi(k) \) and \( \phi(k) \) in terms of the WS wave function of individual bands, Eqs. (14) and (20), calculated without interband coupling. Thus,

\[
\phi_v(k) = \sum_n A_n \phi^{(0)}_{v,n}(k)
\]

(49)

\[
\phi_c(k) = \sum_n B_n \phi^{(0)}_{c,n}(k)
\]

(50)

where index \( n \) labels the WS states [see Eqs. (15) and (18)], \( A_n \) and \( B_n \) are the corresponding expansion coefficients. Substituting expressions (49) and (50) into Eqs. (8) and (9), we obtain the system of eigenvalue equations on expansion coefficients \( A_n \) and \( B_n \):

\[
E A_n = E^{WS}_{v,n} A_n + F \sum_m D_{nm} B_m
\]

(51)

\[
E B_n = E^{WS}_{c,n} B_n + F \sum_m D^*_{nm} A_m
\]

(52)

where \( D_{nm} \)'s are dipole matrix elements, calculated between the WS wave functions of individual bands,

\[
D_{nm} = \left< \phi^{(0)}_{v,n} | D_i(k) | \phi^{(0)}_{c,m} \right> = \frac{1}{2k_0} \int_{-k_0}^{k_0} dk_x D_i(k_x, k_y) \exp \left[ i eF \left( 2 \int_{-k_0}^{k_0} E_i(k', k_y) dk' + (E^{WS}_{v,n} - E^{WS}_{v,m})(k_x + k_y) \right) \right]
\]

(53)
Figure 3.7 Energy spectra of graphene in a constant electric field, parallel to the x-axis. The spectra are calculated numerically for a finite-size system for two values of $k_y$: (a) $k_y = 0$ and (b) $k_y = 0.32(2\pi/a)$. The number of states in each band is 100. Red lines mark the anticrossing points corresponding to $l = 1$ and 2.

In Figure 3.7, the energy spectra of a finite-size system of graphene, calculated numerically from the system of equations (49) and (50), are shown for different values of the y-component of the wave vector $k_y$. At $k_y = 0$ [see Figure 3.7(a)], the system is far away from the Dirac points. In this case, the dipole matrix element as a function of $k_x$ has a broad peak [see Figure 3.3]. For $k_y = 0.32(2\pi/a)$ [see Figure 3.7(b)], the system is close to the Dirac point with the dipole matrix element having a sharp narrow peak. In this case, the values of the anticrossing gaps and the positions of the anticrossing points are close to the analytical expressions (41) and (42), obtained in the model with $\delta$-function profile for the dipole matrix element.

The data, shown in Figure 3.7, illustrate the strong dependence of the energy spectra on the value of $k_y$, i.e., on the shape of the function $D_x(k_x)$. With increasing $k_y \to K_y$, i.e., when the peak in $D_x(k_x)$ becomes sharp, the anticrossing points move to smaller values of the electric field, and the anticrossing gaps become smaller.
In Figure 3.8, the anticrossing gaps and the positions of the anticrossing points are shown as a function of $k_y$ for $l = 1$ and 2 anticrossing points. A general trend is that with increasing $k_y$, both the anticrossing gaps $\Delta_{x}^{(i)}$ and the electric fields $F^{(i)}$ at which the anticrossing points are observed, are decreasing. The arrows in Figure 3.7 show the analytical values of the anticrossing gaps and the positions of the anticrossing points, obtained from Eqs. (41) and (42). These numbers are close to the corresponding numerical values at $k_y \approx K_y = (1/3)(2\pi/a)$, i.e., near the Dirac point (see Figure 3.7).

### 3.3.4 Wannier-Stark states of two-band model: Two Dirac points

By changing the direction of electric field, one can realize a situation when along a line of coupled states there are two Dirac points. For graphene, this happens for a line shown in Figure 3.9(a), i.e., when the angle between the direction of the electric field and axis $x$ is $\pi/6$. Then, for the line shown in Figure 3.9, we introduce one-dimensional wave vector $\kappa$ along the
direction of electric field and write the dipole matrix element in terms of two δ functions, localized at the Dirac points

\[ D_\delta(\kappa) = e\Lambda_1\delta(\kappa - \kappa_1) + e\Lambda_2\delta(\kappa - \kappa_2) \]  

where \( \kappa_1 \) and \( \kappa_2 \) are the coordinates of the Dirac points along the line of coupled states. The wave vector \( \kappa \) changes from 0 to \( \kappa_0 = (2\pi/a_\kappa) \), where \( a_\kappa = 2\pi/\kappa_0 \) determines the period of the system along the direction of electric field.

We follow the same steps as in the case of one Dirac point (see Sec. 3.3.2). Namely, we introduce three regions \( 0 < \kappa < \kappa_1 \), \( \kappa_1 < \kappa < \kappa_2 \), and \( \kappa_2 < \kappa < \kappa_0 \). In each region, the conduction and valence bands become decoupled, and the wave functions have the form of Eqs. (24) and (25). At the boundary between the regions, i.e., at points \( \kappa = \kappa_1 \) and \( \kappa_2 \), the boundary conditions have the form of Eqs. (28) and (29). Combining all these equations and taking into account the periodic boundary conditions at points \( \kappa = 0 \) and \( \kappa_0 \), we obtain the following energy spectra of the coupled WS states:

\[ E_n^{(+)} = \pm \frac{eF}{\kappa_0} \left\{ \cos^{-1} \left[ \cos \Lambda_1 \cos \Lambda_2 \cos \left( \frac{\kappa_0}{eF} \tilde{E}_{c,0} \right) - \sin \Lambda_1 \sin \Lambda_2 \cos \left( \frac{\kappa_0}{eF} \alpha \tilde{E}_{c,0} \right) \right] + 2\pi n \right\}. \]  

(55)

Here, \( \tilde{E}_{c,0} \) is defined in terms of the linear integral over the line of coupled states (see Figure 3.9)

\[ \tilde{E}_{c,0} = \frac{1}{\kappa_0} \int_0^{\kappa_0} E_c(\kappa) d\kappa \]  

(56)

The coefficient \( 0 < \alpha < 1 \) in Eq. (55) is defined by the following relation

\[ \alpha = 1 - \frac{2}{\tilde{E}_{c,0}} \int_{\kappa_1}^{\kappa_2} E_c(\kappa) d\kappa \]  

(57)

In dimensionless variables \( \epsilon_n^{(\pm)} = E_n^{(\pm)}(\kappa_0/eF) \) and \( \tilde{E}_{c,0} = \tilde{E}_{c,0}(\kappa_0/eF) \), Eq. (55) becomes

\[ \epsilon_n^{(\pm)} = \pm \cos^{-1} \left[ \cos \Lambda_1 \cos \Lambda_2 \cos \tilde{E}_{c,0} - \sin \Lambda_1 \sin \Lambda_2 \cos (\alpha \tilde{E}_{c,0}) \right] + 2\pi n \]  

(58)
In Figure 3.9(b), the dimensionless WS energy spectrum (58) is shown for parameters $\Lambda_1 = \Lambda_2 = \Lambda_0 = 0.6$ and $\alpha = 0.7$, which correspond to graphene. A specific feature of this spectrum is a nonmonotonic dependence of the anticrossing gaps on the value of the dimensionless band offset $\tilde{\varepsilon}_c,0$. These gaps have both large and very small values.

![Figure 3.9 Line of coupled states and the WS energy spectrum calculated from eq. (55) and (58).](image)

(a) The blue solid line shows line of coupled states in the reciprocal space. Along this line, there are two inequivalent Dirac points $K$ and $K'$. The direction of electric field is also shown. (b) Dimensionless energies $\varepsilon_n^{(\pm)}$ of WS states, calculated from Eq. (58), are shown as a function of the dimensionless parameter $\tilde{\varepsilon}_c,0$ for different values of integer number $n$. The parameters $\Lambda_1 = \Lambda_2 = \Lambda_0$ and $\alpha$ are: $\Lambda_0 = 0.6$ and $\alpha = 0.7$. (c) The energies $E(\pm)$ of the WS states, calculated from Eq. (55), are shown as a function of Bloch frequency $\hbar \omega_k$, which is proportional to the electric field. The anticrossing points, corresponding to $l = 1$ and 2, are marked by red lines. The parameters are $\Lambda_0 = 0.6$, $\alpha = 0.7$, and $E_{c,0} = 1$ eV.

The positions of the anticrossing points are also irregular. The corresponding energy spectrum in the original units is shown in Figure 3.9(c) as a function of the electric field $F$. The anticrossing gaps have a nonmonotonic dependence on $F$. For example, the anticrossing gap at $l = 3$ is larger than the gap at $l = 2$. This behavior is different from the behavior of the anticrossing gaps of the WS spectrum for systems where the dipole matrix elements are almost constant [20] or have a single peak as a function of the wave vector (see 3.3.2).
3.4 Conclusion

Within a single- (either conduction or valence) band model, the energy spectrum of an electron in graphene in a constant external field has a WS ladder structure with energy levels separated by the Bloch frequency, which is proportional to both the electric field and the lattice period of graphene crystal structure in the direction of electric field. In a two-band model, which is introduced in this chapter, a constant electric field results in mixing of the conduction and valence bands. Due to such mixing, the energy spectrum of graphene as a function of electric field shows anticrossing points with the corresponding anticrossing gaps. These gaps also indicate that a constant electric field opens a gap in the electron energy spectrum of graphene. This is understandable because it reduces symmetry of the system by lifting the equivalence (degeneracy) of the two constituent triangular sublattices. The magnitudes of the gaps depend on the electric field.

The strength of the band mixing in an external electric field is determined by the magnitude of the interband dipole matrix element. The net (integral) interband dipole matrix element has a value of $-e\pi/3$ universally determined by the Pancharatnam- Berry phase.

In graphene, this interband dipole matrix element has a unique dependence on the electron wave vector. Namely, at the Dirac points, it has sharp peaks, i.e., in the reciprocal space, the interband coupling is strong near the Dirac points only. In this case, approximating such a strong dependence of the dipole matrix element on the wave vector by the delta function, one can find an analytical expression for the WS energy spectrum. Such analytical solution predicts both the positions of the anticrossing points and the corresponding anticrossing gaps. As a function of inverse electric field, the anticrossing points are equidistant. In the dimensionless units (relative to the Bloch frequency), the anticrossing gaps have the same value at all anticrossing points.
Thus, in the original energy unit, the anticrossing gaps are proportional to the electric field at the corresponding anticrossing points, and for graphene are \( \Delta^{(l)}_g = (2.54/l) \) eV, where \( l = 1,2,... \) is an integer. Physically, such an anticrossing gap (divided by \( \hbar \)) is the rate of the Zener tunneling through \( l \) unit cells that transfers an electron in a localized WS state from the valence to the conduction band. The largest anticrossing gap \( \approx 2.54 \) eV corresponds to the anticrossing point \( l=1 \) at the electric field \( \approx 3.59 \) V/Å. The weak dependence \( \propto l^{-1} \) of the anticrossing gaps on parameter \( l \) is a unique property of graphene and is due to highly nonuniform, singular profile of the dipole matrix element.

Such high fields, \( F \gtrsim 1 \) V/Å, can be generated only by laser pulses in the visible/near-infrared [21, 22] or terahertz [17] spectral regimes. Graphene in a time-dependent electric field (see, for example, Ref. [33]), when the electron dynamics is described in terms of the passage of the anticrossing points, the anticrossing gaps determine the characteristic time \( \tau_i = h / \Delta^{(l)}_g = 0.26/l \) fs, which characterizes adiabaticity of the dynamics. Namely, if time \( \tau_p \) of the passage of an anticrossing point, which is also the characteristic time of variation of the electric field, is much larger than \( \tau_i \), \( \tau_p > \tau_i \), then the electron dynamics is adiabatic. For example, if \( \tau_i \approx 1 \) fs, then the passages of anticrossing points \( l =1 \) and 2, which have the characteristic time \( \tau_i =0.25 \) and 0.51 fs, are adiabatic, while the passages of the points \( l >2 \) are nonadiabatic or even diabatic. It is evident that no matter what is the frequency range, from visible to terahertz, there always will be several anticrossings with near-resonant frequencies violating adiabaticity. Thus, the rapid adiabatic passage is not possible in graphene; also, Rabi oscillations will be dephased.
4 CHAPTER FOUR: GRAPHENE IN STRONG ULTRAFAST OPTICAL PULSE

4.1 Introduction

Graphene is a promising material, which has received enormous attention both theoretically and experimentally due to its excellent transport and optical properties. In particular, its linear band structure and zero band gap lead to unique optical and electrical properties, making it suitable for various optoelectronic applications [23, 34-41]. An in-depth understanding of the optical and electrical properties is one of the prerequisites for its potential applications.

Interactions of strong fields with solids have been studied from the onset of quantum mechanics. Interest in this area has grown due to the availability of ultrashort pulses with fields comparable to the internal fields in solids [16, 42-46]. Such fields excite reversible electron dynamics and strongly modify properties of the solid within the optical cycle, i.e., on the attosecond time scale [21, 47]. Here we show theoretically that, in contrast, the strong-field interactions of graphene are highly nonadiabatic and irreversible causing significant electron transfer from the valence band resulting in a high population of the conduction band, which persists after the pulse’s end. These interactions result in ultrafast current whose density is orders of magnitude higher than that in dielectrics or metals [21, 48]. Although graphene in the absence of an external field has a zero band gap (it is a semimetal), it does not necessarily mean that the corresponding electron dynamics is irreversible, since in an electric field electrons drift through the entire Brillouin zone, which introduces an effective band offset and a band gap $\sim 8$ eV (see Chapter 3). In this case, similar to dielectrics [45, 47], one should have expected reversible
dynamics. The extraordinary extreme nonlinear properties of graphene and the irreversibility in it are related to its unique electronic structure causing the singularity of the interband coupling near the Dirac points. This singularity results in the irreversible electron dynamics in graphene.

We consider the interaction of ultrashort laser pulses with graphene monolayer. The purely two-dimensional electron dynamics in graphene is characterized by unique dispersion relation, the low energy part of which is relativistic-like with linear dependence of the electron energy on momentum. The behavior of such low energy electrons is described by the Dirac relativistic massless equation. The Fermi energy of undoped graphene is at the Dirac point and, therefore, graphene is a semimetal with zero band gap. This should result in strong interband mixing of the valence band (VB) and the conduction band (CB). Below we consider femtosecond laser pulses whose duration \( \tau_p \) is less than the electron scattering time \( \sim 10–100 \) fs [49-57]. In this case, the electron dynamics is coherent and can be described by time-dependent Schrödinger equation.

In contrast, dynamics of graphene in relatively slow fields, \( \tau_p > 100 \) fs, for which the scattering processes become important, and the electron dynamics is incoherent, was studied within the density matrix approach [58], where a hot-electron Fermi distribution was reported. For circularly polarized long optical pulses, the interaction of electrons in graphene with periodic electric field results in the formation of Floquet states and opening a gap in the energy spectrum [59-62] or graphene-like topological surface states of a topological insulator [63].

4.2 Model and Main Equations

We consider an optical pulse that is incident normally on a graphene monolayer and parameterize it by the following single-oscillation form, which is an idealization of the actual 1.5-oscillation pulses used in recent experiments [21, 47].
\[ F(t) = F_0 e^{-u^2} \left(1 - 2\mu^2\right) \]  

where \( F_0 \) is the amplitude, which is related to the pulse power \( P = cF^2/4\pi \), \( c \) is the speed of light, \( u = t/\tau \), and \( \tau \) is the pulse length, which is set \( \tau = 1 \) fs corresponding to carrier frequency \( \omega \approx 1.5 \) eV/\( \hbar \). Note that due to this parametrization, the pulse has always zero area, \( \int_{-\infty}^{\infty} F(t)dt = 0 \). We will assume that the pulse is linearly polarized, where the plane of polarization is characterized by angle \( \theta \) measured about the \( x \)-axis. Here the \( x \) and \( y \) coordinates are introduced in the plane of graphene and determined by the crystallographic structure of graphene—see Figure 4.1. Graphene has a hexagonal lattice structure, which is shown in Figure 4.1(a). Also, the first Brillouin zone of the reciprocal lattice of graphene, which is a hexagon, is shown in Figure 4.1(b). The blue arrow shows the polarization of the pulse. The points \( K = (2\pi / a)(1/3 \quad 1/\sqrt{3}) \) and \( K' = (2\pi / a)(-1/3 \quad 1/\sqrt{3}) \), which are the vertices of the hexagon, are the Dirac points. The energy gaps at these points are zero and the low energy spectra near these points are described by the Dirac relativistic equation.

![Figure 4.1 Lattice structure and Brillouin zone of graphene along with the polarization of the pulse.](image-url)
The graphene lattice consists of two inequivalent sublattices, which are labeled by “A” and “B”. The vectors $a_1 = a/2(\sqrt{3}, 1)$ and $a_2 = a/2(\sqrt{3}, -1)$ are the direct lattice vectors of graphene. The nearest-neighbor coupling, which is characterized by the hopping energy $\gamma$, is also shown. (b) The first Brillouin zone of reciprocal lattice of graphene. Points $K$ and $K'$ are two degenerate Dirac points, corresponding to two valleys of low energy spectrum of graphene. The blue line with arrows shows polarization of the time-dependent electric field of the pulse. Angle $\theta$ characterizes the polarization of the pulse.

The Hamiltonian of electrons in graphene in the optical field has the form

$$\mathcal{H} = \mathcal{H}_0 + e\mathbf{F}(t)\mathbf{r}$$

(2)

and $\mathbf{F}(t) = [F(t)\cos \theta, F(t)\sin \theta]$. Below we consider the case of $\theta = 0$ only, i.e., the pulse is polarized along the $x$-axis. We consider a nearest neighbor tight-binding model, which describes the coupling between two sublattices A and B of graphene with coupling constant $\gamma = -3.03$ eV [1, 2, 27, 28] —see Figure 4.1. In the reciprocal space, the corresponding Hamiltonian $H_0$ is a $2\times2$ matrix of the form

$$\mathcal{H}_0 = \begin{pmatrix}
0 & \gamma f(k) \\
\gamma f^*(k) & 0
\end{pmatrix}$$

(3)

where $\gamma = -3.03$ eV is the hopping integral and

$$f(k) = \exp\left(i\frac{ak_x}{\sqrt{3}}\right) + 2 \exp\left(-i\frac{ak_x}{2\sqrt{3}}\right) \cos\left(\frac{ak_y}{2}\right)$$

(4)

The energy spectrum of Hamiltonian $H_0$ consists of conduction band ($\pi^*$ or antibonding band) and valence bands ($\pi$ or bonding band) with the energy dispersion $E_c(k) = -\gamma|f(k)|$ (conduction band) and $E_v(k) = \gamma|f(k)|$ (valence band). The corresponding wave functions are

$$\Psi_k^{(c)}(\mathbf{r}) = \frac{e^{i\mathbf{k}\cdot\mathbf{r}}}{\sqrt{2}} \begin{pmatrix} 1 \\ e^{-i\phi_k}\end{pmatrix}$$

(5)

and

$$\Psi_k^{(v)}(\mathbf{r}) = \frac{e^{i\mathbf{k}\cdot\mathbf{r}}}{\sqrt{2}} \begin{pmatrix} -1 \\ e^{-i\phi_k}\end{pmatrix}$$

(6)
Where \( f(k) = |f(k)|e^{i\phi_k} \). The wave functions \( \Psi_k^{(c)} \) and \( \Psi_k^{(v)} \) have two components belonging to sublattices A and B, respectively. When the duration of the laser pulse is less than the characteristic electron scattering time, which is \( \sim 10–100 \text{ fs} \) [49-57], the electron dynamics in external electric field of the optical pulse is coherent and can be described by the time-dependent Schrödinger equation

\[
i\hbar \frac{d\Psi}{dt} = \mathcal{H}\Psi
\]

(7)

where the Hamiltonian (2) has explicit time dependence.

The electric field of the optical pulse generates both interband and intraband electron dynamics. The interband dynamics introduces a coupling of the states of the conduction and valence bands and results in redistribution of electrons between two bands. For dielectrics, such dynamics results in its metallization, which manifest itself as a finite charge transfer through dielectrics and finite conduction band population after the pulse ends. It is convenient to describe the intraband dynamics, i.e., the electron dynamics within a single band, in the reciprocal space. In the reciprocal space, the electron dynamics is described by acceleration theorem, which has the following form:

\[
\hbar \frac{dk}{dt} = eF(t).
\]

(8)

The acceleration theorem is universal and does not depend on the dispersion law. Therefore, the intraband electron dynamics is the same for both conduction and valence bands. For an electron with initial momentum \( \mathbf{q} \), the electron dynamics is described by the time-dependent wave vector, \( k_T(q,t) \), which is given by the solution of Eq. (8),

\[
k_T(q,t) = q + \frac{e}{\hbar} \int_{-\infty}^{t} F(t_1) dt_1.
\]

(9)
The corresponding wave functions are the Houston functions [64], $\Phi_{\alpha q}^{(H)}(r,t)$,

$$\Phi_{\alpha q}^{(H)}(r,t) = \Psi^{(\alpha)}_{k_T(q,t)}(r)e^{-i \frac{e}{\hbar} \int_{-\infty}^{t} dt' E_o[k_T(q,t')]},$$

(10)

where $\alpha = v$ (valence band) or $\alpha = c$ (conduction band).

Using the Houston functions as the basis, we express the general solution of the time-dependent Schrödinger equation (7) in the following form:

$$\Psi_q(r,t) = \sum_{\alpha=v,c} \beta_{\alpha q}(t) \Phi_{\alpha q}^{(H)}(r,t).$$

(11)

The solution (11) is parametrized by initial electron wave vector $q$. Due to universal electron dynamics in the reciprocal space, the states, which belong to different bands (conduction and valence bands) and which have the same initial wave vector $q$, will have the same wave vector $k_T(q,t)$ at a later moment of time $t$. Since the interband dipole matrix element, which determines the coupling of the conduction and valence band states in the external electric field, is diagonal in the reciprocal space, then the states with different initial wave vectors are not coupled by the pulse field. As a result in Eq. (11), for each value of initial wave vector $q$, we need to find only two time-dependent expansion coefficients $\beta_v(q,t)$ and $\beta_c(q,t)$. Such decoupling of the states with different values of $q$ is the property of coherent dynamics. For incoherent dynamics, the electron scattering couples the states with different wavevectors $q$. In this case, the dynamics is described by the density matrix.

The expansion coefficients satisfy the following system of differential equations:

$$\frac{d \beta_{v q}(t)}{dt} = -i \frac{F(t)Q_q(t)}{\hbar} \beta_{v q}(t),$$

(12)

$$\frac{d \beta_{c q}(t)}{dt} = -i \frac{F(t)Q_q^*(t)}{\hbar} \beta_{c q}(t),$$

(13)
where the vector-function $Q_q(t)$ is proportional to the inter-band dipole matrix element

$$Q_q(t) = \mathbf{D}[k_T(q,t)] e^{-\frac{i}{\hbar} \int_{-\infty}^{t} dt_1 \{E_c[k_T(q,t_1)] - E_v[k_T(q,t_1)]\}},$$  

(14)

where $\mathbf{D}(k) = [D_x(k), D_y(k)]$ is the dipole matrix element between the states of the conduction and valence bands with wave vector $k$, i.e.,

$$\mathbf{D}(k) = \langle \psi^{(c)}_k | e^r | \psi^{(v)}_k \rangle.$$  

(15)

Substituting the conduction and valence band wave functions (5) and (5) into Eq. (15), we obtain the following expressions for the interband dipole matrix elements:

$$D_x(k) = \frac{ea}{2\sqrt{3}} \frac{1 + \cos \left(\frac{ak_y}{2}\right) \left[\cos \left(\frac{3ak_y}{2\sqrt{3}}\right) - 2 \cos \left(\frac{ak_y}{2}\right)\right]}{1 + 4 \cos \left(\frac{ak_y}{2}\right) \left[\cos \left(\frac{3ak_y}{2\sqrt{3}}\right) + \cos \left(\frac{ak_y}{2}\right)\right]}$$  

(16)

$$D_y(k) = \frac{ea}{2} \frac{\sin \left(\frac{ak_y}{2}\right) \sin \left(\frac{3ak_y}{2\sqrt{3}}\right)}{1 + 4 \cos \left(\frac{ak_y}{2}\right) \left[\cos \left(\frac{3ak_y}{2\sqrt{3}}\right) + \cos \left(\frac{ak_y}{2}\right)\right]}.$$  

(17)

The system of equations (12) and (13) describes the interband electron dynamics and determines the mixing of the conduction band and the valence band states in the electric field of the pulse. There are two solutions of the system (12) and (13), which correspond to two initial conditions: $(\beta_v q, \beta_c q) = (1, 0)$ and $(\beta_v q, \beta_c q) = (0, 1)$. These solutions determine the evolution of the states, which are initially in the valence band or the conduction band, respectively.

For undoped graphene, all states of the valence band are occupied, and all states of the conduction band are empty. For an electron, which is initially in the valence band the mixing of the states of different bands is characterized by the time-dependent component $|\beta_c q(t)|^2$. We can also define the time-dependent total occupation of the conduction band for undoped graphene from the following expression:
\[ N_{CB}(t) = \sum_{\mathbf{q}} |\beta_{c\mathbf{q}}(t)|^2, \]

where the sum is over the first Brillouin zone and the solution \( \beta_{c\mathbf{q}}(t) \) in Eq. (18) satisfies the initial condition \( (\beta_{c\mathbf{q}}, \beta_{c\mathbf{q}}) = (1,0) \).

Redistribution of electrons between the conduction and the valence bands in time-dependent electric field also generates electric current, which can be calculated in terms of the velocity operator as below:

\[
J_j(t) = \frac{e}{a^2} \sum_{\mathbf{q}} \sum_{\alpha_1 = v,c} \sum_{\alpha_2 = v,c} \beta_{\alpha_1\mathbf{q}}^*(t) \mathcal{V}_{j\alpha_1\alpha_2}^{\alpha_2\alpha_1} \beta_{\alpha_2\mathbf{q}}(t),
\]

where \( j = x,y \) and \( \mathcal{V}_{j\alpha_1\alpha_2}^{\alpha_2\alpha_1} \) are the matrix elements of the velocity operator \( \mathcal{V}_j = \frac{1}{\hbar} \frac{\partial \mathcal{H}_0}{\partial k_j} \) between the conduction and valence band states. With the known wave functions (5) and (6) of the conduction and valence bands, the matrix elements of the velocity operator are

\[
\gamma_{\alpha_1\alpha_2}^{\alpha_1\alpha_2} = \frac{a\gamma}{\sqrt{3}\hbar} \left[ \sin \left( \frac{ak_y}{\sqrt{3}} - \phi_k \right) + \sin \left( \frac{ak_x}{\sqrt{3}} + \phi_k \right) \cos \frac{ak_y}{2} \right],
\]

\[
\gamma_{\alpha_1\alpha_2}^{\alpha_1\alpha_2} = \frac{a\gamma}{\hbar} \cos \left( \frac{ak_y}{\sqrt{3}} - \phi_k \right),
\]

\[
\gamma_{\alpha_1\alpha_2}^{\alpha_1\alpha_2} = -i \frac{2a\gamma}{\sqrt{3}\hbar} \cos \left( \frac{ak_y}{\sqrt{3}} - \phi_k \right) - \cos \left( \frac{ak_x}{\sqrt{3}} + \phi_k \right) \cos \frac{ak_y}{2},
\]

\[
\gamma_{\alpha_1\alpha_2}^{\alpha_1\alpha_2} = -i \frac{2a\gamma}{\hbar} \sin \left( \frac{ak_x}{\sqrt{3}} + \phi_k \right) \cos \frac{ak_y}{2}.
\]

The interband matrix elements of the velocity operator, \( \gamma_{\alpha_1\alpha_2}^{\alpha_1\alpha_2} \), are related to the interband dipole matrix elements, \( \mathcal{V}_{j\alpha_1\alpha_2}^{\alpha_1\alpha_2} = iD_j(\mathbf{k}) [E_{\alpha_1}(\mathbf{k}) - E_{\alpha_2}(\mathbf{k})] / \hbar \) and \( \mathcal{V}_{j\alpha_1\alpha_2}^{\alpha_1\alpha_2} = iD_j(\mathbf{k}) [E_{\alpha_1}(\mathbf{k}) - E_{\alpha_2}(\mathbf{k})] / \hbar \).

Within the nearest neighbor tight-binding model, the graphene has electron-hole symmetry, which results in the relation \( \gamma_{\alpha_1\alpha_2}^{\alpha_1\alpha_2} = -\gamma_{\alpha_2\alpha_1}^{\alpha_1\alpha_2} \). Inclusion into the model the higher order tight-
binding couplings, e.g., second-nearest-neighbor terms, introduces electron-hole asymmetry, which results in different magnitudes of velocity in the conduction and valence bands [65]. This asymmetry is weak and does not change the main results presented below.

If the direction of electric field of the pulse is along the direction of high symmetry of graphene crystal, then the current is generated along the direction of electric field of the pulse only, $J_{\parallel}$. For graphene, the directions of high symmetry correspond to polarization angles $\theta = 0$ and 30°. If the polarization of electric field is not along the direction of high symmetry of graphene, then the current is generated in both the direction of the field, $J_{\parallel}$, and in the direction perpendicular to the field, $J_{\perp}$. Our results show that the vertical component of the current is more than two orders of magnitude smaller than the parallel component of the current. Therefore, we calculate only the parallel component of the current.

The generated current results in charge transfer through the system, which is determined by an expression

$$Q_{tr} = \int_{-\infty}^{\infty} dt \, J_{\parallel}(t).$$

The transferred charge is nonzero only due to the irreversibility of electron dynamics in the optical pulse. For completely reversible dynamics, when the system returns to its initial state, the transferred charge is exactly zero. Indeed, since the current can be expressed in terms of polarization $\mathbf{P}(t)$ of the electron system as $\mathbf{J}(t) = d\mathbf{P}(t)/dt$, then the transferred charge is determined by the residual polarization of the system, i.e., the polarization after the pulse ends, $Q_{tr} = \mathbf{P}(t \to \infty)$. The residual population is nonzero only for irreversible dynamics.
4.3 Results and Discussion

4.3.1 Conduction band population

Electron dynamics in an optical field is determined by two interrelated properties of graphene: (i) zero band gap, which results in strong interband mixing even in a weak electric field, and (ii) strong dependence of interband dipole matrix elements on the wave vector. These matrix elements, $D_x$ and $D_y$, are singular at the Dirac points, K and K', as $\propto 1/\Delta k$, where $\Delta k = |k - k_F|$ is the distance in the reciprocal space from nearest Dirac point; see Figure 4.2. Away from the Dirac points, $D_x \sim D_y \sim ea/2 \approx 1.2 \, e\text{Å}$. At the center of the Brillouin zone (the Γ point), $D_x = D_y = 0$. Thus there is strong interband coupling at the Dirac points and no coupling at the Γ point.

![Interband dipole matrix element $D_x$ as a function of the wave vector $k$. The red lines show the boundary of the first Brillouin zone. The dipole matrix element is singular near the Dirac points (K and K’ points).](image)

A strong optical electric field causes redistribution of electrons between the CB and the VB. The total CB population, $N_{CB}(t)$ [see Eq. (18)]. It is displayed as a function of time $t$ together with the corresponding time-dependent electric field, $F(t)$, in Figure 4.3(a). Its qualitative
features are in sharp contrast with those of dielectrics [20, 47]. First, the electron kinetics is dramatically irreversible: when the pulse is over, the CB population does not return to zero staying at a high residual level \( N_{\text{res}} \) which is close to the maximum CB population during the pulse, \( N_{\text{max}} \). The second, related feature is that there is \( a \sim \pi/2 \) phase shift between \( N_{\text{CB}}(t) \) and the electric field, \( F(t) \): the maximums of the conduction band population occur at zeros of the electric field. In contrast, for dielectrics, the CB population adiabatically follows the field, and their maximums coincide with a good accuracy [20, 47].

Such irreversible electron dynamics takes place for all pulse amplitudes \( F_0 \) as Figure 4.3(b) clearly demonstrates. The maximum CB population is reached at \( t \approx 1 \) fs; the residual (at the end of the pulse) CB population, \( N_{\text{CB}}^{(\text{res})} \), is close to \( N_{\text{CB}}^{(\text{max})} \) in all cases [Figure 4.3(c)]. We have found that the CB population has only a weak dependence on the polarization direction, and the results similar to Figure 4.3 are obtained for other polarizations.

As we interpret, the irreversible electron dynamics is due to the gapless energy dispersion in graphene and the strong dependence of the interband dipole matrix elements, \( D_x \) and \( D_y \), on the wave vector. This causes a unique dependence of the Zener tunneling rate, \( \Delta_l \propto l^{-1} \), where \( l \)
is the number of unit cells through which the electron tunnels to cross the band gap (see Chapter 3); in sharp contrast, for 3D crystals, this dependence on $l$ is exponential. This weak $l$ dependence brings about strong resonance transitions between the VB and CB leading to dephasing (*Landau damping*), which effectively causes irreversibility for our time intervals.

The singularities of the dipole matrix elements at the Dirac points also result in a highly nonuniform distribution of the conduction band population in the reciprocal space, $N_{CB}(k,t) = |\beta_{k}(t)|^2$, which is shown in Figure 4.4. This population dynamics is unusual and dramatic. The electrons are accelerated by the field along its polarization direction ($x$-axis) as determined by the time-dependent wave vector $k(t)$,

$$
\mathbf{k}(t) = \frac{e}{\hbar} \int \mathbf{F}(t) dt
$$

(25)

Initially, for $t < -0.75$ fs, the field is negative which accelerates the electrons to the right in Figure 4.4. At the Dirac points due to the singular and large interband dipoles, the electrons are transferred $\text{VB} \rightarrow \text{CB}$, which shows as two “jets” of high electron population at $k_x \approx 1$ Å$^{-1}$ — see panels for $t = -1.5, -0.75$ fs. Then the field changes its sign, and electrons start to move left and also undergo further $\text{VB} \rightarrow \text{CB}$ transitions leading to the appearance of the jets at $k_x \approx -1$ Å$^{-1}$ and interference fringes at the $k_x \approx 1$ Å$^{-1}$ Dirac point for $t \geq 0.75$ fs. Further, additional electrons are transferred causing the interference fringes at the $k_x \approx -1$ Å$^{-1}$ Dirac points for $t = 1.5$ fs. The distribution becomes completely symmetric at the end of the pulse ($t = 2.25$ fs), which is a consequence of the zero pulse area.
Figure 4.4 Conduction band population as a function of the wave vector at different moments of time. Only the first Brillouin zone of the reciprocal space is shown. The peak electric field of the pulse is $F_0 = 1$ V/Å. Different colors correspond to different values of the conduction band population.

In Figure 4.5, the results shown in Figure 4.4 are redrawn beyond the first Brillouin zone. The spots of high conduction band population form two parallel arrays oriented along axis $x$, i.e. along the direction of the electric field. The number of spots in each array depends on the intensity of the optical pulse.
Figure 4.5 Residual conduction band population in the extended Brillouin zone scheme. Points $K$ and $K'$, which correspond to two valleys of graphene. The red dotted line shows the boundary of the first Brillouin zone. Different colors correspond to different values of the conduction band population as shown in the figure. The polarization of the optical pulse is along axis x.

Residual (after the pulse end) distributions $N_{(res)}(k)$ of the CB electrons in the reciprocal space for various field amplitudes $F_0$ are displayed in Figure 4.6. They exhibit the jets at the Dirac points extended in the direction of the external field, which are modulated by the interference fringes. The extension, $\Delta k$, of the jets increases approximately proportionally to the field; it is defined by the acceleration in the average field during half-period: $\Delta k \sim eF_0 / \omega$. For instance, for $F_0 = 1.5$ V/Å, $\Delta k \sim 1$ Å$^{-1}$, in agreement with Figure 4.6. The spacing between the interference fringes, $\delta k$, is reciprocal to the nonlocality scale, i.e., the length electron displaces
during the optical cycle, $\delta k \sim \omega / v_p \sim 0.2 \text{ Å}^{-1}$, where $v_p \approx 10^5 \text{ cm/s}$ is the Fermi velocity; this estimate is also in agreement with Figure 4.6.

The residual distribution of Figure 4.6 shows the fringes with very high contrast: the maximum population probability, $N_{CB}^{(res)}(k) \approx 1$, and practically zero minimum population probability. Note that these fringes are created by a femtosecond pulse but can be relatively long-lived, decaying with electron collision time $\tau$.

![Figure 4.6 Residual conduction band population for different amplitudes of the optical pulse. Only the first Brillouin zone is shown. The polarization of electric field is along axis $x$.](image)

At low excitation frequencies, we can estimate this time for doped graphene with equilibrium CB electron density $n$ as $\tau = \hbar / \mu \sqrt{\pi n / (e v_p)}$, where $\mu$ is the electron mobility. Setting
\[ \mu \approx 2.5 \times 10^4 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1} \text{ at } n \approx 5 \times 10^{12} \text{ cm}^{-2} \text{ [66, 67]} \text{ and } v_F = 1.15 \times 10^8 \text{ cm/s} \text{ [68]}, \text{ we obtain } \tau \approx 0.6 \text{ ps}. \text{ In contrast, at optical excitation frequencies and high intensities, time } \tau \text{ is reduced and is measured to be } \tau \sim 140 \text{ fs} \text{ [54]; for very high excitation densities, carrier multiplication processes become important, further reducing } \tau \text{ to a few tens of femtoseconds} \text{ [53]. Electron-phonon processes are relatively slow, with scattering time } \tau \geq 600 \text{ fs} \text{ [53]. Even the fastest electron collisions, with tens of femtosecond time, are much slower than the subcycle dynamics of } \lesssim 1 \text{ fs duration predicted in this article. The femtosecond and attosecond momentum imaging [69] is potentially capable of measuring the ultrafast transient dynamics predicted by Figure 4.4.}

![Figure 4.7 Residual conduction band population as a function of energy for different amplitudes. The polarization of the optical pulse is along x-axis.](image-url)
In Figure 4.7 the function $N_{cb}^{(\text{ee})}(k)$ is shown for different amplitudes $F_0$ of the optical pulse. The conduction band population as a function of energy has a single peak structure with a well-defined maximum at finite electron energy. For example, for $F_0 = 0.6 \text{ V/Å}$, the maximum of $N_{c,E}(E)$ is at $E \approx 2 \text{ eV}$. The width of the peak also increases with increasing the pulse amplitude. At $F_0 = 1.5 \text{ V/Å}$ the peak occupies the whole conduction band, i.e. after the pulse ends all the conduction band states are partially occupied by electrons. The conduction band population exactly at the Dirac point, i.e. at zero energy, is small. Such behavior is correlated with the distribution of the conduction band population in the reciprocal space shown in Figure 4.6.

The data are shown for a state with initial wave vector $\mathbf{q}$. The CB population is calculated as $|\beta_{q}(t)|^2$ and the dipole matrix element is defined as $D_{x,(k,(q,t))}$. Two different initial wave vectors in panels (a) and (b) correspond to small and large residual conduction band populations, respectively. The inset in panel (a) illustrates the electron dynamics in the reciprocal space schematically: the electron is transferred along the path “1”→“2”→“3”→“2”→“1”. The polarization of the optical pulse is along axis $x$.

The formation of the localized regions with high conduction band population, which is illustrated in Figure 4.4, Figure 4.5, and Figure 4.6, is due to the singularity of the intraband dipole matrix elements at the Dirac points. The interband dipole matrix elements are large near the Dirac points and are diverging exactly at the Dirac points. An electron with initial wave
vector $\mathbf{q}$ propagates in the reciprocal space along the direction of electric field and the electron wave vector at a moment of time $t$ is given by the function $\mathbf{k}_{\gamma}(\mathbf{q}, t)$; see Eq. (9). The trajectory of such an electron is shown schematically in the inset in Figure 4.8(a), where the electron, which is initially at point “1”, is transferred along the path “1”→“2”→“3”→“2”→“1” during the pulse. Since the area under the pulse is zero, the electron returns to its initial point “1”. Along this closed path the interband coupling, which is proportional to the interband dipole matrix element, is the strongest near the point “2”, closest to the Dirac points. Thus the strongest mixing of the CB and VB states occurs when the electron passes through point “2”. For the closed path “1”→“3”→“1” there are two passages of point “2”. As a result, there are two strong changes in CB population. These two changes can be constructive or destructive, resulting in final large or small CB population, respectively.

These two possibilities are shown in Figure 4.8, where the time-dependent CB population is shown for two initial wavevectors $\mathbf{q}$. The time-dependent interband dipole matrix element, $D_{\chi}$, calculated at wave vector $\mathbf{k}_{\gamma}(\mathbf{q}, t)$, is also shown in Figure 4.8. The two maxima in the time-dependent dipole matrix element correspond to two passages of the point “2” shown in the inset in Figure 4.8(a). For both initial wave vectors [see Figure 4.8(a) and (b)] the maxima of the dipole matrix element are correlated with large changes in the CB population. In Figure 4.8(b) these changes are constructive resulting in large CB population after the pulse ends, while in Figure 4.8(a) the changes are destructive, which results in small final CB population. Whether changes of the CB population are constructive or destructive is determined by the phase accumulated between two consecutive passages of point “2”. The phase is determined by exponential factor in the expression (14) for the vector function $Q_{\mathbf{q}}(t)$. 
4.3.2 Transferred charge

A strong optical pulse applied to metal or dielectric causes transfer of charge parallel to the pulse field; the direction of the transfer (the sign of the transferred charge) is determined by the carrier-envelop phase (CEP) of the pulse [21, 45]. In this article, the maximum of the carrier oscillation and its envelope coincide, which implies zero CEP (effect of the CEP on graphene high-field behavior will be considered elsewhere). In such a case, the transfer in dielectric occurs in the direction of the field maximum, and in metal in the opposite direction [20, 21, 48]. Below we show that graphene (a semimetal) is unique and different from both metals and insulators.

Given that the area of the pulse is zero, the transferred charge is entirely due to optical nonlinearity. Current density $j$ and polarization $P$ are exactly related, $j = \dot{P}$. The density of the net transferred charge per pulse, $Q_\alpha$, is thus determined by the residual polarization after the pulse end, $Q_\alpha = P^{(res)}_{\alpha}$, where $\alpha$ is the direction of the field (charge transfer direction). Hence, in a single-pulse experiment, the charge transfer is strictly zero in the absence of relaxation (i.e., for adiabatic, reversible processes). Consequently, in graphene, where the strong-field processes are highly irreversible, and the residual charges dominate, the charge transfer should be uniquely strong.

In Figure 4.9, the results for induced current and charge transfer is illustrated. Panel (a) displays temporal dynamics of the current. In the first half of the pulse, this current is negative, while in the second half it is positive where also significant relaxation is evident in a strong field, $F_0 = 2 \text{ V/Å}$, case.

The total transferred charge per pulse, $Q_\alpha$, shown in Figure 4.9(b), is positive (as for dielectrics) for $F_0 \leq 1.5 \text{ V/Å}$ and negative for larger fields (i.e., the transfer occurs opposite to the direction of the maximum field, as for metals); $Q_\alpha$ rather weakly depends on doping.
Figure 4.9 The results for induced current and transferred charge density in graphene.
(a) Electric current density in graphene as a function of time for two amplitudes, $F_0 = 1$ V/Å and 2 V/Å.
(b) Transferred charge density through graphene monolayer as a function of $F_0$ for different levels of doping (defined by the Fermi energy $E_F$).

The charge transfer per pulse in bulk silica (quartz) [21] is $Q_u \sim 10^{-5}$ C/m$^2$ at $F_0 \approx 2$ V/Å. To compare with graphene, it should be multiplied by the thickness of the graphene, ~0.1 nm, which yields for quartz an equivalence of $Q_u \sim 10^{-15}$ C/m per atomic monolayer. Our present result is $Q_u \geq 10^{-9}$ C/m. Thus, in strong-field charge transfer, graphene is six orders of magnitude more efficient than quartz.

4.4 Conclusion

To summarize, we have shown that graphene subjected to an ultrafast (one optical oscillation) and strong ($\sim 1$ V/Å) optical pulse exhibits fundamental behavior dramatically different from both insulators and metals. Field-induced, Zener-type VB $\leftrightarrow$ CB electron transfer is deeply irreversible (nonadiabatic): the residual (after-pulse) CB population is close to the maximum one. The reciprocal space (quasimomentum) dynamics is developing on a time scale $\sim 1$ fs forming momentum distribution, which exhibits deep fringes with the population
probability changing in the full interval between one and zero with the periodicity independent of the field amplitude. This unique periodic distribution can be accessed experimentally.

In our calculations above we have described the interaction of optical pulse with graphene within coherent electron dynamics, assuming that the duration of the pulse is longer than the corresponding relaxation times. The relaxation times during ultrafast excitation of graphene have been investigated experimentally [53, 54]. The carrier-carrier scattering in Ref. [54] is observed to occur during 30–140 fs. In Ref. [53], the observed electron-electron scattering kinetics unfolds on times 10 fs or longer. The field-induced processes that we predicted are extremely fast: the populations of the valence and conduction changes within subcycle intervals, on the time scale of 500 attoseconds or shorter. In our article, the superstrong near-single-oscillation pulse is not longer than 4 fs, which is shorter than experimentally observed scattering times, and it drives very significant changes in the electron distribution, which is also highly anisotropic.

The strong optical pulse causes the net charge transfer (per unit width of the graphene, per pulse) $Q_{tr} \sim 10^{-9}$ C/m, which corresponds to a femtosecond pulse of electric current in the plane of graphene with peak density $j \sim 10^{16}$ A/m$^2$. The charge is transferred in the direction of the maximum field for moderate field amplitudes ($F_0 \leq 1.5$ V/Å) and opposite to that for high fields. This ultrafast charge transfer phenomenon is almost independent of graphene doping. The charge transfer in fused silica during propagation of femtosecond optical pulse has been measured experimentally in Ref. [21, 47]. A similar technique can be applied for graphene. The femtosecond currents and charge transfer in graphene may provide a fundamental basis for detection and calibration of ultrashort intense laser pulses. They are promising for petahertz-bandwidth information processing.
CHAPTER FIVE: BUCKLED GRAPHENE-LIKE MATERIALS IN ULTRAFAST AND STRONG LASERS

5.1 Introduction

Novel Dirac materials such as silicene or germanene [70-76] are monolayers of silicon or germanium with hexagonal lattice structures where charge carriers at the Fermi surface are, as in graphene, Dirac fermions [77-85]. Recently, silicene has shown promise for applications in electronics such as field-effect transistors (FETs) [41, 86-88] where, being a semiconductor, it has a natural advantage over graphene that is a semimetal. Below we will consider silicene but all qualitative results are also valid for germanene.

In this chapter we theoretically predict that a single monolayer of silicene (germanene) is controllable at optical frequencies by a normal component of the incident optical field just like the gate voltage controls channel current in FETs. The main difference between silicene and graphene is that due to a larger radius of a Si (or Ge in germanene) atom compared to a C atom, the corresponding hexagon lattice in silicene has a buckled structure [89] consisting of two sublattices that are displaced vertically by a finite distance $L_z \sim 0.5$ Å ; see Figure 5.1(a). As a result, silicene has large spin-orbit interaction, which opens up band gaps at the Dirac points ($\Delta_{so} \approx 1.55–7.9$ meV for silicene [4,5] and $\Delta_{so} \approx 24–93$ meV for germanene [72, 76]). For graphene, the corresponding spin-orbit-induced gap is very small, 25 μeV [90]. The buckled structure of the silicene/germanene lattice also allows for the band gap to be controlled by an applied perpendicular electric field [91]: the band gap increases almost linearly with this electric field.
Phenomena in silicene in a strong optical pulse field are illustrated in Figure 5.1(b) – (e). A strong optical field causes electron transfer in the direction of the force [21, 92]. In fact, a strong optical field in the z-direction (normal to the silicene plane) decreases symmetry of the system from honeycomb (six-order, centrosymmetric) to triangular (third-order, noncentrosymmetric). This leads to the appearance of effects such as optical rectification and induction of currents normal to the in-plane component of the applied electric field.

Microscopically, the z component of the strong field causes transfer of electrons between the sublattices. Assume for certainty that, for the chosen pulse, electrons are transferred from A to B. (Note that the change of the maximum field to the opposite, i.e., change of the carrier-envelope phase of the pulse by \(\pi\), would obviously cause an opposite transfer.) In the case of in-plane field \(F_{2D}\) polarized in the y-direction, there is an electron transfer in both y and x directions; see Figure 5.1(b). The symmetry of the system dictates that with the reversal of \(F_{2D}\) (for the same z component, \(F_z\)) the y-current changes to the opposite, but the x-current does not change, as shown in Figure 5.1(c). This implies, in particular, that the system causes optical rectification in the x-direction, which is due to the absence of symmetry with respect to the reflection in the yz plane for either sublattice.

A fundamentally different scenario takes place for \(F_{2D}\) in the x-direction; see Figure 5.1(d) and 1(e). In this case, there is no current in the y-direction due to symmetry on reflection in the xz-plane. With respect to field \(F_{2D}\) changing to the opposite, the x-current does not have any definite parity, which is rectification in the x direction.
Figure 5.1 Schematic of Buckled 2D nanocrystals and charge transfer mechanism in the ultrafast field.
(a) Hexagonal lattice structure of 2D silicene. The lattice consists of two inequivalent sublattices labeled by “A” and “B”. Sublattices A and B are shifted in the z-direction by distance $L_z$. The angle of incidence of the pulse is $\theta$. (b) Schematic of in-plane electron transfer induced by in-plane pulse electric field $F_{2D}$ directed along the y-axis as shown. The curved red arrows indicate the electron transfer between the sublattices. (c) The same as (b) but for the opposite $F_{2D}$. (d) The same as (b) but for the field directed along the x-axis. (e) The same as (d) but for the opposite $F_{2D}$. The z component of the pulse field has the same direction in all cases.
To provide for the field-effect control of optical phenomena in silicene, the $z$ component of the pulse electric field should be strong enough: $F_z \geq h\omega / (eL_z) \sim 2 \text{ V/Å}$, where $\omega$ is the optical frequency. Then, necessarily, the pulse should be very short, on the femtosecond scale, to allow the processes to be completed before significant damage to the lattice may have occurred; see Section 5.2 below. For such fields, there may be partial adiabaticity (reversibility) set on, which we will show below in Section 5.3.

5.2 Theory and Model Description

We study electron dynamics in buckled Dirac systems (silicene/germanene) in the electric field of the optical pulse, which has a duration of few femtoseconds. We assume that the pulse has the following profile

$$F(t) = F_0 e^{-u^2} (1 - 2u^2)$$

(1)

Where $F(t)$ is the electric field and $F_0$ is the amplitude, which is related to the pulse power $P = cF_0^2 / 4\pi$, $c$ is the speed of light, $u = t/\tau$, and $\tau$ is the pulse length, which is set $\tau = 1 \text{ fs}$ corresponding to carrier frequency $h\omega \approx 1.5 \text{ eV}$. Note that due to this parameterization, the pulse always has zero area, $\int_{-\infty}^{\infty} F(t)dt = 0$.

We consider p-polarized laser pulse with polarization direction parallel to the plane of incidence, orientation of which is determined by an angle $\phi$ measured relative to axis $x$. Here the $x$ and $y$ coordinate systems are introduced in the plane of silicene/germanene and are determined by their crystallographic structure - see Figure 5.2. The incident angle of the laser pulse is $\theta$.

Similar to graphene, the silicene/germanene monolayer has a hexagonal lattice structure, which is shown in Figure 5.2(a). The lattice has two sublattices, say "A" and "B", and is
determined by two lattice vectors \( a_1 = a / 2(\sqrt{3}, 1) \) and \( a_2 = a / 2(\sqrt{3}, -1) \), where \( a \) is the lattice constant, which is 3.866 Å for silicene and 4.063 Å for germanene. The distance between the nearest neighbor atoms of silicene/germanene is \( a / \sqrt{3} \). The first Brillouin zone of the reciprocal lattice is a hexagon and is shown in Figure 5.2(b). The points \( \mathbf{K} = \frac{2\pi a}{a} \left( \frac{1}{\sqrt{3}}, \frac{1}{3} \right) \) and \( \mathbf{K}’ = \frac{2\pi a}{a} \left( \frac{1}{\sqrt{3}}, -\frac{1}{3} \right) \) are the Dirac points.

Figure 5.2 Representation of direct and reciprocal space (first Brillouin zone) of Silicene/Germanine. (a) Hexagonal lattice structure of 2D silicene/germanene consists of two inequivalent sublattices, which are labeled by "A" and "B". The vectors \( a_1 = a / 2(\sqrt{3}, 1) \) and \( a_2 = a / 2(\sqrt{3}, -1) \) are the direct lattice vectors. The nearest neighbor coupling, characterized by the hopping integral \( \gamma \), is also shown. (b) The first Brillouin zone of silicene/germanene. Points \( \mathbf{K} \) and \( \mathbf{K}’ \) are two degenerate Dirac points, corresponding to two valleys of the low energy spectrum of silicene/germanene. Blue line with arrow shows in-plane (x-y plane) polarization of the time-dependent electric field of the pulse. The in-plane polarization is characterized by azimuthal angle \( \varphi \), i.e. angle between the x−y component \( \vec{F}_{2d} \) of the electric field of the pulse and \( x \)-axis.

Due to a larger atomic size compared to the carbon atom, the silicon and germanium form the buckled crystal structure with a relative shift of sublattices A and B in the \( z \)-direction by distance \( L_z \). This distance is 0.46 Å and 0.66 Å for Silicene and Germanene, respectively.
Graphene monolayer, for which the spin-orbit interaction is small (around 0.03 meV), the energy gaps at the Dirac points are zero and the low energy spectra are described by the relativistic Dirac equation. For silicene/germanene, the spin-orbit interaction (around 10-100 meV) opens a finite gap in the range of 10-100 meV [91]. Although the finite gap in the energy spectrum of silicene/germanene system modifies the low-energy electron transport as well as its weak magnetic field correlation properties, spin-orbit interaction has a negligible effect on the electron dynamics in strong electric field of the optical pulse. Such a strong field introduces the energy scale on the order of a few eV, which is much larger than the energy scale of spin-orbit coupling in buckled Dirac materials. At the same time, the buckled structure of silicene/germanene introduces a strong sensitivity of the system to external perpendicular electric field [91]. Therefore, if the electric field of the optical pulse has a component perpendicular to the layer, then the electron dynamics in the laser pulse can be strongly modified. Hence, in this chapter we disregard the effect of spin-orbit interaction in electron dynamics but take into account their buckled structure, i.e. sensitivity to perpendicular electric field.

The Hamiltonian of an electron in silicene/germanene in the field of the optical pulse has the form

\[ \mathcal{H} = \mathcal{H}_0 + e \mathbf{F}_{2d}(t) \mathbf{r} + \frac{eL_F F_z(t)}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, \]

where \( \mathcal{H}_0 \) is the field-free electron Hamiltonian, \( \mathbf{r} = (x, y) \) is a 2D vector, \( \mathbf{F}_{2d} = (F_x(t), F_y(t)) = F(t) \sin \theta (\cos \phi, \sin \phi) \), and \( F_z(t) = F(t) \cos \theta \). Here the matrix form of the Hamiltonian corresponds to two components of the wave functions \( \psi_A \) and \( \psi_B \), which describe the amplitudes of an electron to be on the lattice site A and B, respectively.
As we mentioned above, the field-free electron Hamiltonian, $H_0$, is described by the nearest neighbor tight-binding model of silicene/germanene without spin-orbit terms. This Hamiltonian is the same as the free-field Hamiltonian of graphene (see Chapter 2) and describes the tight-binding coupling between two sublattices ”A” and ”B” - see Figure 5.2. In the reciprocal space, the Hamiltonian $H_0$ is a $2 \times 2$ matrix of the form

$$
\mathcal{H}_0 = \begin{pmatrix}
0 & \gamma f(k) \\
\gamma f^*(k) & 0
\end{pmatrix}
$$

where $\gamma = -1.6 \text{ eV}$ is the hopping integral of silicene and

$$
f(k) = e^{\frac{ik_k}{\sqrt{3}}} + 2e^{\frac{-ik_k}{2\sqrt{3}}} \cos\left(\frac{ak_k}{2}\right)
$$

The energy spectrum of Hamiltonian $H_0$ consists of the conduction ($\pi^*$ or anti-bonding band) and valence bands ($\pi$ or bonding band) with the energy dispersion $E_c(k) = -\gamma |f(k)|$ (CB) and $E_v(k) = \gamma |f(k)|$ (VB). The corresponding wave functions of the conduction and valence bands are

$$
\Psi^{(c)}_k(r) = e^{ikr} \left( \begin{array}{c}
1 \\
ed^{i\hbar k}
\end{array} \right), \quad \Psi^{(v)}_k(r) = e^{ikr} \left( \begin{array}{c}
-1 \\
ed^{i\hbar k}
\end{array} \right)
$$

where $f(k) = |f(k)| e^{i\phi}$. The wave functions $\Psi^{(c)}_k$ and $\Psi^{(v)}_k$ have two components corresponding to sublattices A and B.

The characteristic electron-electron scattering time $\tau_{e-e}$ in silicene/germanene similar to graphene is around 10-100 fs [49-57]. The duration of the pulse in our problem ($\approx 10$ fs) is less than the characteristic scattering time $\tau_{e-e}$. Therefore, the electron dynamics in external electric
field of the optical pulse is coherent and can be described by the time-dependent Schrödinger equation

$$i\hbar \frac{d\Psi}{dt} = \mathcal{H}\Psi$$  \hspace{1cm} (6)$$

where the Hamiltonian (2) has explicit time dependence. The electric field of the optical pulse generates both interband and intraband electron dynamics. The interband dynamics introduces a coupling of the states of the conduction and valence bands and results in redistribution of carriers between two bands. An equivalent theoretical study for dielectric, which then confirmed experimentally, has shown a resultant metallization into the system that manifests itself as a finite charge transfer through dielectrics and finite conduction band population after the pulse ends [21, 47].

Within this formalism, the electron dynamics in the reciprocal space is described by acceleration theorem, which has the following form

$$\hbar \frac{d\mathbf{k}}{dt} = e\mathbf{F}_{2d}(t)$$  \hspace{1cm} (7)$$

The acceleration theorem is universal and does not depend on the dispersion law. Hence, the intraband electron dynamics is equivalent for both the conduction and valence bands. Time-dependent wave vector $\mathbf{k}(\mathbf{q}, t)$ for an electron with initial momentum $\mathbf{q}$, can be found from Eq.(7) as

$$\mathbf{k}_f(\mathbf{q}, t) = \mathbf{q} + \frac{e}{\hbar} \int_{-\infty}^{t} \mathbf{F}_{2d}(t') dt'$$  \hspace{1cm} (8)$$

Using the Houston functions [64] as the basis,
with $\alpha = v$ (VB) or $\alpha = c$ (CB), the general solution of the time-dependent Schrödinger equation is expressed in the following form

$$
\Psi_{q}(r,t) = \sum_{\alpha=v,c} \beta_{\alpha q}(t) \Phi_{\alpha q}(r,t)
$$

(10)

The solution (10) is parameterized by initial electron wave vector $\mathbf{q}$. Due to the fact that the intraband electron dynamics in the reciprocal space is universal, i.e., is the same for both the conduction and valence bands, and is described by universal acceleration theorem (7), the equations which describe the coherent electron dynamics in the field of the pulse become decoupled, that strongly simplifies the problem.

Substituting Eq. (10) into the time-dependent Schrödinger equation (6) and taking into account Eqs. (5) and (9), we obtain that the expansion coefficients $\beta_{\alpha q}$ satisfy the following system of differential equations

$$
\frac{d\beta_{\alpha q}(t)}{dt} = -i \frac{\mathbf{F}_{2q}(t) \mathbf{Q}_{q}(t)}{\hbar} + e \mathbf{F}_{\mathbf{z}}(t) \tilde{L}_{\mathbf{z}}(t, \mathbf{q}) \beta_{\alpha q}(t)
$$

(11)

$$
\frac{d\beta_{c q}(t)}{dt} = -i \frac{\mathbf{F}_{2q}(t) \mathbf{Q}_{q}^{*}(t)}{\hbar} + e \mathbf{F}_{\mathbf{z}}(t) \tilde{L}_{\mathbf{z}}(t, \mathbf{q}) \beta_{c q}(t)
$$

(12)

where the function $\tilde{L}_{\mathbf{z}}(t)$ which is given by the following expression

$$
\tilde{L}_{\mathbf{z}}(t, \mathbf{q}) = L_{\mathbf{z}} e^{\frac{i}{\hbar} \int_{\mathbb{R}} d'r' (E_{r+} - E_{r'})}
$$

(13)

is due to the buckled structure of silicene/germanene and determines the interband coupling corresponding to the perpendicular component of the electric field of the pulse. The vector function $\mathbf{Q}_{q}(t)$ is proportional to the in-plane interband dipole matrix element.
\[ Q_q(t) = D[k_q(q, t)] e^{i \frac{t}{\hbar} \int_{-\infty}^{t} dt' \{ E_i(k_q(t')) - E_i(k_q(q, t')) \}} \]  

(14)

\[ D(k) = [D_x(k), D_y(k)] \] is the interband dipole matrix element, which determines the coupling of the conduction and valence band states with wave vector \( k \) in external electric field and is equal to

\[ D(k) = \langle \Psi_k^{(c)} | e r | \Psi_k^{(v)} \rangle \] 

(15)

Substituting Eq. (5) into Eq. (15), we obtain

\[ D_x(k) = \frac{ea}{2\sqrt{3}} \left( 1 + \cos k_y a/2 \left[ \cos \sqrt{3}k_y a/2 - 2 \cos k_y a/2 \right] \right) \] 

(16)

\[ D_y(k) = \frac{ea}{2} \left( \sin k_y a/2 \sin \sqrt{3}k_y a/2 \right) \] 

(17)

The system of equations (11)-(12) describes the interband electron dynamics and determines the mixing of the CB and the VB states in the electric field of the pulse. For undoped silicene/germanene all states of the VB are initially occupied, and all states of the CB are empty. Then the initial condition for the system (11)-(12) is \( (\beta_{q_x}, \beta_{q_y}) = (1, 0) \) and the mixing of the states of different bands is characterized by \( |\beta_{q}(t)|^2 \). We also define the total time-dependent population of the CB as the following expression

\[ \mathcal{N}_c(t) = \sum_q |\beta_{q}(t)|^2 \] 

(18)

where the sum is over the first Brillouin zone and the solution satisfies the initial condition \( (\beta_{q_x}, \beta_{q_y}) = (1, 0) \). The CB population \( \mathcal{N}_c(t) \) characterizes the electron dynamics in silicene/germanene system and determines whether the dynamics for the entire system is
reversible or not. Namely, the dynamics is reversible if the CB population at the end of the pulse becomes small compared to the maximum CB population throughout the pulse.

### 5.3 Results and Discussion

#### 5.3.1 Band population dynamics in strong pulse field

The principal distinction of silicene from graphene is that the sublattices, A and B, are separated “vertically” (i.e., in the z-direction) by an appreciable distance, $L_z \approx 0.5 \, \text{Å}$; see Figure 5.1(a). The strong field of the optical pulse causes nonperturbative nonlinear changes in the material. Such phenomena are sensitive to the maximum field of the pulse, which is amplitude $F_0$. For our choice of pulse Eq. (1), the maximum of the carrier oscillation occurs at the maximum of the pulse envelope. That is, the carrier-envelope phase (CEP) is zero; see Figure 5.3(a) illustrating the pulse waveform.

The CB population calculated in accord with Eq. (19) for pulse polarized in the $yz$-plane is displayed in Figure 5.3(b) as a function of time $t$ for different field amplitudes and incidence angle $\theta = \pm 80^\circ$. Note that because silicene is symmetric with respect to reflection in the $xz$-plane, the results for both $80^\circ$ and $-80^\circ$ are identical. The two most prominent features of this dynamics are that (i) the dependence on the pulse amplitude is very nonlinear, and (ii) the residual (after the pulse end) populations, $N_{(res)}$, are close to the maximum populations during the pulse. The latter property is similar to that of graphene (see Chapter 4). However, it is in sharp contrast to that in silica, cf. Refs. [20] (theory) and [21] (experiment), where the residual CB populations are relatively small. This large residual CB population for silicene suggests a lack of adiabaticity, which is likely due to a relatively small distance of the transfer between the two sublattices in the $xy$-plane, $L_{xy} = a/(2\sqrt{3}) \approx 0.7 \, \text{Å}$, in this case. Note that the adiabaticity parameter is...
\[ \delta = \hbar \omega / (e F_y L_{xy}) . \] Adiabaticity requires \( \delta \ll 1 \) while, in our case, even at the strongest fields, the adiabatic parameter is not too small, \( \delta > 1 \).

The response for the case of the pulse polarized in the \( xz \)-plane is displayed in Figure 5.3(c) and 3(d). In stark contrast to the case of the \( yz \)-polarization considered above in the previous paragraph, here there is a dramatic difference between \( \theta = 80^\circ \) and \( \theta = -80^\circ \). This is due to the violation of reflection symmetry induced by the \( z \) component of the maximum field. For the case illustrated, this field promotes the transfer of electrons predominantly toward the \( B \) sublattice; cf. Figure 5.1(a).

For \( \theta = 80^\circ \) as shown in Figure 5.3(c), the \( x \)-component of the maximum field, \( F_x < 0 \), promotes transfer of electrons from left to right (in the direction \( x > 0 \)) according to their negative charge; cf. Figure 5.1(d). The distance of transfer is the same as in the case of the \( yz \)-polarized field \( L_{xy} = a/(2\sqrt{3}) \approx 0.7 \) Å and adiabaticity is violated since \( \delta = \hbar \omega / (e F_y L_{xy}) \geq 1 \).

Correspondingly, the residual CB populations \( N_e^{(res)} \) are again close to their corresponding maxima during the pulse.
Dramatically different behavior takes place for the reciprocal incidence, $\theta = -80^\circ$, where the CB population kinetics is displayed in Figure 5.3(d). For relatively weak fields, $F_0 = 0.5–1.5$ V/Å, the kinetics is essentially irreversible, where the maximum CB population is attained at the end of the excitation pulse, similar to the case of Figure 5.3(c) considered above in the previous paragraph. In sharp contrast, for stronger fields, $F_0 = 2–3$ V/Å, there is partial reversibility: at the end of the pulse, the CB population is reduced by a factor of $\approx 2$ with respect to its maximum.
This is related to improved adiabaticity, i.e., decreased adiabaticity parameter,
\[ \delta = \frac{\hbar \omega}{(eF_L a)} < 1 \]
where \( L_{\alpha} = a / \sqrt{3} \approx 1.4 \) Å is the horizontal transfer distance; see Figure 5.2(a). This distance is twice longer than for the case of Figure 5.1(c) and (d) corresponding to the polarizations in Figure 5.3(b) and (c).

Note that the adiabaticity in the case of Figure 5.3(d) is incomplete; for comparison, in the case of silica (quartz) a nearly perfect adiabaticity has been predicted and observed [20, 47]. This high degree of adiabaticity is most certainly related to a wide band gap, \( \Delta_g \) (see also Ref. [45]) and to a significantly larger lattice constant, \( a \approx 5 \) Å, in quartz. Both these factors determine adiabaticity, which is pronounced when \( \frac{\hbar \omega}{\Delta_g} \ll 1 \) and \( \frac{\hbar \omega}{(eaF_0)} \ll 1 \). Thus one should not expect near-perfect adiabaticity in graphene (Chapter 4), silicene, and germanene where \( \Delta_g \) is negligible, and \( a \) is relatively small.

### 5.3.1.1 X-polarized Pulse

To further signify the reversibility of electron dynamics, we show in Figure 5.4 the maximum and residual CB populations, \( N_{\text{max}} \) and \( N_{\text{res}} \), for both positive and negative angles of incidence, \( \theta = 80^\circ \) and \( \theta = -80^\circ \). Since we do not take into account the relaxation processes, the CB population after the pulse remains constant. The maximum CB population is defined during the pulse and corresponds to the local maximum of CB population as a function of time, which is realized at \( \tau \approx 0 \div 0.5 \) fs.
Figure 5.4 Maximum and residual CB populations in Silicene as functions of the peak electric field. The incident angle is (a) \(\theta = 80^\circ\) and (b) \(\theta = -80^\circ\). The in-plane polarization is along axis \(x\), i.e. \(\varphi = 0\).

The resultant data, presented in Figure 5.4, show that for positive angle of incidence, the maximum CB population increases monotonically with pulse's amplitude, while the residual CB population saturates at large amplitudes, \(F_0 > 1.5\ \text{V/Å}\), at a value of \(N_{\text{res}} \approx 5\%\) with small oscillations of \(N_{\text{res}}\) between 3 to 5 percent. For a negative angle of incidence [see Figure 5.4(b)], both maximum and residual CB populations increase with the increment of the field intensity. Such a behavior illustrates irreversible electron dynamics for the case of negative elevation angles. Thus the reversible electron dynamics is realized only at a positive angle of incidence and large intensities of the laser pulse.

To characterize the strength of the reversibility of electron dynamics, we show in Figure 5.5 the ratio of maximum to residual CB populations, \(N_{\text{max}} / N_{\text{res}}\), for two positive angles of incidence, \(\theta = 70^\circ\) and \(80^\circ\). At small amplitudes, this ratio is close to 1, which corresponds to
irreversible electron dynamics. The range of field amplitudes, at which the dynamics is irreversible, increases with decreasing the angle $\theta$. Namely, for $\theta = 70^\circ$ the electron dynamics is irreversible at $F_0 < 2.2$ V/Å, while for $\theta = 80^\circ$ it is irreversible at $F_0 < 1.5$ V/Å. The ratio $N_{\text{max}} / N_{\text{res}}$ reaches its smallest value of $\approx 0.3$ at $F_0 \approx 2.5$ V/Å.

![Figure 5.5 The ratio of residual to maximum CB populations for silicene monolayer vs Field Amplitude. The angle of incidence of the pulse is $\theta = 70^\circ$ (red line) and $\theta = 80^\circ$ (black line). The in-plane polarization of the pulse is along x-axis, i.e. $\varphi = 0$.](image)

In addition to the total CB population, the electron dynamics is characterized by the distribution of the CB population in the reciprocal space, which is given by the following function $|\beta_{\xi}(t)|^2$. We show such residual (after the pulse ends) distribution in Figure 5.6 and Figure 5.7 for positive $\theta = 80^\circ$ and negative $\theta = -80^\circ$ angles of incidence, respectively. In both cases the distribution functions are highly nonuniform with the fringes of very high contrast: the maximum CB population probability $\approx 1$, and almost zero minimum population probability. Such high nonuniformity has also been observed in graphene (see Chapter 4).
Figure 5.6 Residual CB population of silicene in the first BZ for different amplitudes of the optical pulse. Only the first Brillouin zone is shown. The polarization of electric field is along x-axis. The angle of incidence of the pulse is \( \theta = 80^\circ \). The results are shown for silicene monolayer.

Figure 5.7 illustration of Residual CB population, similar to Figure 5.6, but for \( \theta = -80^\circ \)

The data also show that for positive and negative \( \theta \), the residual CB population probabilities \( |\beta_{\alpha}(t)|^2 \) exhibit very different structures. We identify two regions in the first
Brillouin zone: region (i) \(|k_y| > 2\pi / 3a\) and region (ii) \(|k_y| < 2\pi / 3a\). The boundaries between these two regions, \(k_y = \pm 2\pi / 3a\), are parallel to the in-plane polarization of the optical pulse, i.e. x-axis. For a positive angle of incidence, \(\theta = 80^\circ\), the CB population is large in the region (i) with high contrast fringes, and it is small in the region (ii) with weak contrast fringes. The inverse structure occurs for the negative angle of incidence, \(\theta = -80^\circ\). In this case, the CB population is large in the region (ii) and small in region (i). Since the area of region (i) is smaller than the area of region (ii), the total residual CB population \(N_{\text{res}}\) for positive angle \(\theta\) is less than the corresponding residual CB population for negative angle \(\theta\).

5.3.1.2 Y-polarizes pulse

In the previous section, the plane of incidence was x-z plane, i.e., in-plane polarization angle was \(\phi = 0\). In this case, the system shows both reversible and irreversible dynamics depending on the angle of incidence and pulse intensity. The dynamics is also sensitive to the sign of the angle of incidence. For polarization of the light in the y-z plane, which corresponds to angle \(\phi = 90^\circ\), the system is symmetric with respect to the sign change of the angle of incidence, \(\theta \rightarrow -\theta\). Such symmetry follows from the crystal structure of silicene/germanene shown in Figure 5.2. The results of calculations also show that the electron dynamics in both cases, positive and negative angles \(\theta\), are the same.

In Figure 5.8 we show the distribution of the CB population in the reciprocal space, \(|\beta_k(t)|^2\), for Y-polarized optical pulses. The distribution, in this case, shows some fringes with less pronounced contrast as in the case of X- polarized light. For a negative angle of incidence, the distribution of the CB population can be obtained from the corresponding distribution for
positive angle by projecting it over the axis, which also illustrates the symmetry of electron dynamics with respect to the change of sign of the angle of incidence.

![Graph showing the residual CB population of silicene in the first BZ for y-polarized laser](image)

Figure 5.8 Residual CB population of silicene in the first BZ for y-polarized laser. The polarization of electric field is along y-axis ($\varphi = 90^\circ$). The angle of incidence of the pulse is $\theta = 80^\circ$.

### 5.3.2 Effective interband coupling

The interband electron dynamics of silicene/germanene in the field of the optical pulse with angle of incidence $\theta$ and in-plane polarization $\varphi$ is determined by an effective interband coupling function

$$D_{\chi}^{\text{eff}}(k) = [D_{\gamma}(k) \cos \varphi + D_{\gamma}(k) \sin \varphi] \cos \theta + eL_z \sin \theta$$  \hspace{1cm} (20)

The first term in this expression is singular (diverging) at the Dirac points and has the same functional structure as the interband dipole coupling of graphene. In graphene, such singular behavior of the interband coupling results in highly irreversible electron dynamics. The second term in Eq.(20) is due to buckled structure of silicene/germanene and is a constant in the
reciprocal space. This term creates a positive (for positive angles $\theta$) or negative (for negative angles $\theta$) shift of the interband coupling.

The intraband electron dynamics in the time-dependent electric field of the optical pulse is described by acceleration theorem, Eq. (7), which determines the time-dependent wave vector $k_T(q,t)$ [see Eq. (8)] for an electron with initial wave vector $q$. Thus, at a moment of time $t$, the mixing of the conduction and valence bands is determined by the effective interband coupling $D_{\text{eff}}(k)$, calculated at the wave vector $k_T(q,t)$. Due to the singularity of the first term in Eq. (20), the interband coupling due to this term occurs only when the electron wave vector $k_T(q,t)$ is near the Dirac points, i.e. within a short time interval. The interband coupling contribution due to the second term in Eq. (20), is a constant in the reciprocal space, which results in “constant” interband mixing at all $k$-points along the electron trajectory throughout the Brillouin zone. Depending on the sign of the second term in Eq. (20), i.e. depending on the sign of the angle of incidence, this part of the interband coupling enhances or suppresses the interband mixing introduced by the singular part of the interband coupling function (20). To characterize the effective interband coupling function $D_{\text{eff}}(k)$ we show in Figure 5.9 the sign of $D_{\text{eff}}(k)$ in the first Brillouin zone for different orientations of the incident pulse.

For zero angle of incidence, the effective interband coupling has central symmetry distribution for both X- and Y-polarization of the pulse [see Figure 5.9(a), (d)]. For a finite angle of incidence, the distribution of the effective interband coupling is quite different for the two polarizations of the optical pulse. For Y-polarized light, the distributions of the sign of function $D_{\text{eff}}(k)$ for positive and negative angles of incidence are similar and related by reflection upon the $k_y$ axis [Figure 5.9(e), (f)]. As a result, the electron dynamics for an electron with initial wave vector $q$ for a positive angle of incidence is identical to the electron dynamics with initial wave
vector $\mathbf{q}$ for a negative angle of incidence. Therefore, the response of the silicene/germanene system is symmetric with respect to the change of the sign of angle $\theta$.

A completely different situation occurs for X-polarized light [see Figure 5.9(b), (c)]. In this case, the interband coupling function is quite different for positive and negative angles of incidence. For positive $\theta$ [Figure 5.9(b)], in the domain $|k_x| < 2\pi / 3a$, there is a small region with negative interband coupling. The magnitude of the interband coupling in this region is large due to the singular first term in Eq. (20). In this domain, $|k_x| < 2\pi / 3a$, there is also a large region with positive interband coupling through which the main contribution comes from the small second term in Eq. (20). For X-polarized light, the electron moves in the reciprocal space along $k_x$ axis. Thus, if the initial wave vector is in the domain $|k_x| < 2\pi / 3a$, then the electron moves through a small region with a large negative effective interband coupling and a large region with small positive interband coupling, resulting in an effective cancellation of the interband mixing. Therefore, in the domain $|k_x| < 2\pi / 3a$ the residual CB population is small and is quite consistent with the distribution of the CB population probabilities shown in Figure 5.6.

For a positive angle of incidence, in the domain $|k_x| > 2\pi / 3a$ the effective interband coupling function is always positive [see Figure 5.9(b)], i.e. both terms in Eq. (20) are positive, which finally results in strong interband mixing and large residual CB population in this region. Such behavior is consistent with CB population probabilities shown in Figure 5.6. For the negative angle of incidence, the situation is opposite [see Figure 5.9(c)]. Now, in the domain $|k_x| < 2\pi / 3a$ the effective interband coupling is negative everywhere, which results in a strong interband mixing and irreversible electron dynamics in this region [see also Figure 5.7]. In the
domain $|k_x| > 2\pi/3a$, there are regions with both positive and negative interband coupling constants, resulting in partial cancellations of the conduction and valence band mixing and suppression of the residual CB population, which is also consistent with the results shown in Figure 5.7.

Figure 5.9 Sign of effective interband coupling function for different polarizations of the optical pulse. The black and red dots correspond to positive and negative values of $D_{\text{eff}}(k)$, respectively. The angle of incidence of the optical pulse is (a), (d) $\theta = 0$; (b), (e) $\theta = 80^\circ$; (c), (f) $\theta = -80^\circ$. The polarization of electric field of the pulse is along $x$-axis ($\phi = 0$) [(a), (b), and (c)] and $y$-axis ($\phi = 90^\circ$) [(d), (e), and (f)]. The results are shown for silicene monolayer.
5.3.3 *Ultrafast currents induced by strong pulse*

Electrical current is due to displacement of charges caused by the applied pulse field. For free classical electrons, this current is proportional to their mean velocity, i.e., to the integral of the field, often referred to as vector potential,

\[ A(t) = -e \int_{-\infty}^{t} F_{2d}(t') dt' \]  

(26)

In contrast to free electrons, as we have argued above in Section 5.3.1, the strong field acting on the electrons in a crystal lattice of silicene causes effective symmetry reduction from honeycomb to triangular and, in particular, the dependence of electron dynamics on the sign of the maximum field; cf. Figure 5.3(c) and (d). The observed partial adiabaticity is also due to the presence of the periodic lattice and defined by its period in the field direction.

The effective reduction of symmetry to triangular (where there is no inversion center) caused by the strong normal (z) field component causes the currents in the silicene lattice to be highly anisotropic and nonreciprocal as we show below in this section. Let us denote \( J_{xx} \) an x-component of the current density induced by the field polarized in the xz-plane with the maximum in the negative x-direction as shown in Figure 5.3(c). Similarly, we denote \( J_{xx} \) the x-component of the current density caused by the field with the maximum in the positive x-direction as in the case of Figure 5.3(d). Note that generally \( J_{xx} = J_{xx} \) (as would have been the case for free electrons) due to the low, triangular effective symmetry.

Similarly, we introduce current density \( J_{yx} \) as the y-component of the current density induced by the yz-polarized pulse. Note that in this case, the presence of the xz-symmetry plane dictates that \( J_{yx} = J_{yx} \). Interestingly enough, the in-plane field in the y-direction causes also a current in the x-direction [cf. Figure 5.1(b) and (c)], whose density we will denote as \( J_{yx} \). Note
that due to the symmetry, this current is invariant with respect to inversion in the xz-plane; i.e.,
\[ J_{yx} = J_{ix} . \]

In Figure 5.10, we plot the temporal behavior of the current density for the four independent cases of the pulse polarization and current direction, \( XX, iX, YY \) and \( YX \), as indicated in the panels; the currents in all other cases are either related to these cases by symmetry, as presented in the previous two paragraphs, or equal zero as, e.g., \( J_{xy} \) and \( J_{xy} \). For the \( XX \) case shown in Figure 5.10(a), in the relatively weak fields, \( F_0 \leq 1 \) \( \text{V/Å} \), the current density, \( J_{xx} \), qualitatively follows the vector potential, \( A(t) \) reaching (negative) maximum at approximately quarter oscillation period and turning to zero at the maximum field (\( t = 0 \)). Kinetics \( J_{xx}(t) \) is approximately antisymmetric with respect to point \( t=0 \), which shows that this process is nearly time reversible.

However, at higher fields, the behavior in Figure 5.10(a) becomes nontrivial. The first manifestation of this behavior appears at \( F_0 = 1.5 \) \( \text{V/Å} \) where instead of a pronounced minimum (maximum negative current) there is a plateau, which turns to a maximum for \( F_0 \geq 2 \) \( \text{V/Å} \). We attribute this behavior to electrons that are compelled by the field force to drift in the reciprocal space across the Dirac point. We will discuss this behavior in more detail in conjunction with Figure 5.10(c).
A phenomenon of fundamental importance is the loss of adiabaticity in higher fields, which manifests itself in the lack of antisymmetry with respect to point $t = 0$ in Figure 5.10(a).
Note that nonadiabaticity also implies irreversibility\(^2\) and, consequently, violation of time-reversal symmetry (also called \(T\)-invariance or \(T\)-symmetry). This violation of adiabaticity is related to a gradual transfer of population between the A and B sublattices, as we discussed above in Sec. 5.3.1. Such transfer is not instantaneous; one can estimate the characteristic time it requires as \(t_r \sim \pi \hbar / (eL_e F_0)\). For a high field used, \(F_0 \sim 2 \text{ V/Å} \), we obtain \(t_r \sim 1 \text{ fs}\). This is in full qualitative agreement with the results of Figure 5.10(a), where the time-reversal asymmetry becomes pronounced for high fields and times longer than \(\sim 1 \text{ fs}\) from the moment the pulse is applied.

One of the consequences of the \(T\)-invariance violation is nonzero values of the transferred charge and of the residual polarization—see Eq. (25) and Figure 5.12 and the corresponding discussion—violating the \(T\)-symmetry and adiabaticity. This implies that the system’s dynamics is irreversible (nonadiabatic), which may surprise one because the system is completely Hamiltonian. This is due to the fact that the central frequency of the laser radiation, \(\hbar \omega \approx 1.5 \text{ eV}\), is close to the transition frequency between the electron states localized at the two sublattices, \(\hbar \Delta \omega \sim \pi \hbar / t_r = eL_e F_0 \sim 1.4 \text{ eV}\). This causes resonant absorption leading to dephasing—collisionless relaxation widely known as Landau damping [93].

Current kinetics for the \(\bar{XX}\) case displayed in Figure 5.10(b) is qualitatively similar to that for the \(XX\) case discussed above in the previous three paragraphs. However, the symmetry reduction caused by the nonlinear interaction with a controlled (zero in our case) CEP causes current \(J_{\bar{XX}}\) to differ quantitatively from \(J_{XX}\), which difference is pronounced in the second

\(^2\)Nonadiabaticity implies increase of entropy from the statistical or thermodynamic standpoint. Hence, nonadiabatic processes are irreversible. Examples of irreversible processes are seen in panels (b) and (c) of Figure 5.3, while panel (d) shows partially reversible processes.
half-period \( (t > 0) \) where the \( T \)-asymmetry of the current becomes evident. The latter is due to the nonadiabaticity, already mentioned above in the discussion of Figure 5.10(a): the transfer of the electrons between sublattices occurs during a finite period of time, \( t_r \sim \frac{\pi \hbar}{(eL_z F_0)} \sim 1 \) fs, comparable with the half optical period in our case.

The \( YY \) case illustrated in Figure 5.10(c) is not related by crystal symmetry or other invariances to the \( XX \) and \( \bar{XX} \) cases considered above. However, the kinetics of \( J_{yy} \) is qualitatively similar to, though quantitatively different from, the previous two cases. Note that there is a strict symmetry \( J_{yy} = -J_{yy} \). Here also the \( T \)-symmetry is violated: the kinetics in the first and second half-periods is dramatically different. Note that in this case, current at the end of the pulse may not vanish, which is certainly due to the absence of collisions and other interactions in the model. Note that the electron-electron collisions are the fastest interaction-induced relaxation process. However, it takes the electron-electron collisions \( \sim 10-20 \) fs in a similar two-dimensional system, graphene, to make an effect, which is too long for our pulse whose entire duration is less than 4 fs.

The results for current \( J_{yx} \) (in the x direction induced by the field in the y-direction) are displayed in Figure 5.10(d). Note that exactly \( J_{yx} = J_{fx} \) due to symmetry. Without an electric field applied, silicene is a center-symmetric solid. Therefore for low fields current \( J_{yx} \) should vanish. This is, in fact, the case with a good accuracy for \( F_0 = 0.5 \) V/\( \text{Å} \), as one can see in Figure 5.10(d). With field increasing, there is an increased current \( J_{yx} \). Predominantly, it is directed along the negative x-axis, as is understandable from comparison with Figure 5.1(b) and (c). Note that magnitude of this current is approximately an order of magnitude smaller than \( J_{yy} \).
Figure 5.11 Electron momentum distribution in the first Brillouin zone in the CB for a \( Y \)-polarized pulse with maximum field \( F_0 = 2.5 \) V/Å at two different time.

(a) Distribution at the moment of time \( t = -1.3 \) fs corresponding to the maximum negative current \( J_{YY} \). (b) Distribution at time \( t = -0.7 \) fs corresponding to the maximum positive oscillation of current \( J_{YY} \).

The origin of the current oscillations for strong fields, \( F_0 \geq 2 \) V/Å, in Figure 5.10(a)–(c) can be understood from the electron momentum distribution. Consider for certainty the \( YY \) case, where the current is shown in Figure 5.10(c). The corresponding momentum distribution for electrons in the CB for pulse field amplitude \( F_0 = 2.5 \) V/Å is displayed in Figure 5.11(a) for the moment of time \( t = -1.3 \) fs, corresponding to the minimum (the maximum negative value) of the current, \( J_{yy} \). At this instance, which just precedes the current oscillation, excess electron population (depicted by green) is concentrated at \( k_y < 0, k_x = +0 \) (i.e., at small positive values of \( k_x \)). This excess population is formed due to field force \( eF_y(t) > 0 \) that propels the electrons across the \( K \)-points at \( k_y \approx 0.6 \ \text{Å}^{-1}, k_x \approx \pm 1 \ \text{Å}^{-1} \) into the second Brillouin zone in the extended picture; these electrons appear in the first Brillouin zone at the \( K \) point at \( k_y \approx -1 \ \text{Å}^{-1}, k_x = +0 \). Generally, the interband electron transfer occurs predominantly at the \( K \) points where the dipole
matrix elements, which couple the VB and the CB, are singular. This singular coupling also generates electron distributions that are dramatically different for \( k_x > 0 \) and \( k_x < 0 \). This asymmetry is due to the lack of the center symmetry in the presence of strong field \( F_z \); i.e., it has the same origin as current \( J_{yx} \) described above in the previous paragraph. Note that there is also the second localization of electrons around the \( K' \) point at \( k_x \approx 1 \ \text{Å}^{-1} \), which is also sharply asymmetric in the x-direction for the same reason.

A dramatically different electron distribution is displayed in Figure 5.11(b) for \( t = -0.7 \) fs when current \( J_{yy} \) experiences the maximum upswing. This is caused by a significant number of electrons in the CB with \( k_y > 0 \) which appear due to drift in the reciprocal space under force \( eF_y > 0 \). These electrons make a positive contribution to the current (their group velocity \( v_g < 0 \); correspondingly, due to \( e < 0 \), their contribution to \( J_{yy} \) is positive). The momentum distributions in Figure 5.11 also appear discontinuous due to the same reasons as in Figure 5.11(a) discussed in the previous paragraph.

![Figure 5.12 Charge transferred in the plane of the silicene as a function of the maximum pulse field.](image)
Four cases are displayed: $Q_{XX}$, $-Q_{XX}$, $Q_{YY}$, and $Q_{YX}$, as labeled in the figure. All other components of the charge density transferred are either zero or related to these four cases.

The currents described above in conjunction with Figure 5.10 cause transfer of charge across the system and accumulation of charges by the end of the pulse as given by Eq. (25). Such charge $Q$ transferred through the system is displayed as a function of the field amplitude, $F_0$, in Figure 5.12 for four independent combinations of the field and current directions, $XX$, $YX$, $YY$, and $YX$. A remarkable property of these results is that in all cases, except for $YX$, the transferred charge changes its sign as the field amplitude increases. This can be attributed to the increased number of electrons experiencing the Bragg reflections at the Brillouin zone boundary, especially at the (Dirac) $K$ points, with the field increase. Thus this sign change of the transferred charge has the same origin as the current oscillations in Figure 5.10 as described above. This charge accumulated at the pulse end is an experimentally observable quantity just as the previous experiments on currents in dielectrics [21, 94]. On the order of magnitude, this accumulated charge in Figure 5.12 is $Q \sim 1 \text{fC}/\mu\text{m}$. For $a \sim 1 \mu\text{m}$ focused spot, this gives $a \sim 1 \text{fC}$ transferred charge. Such a charge is on the same order of magnitude as in experiments Refs. [21, 94] and is, in principle, reliably observable.

5.4 Concluding Discussion

In this chapter we studied the effects of reduction of fundamental symmetries in buckled two-dimensional crystals such as silicene and germanene induced by a strong ultrashort pulse. In our case, the interaction with the pulse field is a dominant term in the Hamiltonian. Correspondingly, we neglect effects of the electron-electron interaction within the time frame of the experiment: $\sim 1$–$2$ fs duration of the pulse. Importantly, the phenomena considered are
symmetry-defined and, therefore, are qualitatively robust with respect to the effects of electron-electron interaction.

At high optical fields \( F \sim 1-3 \text{ V/Å} \), breakdown of the material may potentially, but not necessarily, occur. It is known experimentally \([21, 47]\) that for ultrashort (\( \sim 1.5 \text{ optical oscillation} \)) near-IR strong pulses, the breakdown of 3D dielectrics silica and quartz occur at very high fields, \( F \gtrsim 2.7 \text{ V/Å} \). Gold electrodes also survive such pulses \([21]\). The experimental situation with a similar breakdown of graphene, silicene, and germanene is still unknown. In any case, the charge transfer considered in the present article occurs on a scale of half optical period, a fraction of a femtosecond, and can be measured per a single pulse even if the material in the laser focus is eventually damaged (the lattice damage will form at times on the order of vibrational periods, i.e., tens of femtoseconds).

The accumulation of charge, \( Q \), transferred through the system implies a dramatic manifestation of fundamental symmetry violation. This charge accumulation violates simultaneously the parity symmetry (\( P \)-symmetry) and the charge-inversion symmetry (\( C \)-symmetry). This violation happens due to the fact that our pulse is short and has a controlled CEP (zero in our case): the maximum field is reached at the maximum of the envelope (instance \( t = 0 \)). Due to the strong nonlinearity of the system for fields \( F_0 \gtrsim 1 \text{ V/Å} \) applied, this maximum field defines a selected direction in the system plane for the force acting on electrons. This causes the violation of the \( C \)- and \( P \)-symmetries. This is actually a general property for systems subjected to short, strong, CEP-controlled pulses. It takes place in both two-dimensional solids such as graphene, silicene, germanene, and also conventional three-dimensional solids such as fused silica, sapphire, etc. In particular, it was a fundamental origin for the charge transfer in silica and quartz in the original experiments \([21]\).
The symmetry violation specific for silicene is related to the electron transfer between the sublattices caused by the normal field component \( F_z \), which effectively reduces the system’s symmetry from hexagonal to triangular. This causes nonreciprocity, \( J_{\tilde{xx}} = -J_{xx} \), and the appearance of a cross current, \( J_{xy} \neq 0 \). Note that anisotropy in the xy-plane, \( J_{\tilde{xx}} = -J_{xx} \), is inherent in both silicene and graphene.

Our zero-CEP pulse is \( T \)-symmetric; in the absence of the \( T \)-symmetry violation, the current should be \( T \) odd, which would preclude the accumulation of charges after the pulse. However, we have seen from the results of Figure 5.10 (a)–(c) that the current is not antisymmetric in time; i.e., there is a significant violation of the \( T \)-symmetry, which we attribute to the Landau damping. This is inherent in both graphene and silicene and is due to the absence of a significant band gap; this is in contrast to silica that is almost perfectly \( T \)-reversible. An additional contribution to \( T \)-irreversibility stems from the fact that the frequency associated with the electron transfer in the normal direction, \( eF_z L_z / \hbar \), is on the same order as the carrier frequency of the pulse. This causes resonant absorption of the excitation pulse and the Landau damping, specific for the silicene (and also germanene). If adiabaticity were present, it would have guaranteed reversibility and would have forbidden the charge accumulation.

Finally, we note a close analogy of silicene with the field-effect transistor (FET) [41, 86-88]. In FETs, the gate field, applied normally to the conducting channel, changes the carrier populations in it and, thereby, controls its conductance. Analogously, in silicene, the normal field component, \( F_z \), transfers carriers to one of the sublattices, A or B, thereby changing the system’s response to the in-plane field. A fundamental difference (and advantage) of silicene is that such a “device” works at optical frequencies, with the response time on the (sub)-femtosecond scale.
This opens a potential for many applications of silicene in future petahertz-speed devices and applications.
6 CHAPTER SIX: GRAPHENE UNDER A FEW-CYCLE CIRCULARLY POLARIZED PULSE: ATTOSECOND INTERFEROMETRY, CHIRALITY, AND BERRY PHASE

In Section 2.5 and 2.6, we described how the chiral Hamiltonians of monolayer graphene is correlated to the Berry’s phase. We showed that if electron momentum (or wave vector) in reciprocal space make a close loop, which encircles the Dirac point, then its chiral wave function undergoes a phase change of $\pi$ known as Berry’s phase. In this chapter we aim to manifest the chiral nature of graphene related to the Berry phase.

6.1 Introduction

Graphene is a two-dimensional material with remarkable electronic properties: it is a gapless semiconductor (or, semimetal) where the valence band (VB) and conduction band (CB) touch each other at the Dirac points ($K$ and $K'$ points) in the reciprocal space where electrons and holes behave as massless fermions [24, 66, 95]. Electron band structure in graphene’s reciprocal space is determined by its spatial and time-reversal symmetry. It is chiral, topologically nontrivial, and characterized by a nonzero Berry phase of $\pm\pi$ [4, 6, 96, 97] acquired by the electronic wave function when circling a $K$ or $K'$ point – see Figure 6.1(a). This topologically nontrivial chiral structure of graphene manifest itself in the quantum Hall effect [24, 66, 95] and in angle-resolved photoemission spectroscopy (ARPES) [8]. The Berry phase has been observed in an optical- lattice quantum simulation of graphene in the presence of a magnetic field gradient (using the Stern-Gerlach effect) [97]. Similar measurements in natural graphene would require magnetic fields too high to be realistic. Note that the area of the present
study is ultrafast electron kinetics in unbiased graphene and not graphene plasmons \cite{49} that are absent in this case.

In this dissertation, we propose attosecond strong-field interferometry in graphene, which, without the involvement of magnetic fields, reveals its chiral nature related to the Berry phase, and fundamentally allows measurement of the dynamic phase. It contains rich information about the electronic structure, attosecond excitation dynamics, and, potentially, ultrafast relaxation in graphene. The idea of such strong-field interferometry is presented in Figure 6.1(b)–1(f).

The quantum motion of an electron in the reciprocal space is known to be deterministic as expressed by the Bloch acceleration theorem, $\hbar \mathbf{k}(t) = \hbar \mathbf{k}_0 + e \mathbf{A}(t)$, where the vector potential is defined as $\mathbf{A}(t) = -\int_{-\infty}^{t} \mathbf{F}(t') dt'$, $\mathbf{k}(t)$ is the electron crystal momentum at time $t$, $\mathbf{k}_0$ is the crystal momentum at the initial time, $e$ is unit charge, and $\mathbf{F}(t)$ is the optical electric field on graphene. We used optical pulses with a given number of oscillations defined in terms of Hermite polynomials \cite[see Sec. 6.2]{64}. Each oscillation is circularly polarized. For a one-optical-oscillation ultrashort circularly polarized pulse, an example of the vector potential is displayed in Figure 6.1(b) by the dashed red line. Assuming vacuum wavelength of 1500 nm, the optical period is $T = 5$ fs.

We consider laser pulses shorter than the electron scattering time $\sim 10–100$ fs \cite{49-57}. Hence the electron dynamics is coherent and can be described by time-dependent Schrödinger equation. We solve numerically the time-dependent Schrödinger equation in the basis of the Houston functions \cite{64}. Time-dependent expansion coefficients, $\beta_{i\mathbf{k}_0}(t)$ and $\beta_{\mathbf{k}_0}(t)$, of the electron wave function in this basis determine the amplitudes for an electron with initial wave vector $\mathbf{k}_0$ to be in VB and CB, respectively. In graphene, the dipole matrix element $\mathbf{D}(\mathbf{k})$ between
the VB and CB is singularly enhanced in the vicinity of the Dirac points [92], where most of the
transitions VB ↔ CB occur (refer to Section 4.3.1, in particular Figure 4.2).

The set of the initial points for electron trajectories \( k(t) \), which pass through the K point,
is a curve mirror-symmetric to the trajectory, as shown by the dark blue lines in Figure 6.1(b)–
1(d). This curve is a separatrix: electron trajectories that originate inside the separatrix encircle
the K-point and thus accumulate the Berry phase [Figure 6.1(c)], while those outside do not
[Figure 6.1(d)]. Due to the dipole singularity mentioned above in the previous paragraph, after an
optical period, when the electron crystal momentum returns back to \( k_0 \), the electrons excited to
the VB will be situated in the vicinity of the separatrix. In the real-space Aharonov-Bohm effect
[98], the incident electrons diffract and propagate to the observation point by two pathways
around the magnetic flux region. In our case, there is no diffraction in the reciprocal space: the
final electron momentum \( k \) is the same as the original one, \( k_0 \). Thus a single oscillation pulse
does not create any interference fringes in the reciprocal space—cf. Figure 6.2(a) to be discussed
in detail later.
Figure 6.1 Schematic of a self-referenced interferometry in graphene employing 2-cycle circular pulse. (a) Electron spectrum of graphene in the first Brillouin zone in the tight binding model. The six Dirac points are indicated as K and K', and the directions of coordinate axes are shown. (b)–(d) For a circularly polarized single-oscillation pulse, the separatrix is shown by solid blue lines and the electron trajectories starting at \( k_0 \) points are depicted by dashed red lines. For (b), (c), and (d), respectively, the \( k_0 \) point is on, inside, and outside of the separatrix. (e) and (f) Graphene as a self-referenced interferometer. The optical pulse contains two periods with opposite circularity: the first period, with some amplitude \( F_0 \), has the field rotating clockwise, and the second period with amplitude 0.75\( F_0 \) has the field rotating counterclockwise. The electron motion in the VB is denoted by solid lines and in the CB by dashed lines. The red color highlights the segments of the trajectories where the electron motion for (e) and (f) occurs in different bands. (g) and (h) differ from (e) and (f) by the opposite circularity of the second period.
To have the desired interference of electrons, consider a pulse causing two passages in the K-point vicinity as schematically shown in Figure 6.1(e) and (f). This pulse contains two periods with opposite circular polarizations, counter-rotating with respect to each other—an example of the optical fields is shown in the inset in Figure 6.3. Ultrashort pulses containing opposite circular polarizations were synthesized for applications to generalized double optical gating (GDOG) [99].

In the case of counter-rotating polarizations, there are two pathways leading to the final momentum \( \mathbf{k}_0 \): (i) As shown in Figure 6.1(e), an electron starts at \( \mathbf{k}_0 \), moves to the \( K \)-point, where it undergoes a transition \( \text{VB} \rightarrow \text{CB} \), and then returns to \( \mathbf{k}_0 \) and travels the second cycle entirely within the CB; (ii) Illustrated by Figure 6.1(f), the electron dwells in the VB during the entire first cycle and undergoes the \( \text{VB} \rightarrow \text{CB} \) transition in the vicinity of the \( K \)-point during the second cycle returning eventually to the \( \mathbf{k}_0 \) point. These two pathways are indistinguishable and their corresponding amplitudes, \( A_1 \) and \( A_2 \), interfere: the resulting population probability contains an interference term,

\[
2 \text{Re}(A_1 A_2^*) = 2|A_1 A_2| \cos(\varphi_1 - \varphi_2).
\]

Note that the phase difference \( \varphi_1 - \varphi_2 \) between the two amplitudes, \( A_1 \) and \( A_2 \), accumulates only along the portions of their reciprocal space trajectories denoted by red in Figure 6.1(e)-(f). This interferometer does not need an external reference source and, therefore, is self-referenced.

6.2 Model Description

We study electron dynamics in graphene in the electric field of the optical pulse with a circular polarization, which has duration of few femtoseconds. The source is a laser pulse with the stabilized-carrier-envelope phase (CEP) and optical waveform which gives a strong electric
field with controlled amplitude and phase. The electric fields in such optical pulses are high and comparable to the internal fields acting on electrons in graphene’s unit cell.

Consider ultrashort optical pulse with circular polarization. We start with a pulse consisting of two optical oscillation periods. These two periods may differ by the field amplitudes and directions of circular polarizations. We consider two cases: (i) the two optical periods have the same (say, left) circular polarization and (ii) the two optical periods have opposite (say, left and then right) circular polarizations.

Consider for certainty a graphene monolayer positioned in the x-y plane with the excitation light wave incident in the z direction. The pulsed laser is defined by its field vector (considered to be uniform inside graphene), \( \mathbf{F} = \{F_x, F_y, 0\} \), which is parameterized in the form (derived from Hermite polynomials of the first and second order) as

\[
F_x(t) = -F_0 \left\{ e^{-u^2} \left[ 1 - 2u^2 \right] \mp \alpha e^{-(u-u_0)^2} \left[ 1 - 2(u-u_0)^2 \right] \right\},
\]

\[
F_y(t) = 2F_0 \left\{ u e^{-u^2} + \alpha (u-u_0) e^{-(u-u_0)^2} \right\},
\]

(1)

Here, \( \mp \) determines the circularities (the upper sign is for identical and the lower for opposite circular polarizations); \( F_0 \) is the amplitude of the first optical period, and \( \alpha F_0 \) is the amplitude of the second optical period; \( u = t / \tau \), \( u_0 = t_0 / \tau \), where \( \tau \) is approximately quarter optical oscillation period and \( t_0 \) is approximately a half pulse length. In specific computations, we set \( \tau = 1 \) fs and \( t_0 = 5 \) fs. There has been an extensive discussion about the dominating process over the early time window of excited carriers in the Conduction Band (CB) [49-57]. Gierz, et al., have observed and reported that “due to lack of holes at the top of the Valence Band (VB) of graphene,” impact ionization dominates in the first few femtoseconds after absorption of the pump pulse. Using an ultrashort XUV pulse (<8 fs) to perform time- and angle- resolved
photoemission spectroscopy (TR-ARPES) in graphene, they observed an apparent increase in the CB of carrier density in the first 25 fs after photoexcitation [100]. Therefore, for our study where the duration of the pulse is less than the characteristic scattering time of electrons, the system is Hamiltonian and is described by the time-dependent Schrödinger equation (TDSE)

\[ i\hbar \frac{\partial \psi(t)}{\partial t} = \hat{H}(t)\psi(t) \]  

(2)

Within the length gauge, the Hamiltonian operator takes the following form:

\[ \hat{H} = \hat{H}_0 + e\mathbf{F}_L(t)\mathbf{r} \]  

(3)

where \( \hat{H}_0 \) is the field-free electron Hamiltonian, \( \mathbf{r} = (x, y) \) is a two-dimensional radius vector.

Since the wavelength of visible or infrared light is much larger than the size of a unit cell, and electron velocities are much smaller than the speed of light, we can use the dipole approximation, which neglects the spatial dependence of the laser field while solving the TDSE.

The field-free electron Hamiltonian operator, \( \hat{H}_0 \), is described by the tight-binding model with the nearest neighbor hopping (Chapter 2). The electric field of the optical pulse generates both interband and intraband electron dynamics. The interband dynamics introduces a coupling of the states of the CB and VB and results in redistribution of electrons between the two bands. The quantum motion of an electron in the reciprocal space is expressed by the Bloch acceleration theorem [9].

\[ \hbar \frac{d\mathbf{k}(t)}{dt} = -e\mathbf{F}_L(t) \]  

(4)

which is universal and does not depend on the dispersion law. For an electron with initial crystal momentum \( \mathbf{q} \), the temporal dynamics is described by the time-dependent wave vector \( \mathbf{k}(t) \) as
\[ k(t) = q + \frac{e}{\hbar} A_L(t) \]  \hspace{1cm} (5)

where the vector potential of the field is defined as

\[ A_L(t) = -\int t' F_L(t') dt' \]  \hspace{1cm} (6)

The general solution of the time-dependent Schrödinger equation (2) for the coherent dynamics of electrons utilizes Houston functions [64] as the basis and is expressed in the following form

\[ \Psi_q(r,t) = \sum_{\alpha=v,c} \beta_{\alpha q}(t) \Phi_{\alpha q}^{(H)}(r,t) \]  \hspace{1cm} (7)

where \( \alpha = v \) (VB) or \( \alpha = c \) (CB). \( \beta_{\alpha q}(t) \) are the time-dependent expansion coefficients and \( \Phi_{\alpha q}^{(H)}(r,t) \) are the Houston functions. In principle, for each value of initial wave vector \( q \), we need to find only two time-dependent expansion coefficients \( \beta_{v q}(t) \) and \( \beta_{c q}(t) \). The procedure to solve the Schrödinger equation and find the expansion coefficients of the electron wave function is explained in Chapter 4.

For undoped graphene, before the involvement of the laser, all states of the VB are initially occupied, and all states of the CB are empty. Hence the initial condition is \( (\beta_{v q},\beta_{c q}) = (1,0) \). The electric field of the optical pulse generates both interband and intraband electron dynamics. The interband dynamics introduces a coupling of the states of the conduction and valence bands and results in redistribution of electrons between two bands. The amount of such a mixing is determined by \( \beta_{v q} \) and \( \beta_{c q} \) in VB and CB, respectively. From that, we can
deduce that the population distribution of electrons being in the CB is characterized by $|\beta_{cq}(t)|^2$.

Similarly, one can interpret $|\beta_{cq}(t)|^2$ as the probability amplitude of holes in the VB.

Note that due to dipole approximation (which is quite reasonable in our theory since the wavelength of the optical pulse is much less than the crystallographic vector of graphene) the states with different crystal moment $q$ are not coupled by the pulse field. Furthermore, the total time-dependent population of the CB as the following expression

$$N_{CB}(t) = \sum_{q}|\beta_{cq}(t)|^2$$

where the sum is over the first Brillouin zone.

6.3 Results and Discussion

We use theory and parameters described above in Section 6.2. We solve the Schrödinger numerically in the representation of the Houston functions. The results obtained are presented and discussed below in this section.

This process of the electron interferogram formation in the first Brillouin zone for a pulse containing two optical periods with opposite circularities is illustrated in Figure 6.2. After the first full cycle (for $t = 2.5$ fs), the CB electron distribution density, $|\beta_c(k,t)|^2$, is shown in panel (a), and the real part of the CB population amplitude, $\text{Re}\beta_c(k,t)$, is displayed in panel (d). The first optical oscillation populates the CB along the corresponding separatrix but does not produce any interference fringes [panel (a)], while the population amplitude does show both the fringes and the Berry phase discontinuity by $\pi$ [panel (d)].
Figure 6.2. Graphene interferograms in reciprocal space in the vicinity of the K point at different time.
(a)–(c) For the instances of time \( t \) indicated, distributions of the CB population, \( |\beta_c(k,t)|^2 \), and (d)–(f) real part of the CB excitation amplitude, \( \text{Re}\beta_c(k,t) \). (a) The population distribution at the end of the first optical oscillations, \( t = 2.5 \) fs (the pulse start is set at \( t = -2.5 \) fs). Blue lines show the separatrices for the two oscillations and arrows indicate the directions of the optical electric field rotations. (b) The same as in (a) but for time \( t = 4.5 \) fs, i.e., in the initial stage of the second (counterclockwise) oscillation. (c) The same as in panel (b) but after the second oscillation is completed. (d)–(f) The same as (a)–(c) but for the CB excitation amplitude. The green arrows indicated the region where the bifurcations of the interference fringes occur.

During the second optical cycle, whose field amplitude, \( \alpha F_0 \), is 75% of the first cycle amplitude, \( F_0 (\alpha = 0.75) \), there is gradual formation of the interference fringes in the direction of the electric field rotation along the second (smaller) separatrix [Figure 6.2(b)], which is fully completed at the pulse end at \( t = 7.5 \) fs [Figure 6.2(c)]. The interference fringes have characteristic bifurcations in the vicinity of the second separatrix as marked by the green arrows. The interferogram in Panel (f) shows that at the positions of these bifurcations, the dynamic phase changes very rapidly. Note that the Berry phases accumulated in the first and second quantum
pathways to the final state [shown in Figure 6.1(e) and (f)] are equal and, therefore, cancel out and do not show themselves as any discontinuities in the population interferograms [panel (c)]. These population interferograms [panel (a)-(c)] can be directly observed by femtosecond ARPES.

The resulting reciprocal-space interferogram (the distribution of the CB population) in the extended Brillouin zone picture is displayed in Figure 6.3. This distribution is highly chiral: there is pronounced right-left asymmetry determined by the chirality of the optical pulse (changing the circularity to the opposite would cause the distribution to be mirror-reflected in the yz-plane—see Figure 6.4 and its discussion). The interferograms at both the K and K' points are different, which reflects the intrinsic graphene chirality related to the Berry phase of graphene’s reciprocal space.
Figure 6.3 CB population after a two-oscillations pulse in the extended Brillouin zone picture. Residual CB population in graphene after a two-oscillations pulse where the first optical cycle is left circularly-polarized with amplitude $F_0 = 0.5$ V/Å, and the second cycle is right circularly-polarized with amplitude $0.75F_0$ (this waveform is shown in the inset). The separatrices are indicated by blue lines superimposed on the distributions.

The origin of this chirality can be understood from Figure 6.1(e) and 1(f). When the second (counter-clockwise) oscillation begins at the initial point $k_0$, which is close to the $K$-point and is situated to the right of it, as shown in panel (e), the interfering portions of the trajectories (shown by the red) are short. The corresponding fringes are seen in Figure 6.2(b) in the lower right part of the interferogram. In this case, the time between the first and second passage of the $K$-point is minimal, so any dephasing is small. Hence the phase increases fastest along the separatrix, which means that the fringes are normal to the separatrix, as seen in Figure 6.2(c) and
Figure 6.3. For the \( \mathbf{k}_0 \) points farther along the separatrix from the K-point, the time between the first and second passage of the \( K \)-point increases up to the optical period, \( T \). For such short pulses, the spectral width is large, \( \Delta \omega \sim T^{-1} \). This large spectral width translates into a very fast collisionless dephasing (Landau damping [101]) whose time is \( \sim \Delta \omega^{-1} \sim T \). Thus, at the left part of the interferogram, corresponding to longer times, there is little phase-difference along the separatrices, and the fringes tend to be parallel to the separatrices. To verify that the bifurcations originate from the second oscillation being of smaller amplitude, we have performed calculations for a pulse, which contains two periods with equal amplitudes; the same high degree of chirality is present, but the bifurcations are absent.

Figure 6.4 Same as Figure 6.3 but with for a pulse with opposite chirality. The first oscillation has its electric field rotating counter-clockwise, and the second oscillation does clockwise.
Figure 6.4 demonstrates properties of exact spatial symmetry of graphene, namely, its symmetry on reflection in the $yz$-plane. This reflection leaves the system invariant but changes the sense of rotation of the field. As a result, the interferogram in Figure 6.4 is mirror-reflected in the $yz$ axis with respect to that in Figure 6.3.

![Image](image.png)

Figure 6.5 The same as in Figure 6.3 but for an optical pulse where the two optical periods have the same amplitudes and circular polarizations.

In sharp contrast to Figure 6.3 and Figure 6.4, a similar pulse consisting of two subpulses with identical circularity does not cause any interferogram chirality—see Figure 6.5. The reason is that in this case the interfering segments of trajectories, shown in Figure 6.1(g) and (h) by red lines, are extended over the entire optical period. This leads to two consequences. First, the time
between the two interfering passages through the $K$ point, in this case, is exactly the period $T$, there is strong dephasing, which causes the fringes to be mostly parallel to the separatrix—cf. Figure 6.5. Second, because the field amplitudes for the two oscillations are equal, the amplitudes for the two pathways are complex-conjugated, $A_1 = A_2^*$, causing the distributions to be achiral (symmetric with respect to the reflection in the $yz$-plane). However, the local distributions for the $K$ and $K'$ points are still different, which is due to the internal chirality of graphene’s reciprocal space (Berry phase $\pm \pi$).

Figure 6.6 Residual CB population for a pulse which contains three left polarization followed by three oscillations with right polarization.
Although pulses with two optical oscillations are well within the state-of-the-art—see, e.g., Ref. [45], circularly polarized pulses with two optical oscillations, to our best knowledge, have not yet been synthesized and published. Therefore we present in Figure 6.6, the CB electron distribution caused by a pulse similar to those used in GDOG [99], which contains three optical oscillations with left circular polarization followed by three oscillations with right polarization—see inset in Figure 6.6. Also, in this case, the CB electron population distribution is highly chiral and different for the $K$ versus $K'$ points, which reflects the chirality of both the optical pulse and graphene. The resulting interferograms are, understandably, more complex that for the previous cases of two optical oscillations.

### 6.4 Conclusions

In conclusion, we have proposed a self-referenced interferometry in graphene in the reciprocal space. A strong (~0.5 V/Å) ultrashort (~5 fs) optical pulse is populating the CB on subcycle times (~100 as). Circular polarization of the pulse causes the electron to circle in the reciprocal space accumulating the dynamic phase along this closed trajectory. Circling a Dirac ($K$ or $K'$) point also adds the Berry phase of $\pi$ or $-\pi$. The electron VB $\leftrightarrow$ CB transitions occur predominantly in the vicinity of the Dirac point. The quantum excitation amplitudes corresponding to different optical cycles interfere, and their fringes reflect both the dynamic and Berry phases. The fringes of the population are due to the dynamic phase only; they are fundamentally observable using femtosecond ARPES. These fringes carry rich information of the electronic spectra and interband dynamics near the Dirac points and the chirality of the pulse. These interference fringes of electron population are identical separately for the three $K$ points and the three $K'$ points and different between the $K$ versus the $K'$ points. This reflects the local chirality in the reciprocal space related to the topological Berry curvature, flux, and phase.
The previous work on Berry phase interferometry in the reciprocal space [97] was done in a magnetic field gradient. In sharp contrast, we do not employ a magnetic field (which for graphene would have been too high to be realistic). Our interfering amplitudes are those for an electron passing in the vicinity of a Dirac point at different times, i.e., the “slits” of our interferometer are separated in time, not in space (real or reciprocal). The interference fringes are separated by some crystal momentum $\Delta k$, which is, in the order of magnitude, the width of the region around a Dirac point where the interband transitions take place—this can be estimated from Figure 6.2(a) as $\Delta k \sim 0.1 \text{ Å}^{-1}$. Correspondingly, time interval $\Delta t$ between the formation of fringes can be estimated from the Bloch acceleration theorem as $\Delta t \sim 5\Delta k / (eF_0) \sim 150$ as—in qualitative accord with kinetics in Figure 6.2(b) and 2(c). This dynamics of the interferogram formation provides an attosecond “clock” that may be useful in studying the fastest electron dynamics in nature, which takes place in graphene subjected to strong optical fields.

Fundamentally, the predicted attosecond kinetics in the reciprocal space can be visualized using ARPES with attosecond ultraviolet or XUV pulses, which are realistic at the present state of the art [21, 102]. Note that in our case, the goal is to measure accurately only the momentum distribution of electrons in the CB as a function of time but not the full electronic dispersion relation as in conventional continuous-wave ARPES. Therefore only the momentum distribution should be measured accurately; in contrast, the energy resolution should only be sufficient to distinguish electrons coming from the CB versus those from the VB. Because the phenomena of interest encompass a significant part of the Brillouin zone, this sufficient energy resolution is in the range from $\sim 0.1$ eV, which has experimentally been achieved with optical attosecond pulses (pulse duration $\sim 300$ as) [102] to $\sim 0.5$ eV obtained with XUV attosecond pulses (pulse duration $\sim 100$ as) [21].
Another possibility is to use ARPES to measure the resulting electron interferogram after the pulse. This will persist during a period limited by the electron collision times in the CB, which has been found to be >10 fs. This would further dramatically relax requirements to temporal resolution and, consequently, improve the energy resolution needed to study the vicinity of the Dirac points. Although the sensitivity of the electron interferogram in graphene to the electron collisions, i.e., electron momentum relaxation, is potentially a limiting factor, it also has “silver lining”: it can be used as a clock to monitor this ultrafast relaxation dynamics with unprecedented speed. This is defined by ~100 as, the time of fringe formation and ~100–500 as, potential temporal resolution of ultrafast ARPES (see the previous paragraph).

The proposed graphene interferometry provides an approach for extracting information about both electronic and topological properties of graphene and about the strong ultrafast circularly-polarized optical pulses with potentially attosecond temporal resolution. These may provide unique opportunities for attosecond metrology and light-wave driven nanoelectronics.
CHAPTER SEVEN: Topological properties of graphene on a corrugated substrate subjected to chiral excitation radiation

7.1 Introduction

Topological properties of quantum mechanical Hilbert space have had pronounced influence on physics as a whole and condensed matter physics in particular [5, 30, 103, 104]. Nontrivial topological properties of graphene in the reciprocal $k$-space are due to the presence of nonzero Berry curvature $\Omega(k)$, which is a geometric counterpart of a magnetic field localized at the Dirac points [30, 97]. The Berry connection, $A(k)$, is a geometric counterpart of the vector potential, which yields the Berry curvature by applying the curl operation, $\Omega(k) = \partial_k \times A(k)$. The flux of $\Omega$ is equal to the circulation of $A$ around the K or K’ points and is equal to $\pm\pi$, correspondingly. The Berry flux is a topological counterpart of the Aharonov-Bohm phase [98, 105] (also considered by Ehrenberg and Siday [106]) caused by a localized magnetic field. In a sense, each of the Dirac points can be thought of a solenoid containing a magnetic flux leading to the Bohm-Aharonov $\pm\pi$ phase shift for the electron wave function caused by circling around the Dirac point [97]. The total flux of all the Dirac points is zero corresponding to the zero Chern number.

While the Berry phase in the reciprocal space is analogous to the Aharonov-Bohm phase [6] in the real space, there is a fundamental difference in the ways it can be observed. In the real space, an electron wave can diffract around the region containing magnetic flux and, then, interfere with itself exhibiting fringes shifted due to the Aharonov-Bohm phase [105]. In a sharp contrast, in the reciprocal space, an electron motion in the absence of a magnetic field is
deterministic and diffractionless due to the Bloch acceleration theorem [9] where the crystal momentum, $\mathbf{k}(t)$, as a function of time $t$ evolves as

$$\mathbf{k}(t) = \mathbf{k}_0 + \frac{e}{\hbar c} \mathbf{A}_L(t), \quad \mathbf{A}_L(t) = -e \int \mathbf{F}(t) dt$$

(1)

where $e$ is the unit charge, $\hbar$ is the reduced Planck constant, $\mathbf{F}(t)$ is the optical electric field, $\mathbf{A}_L(t)$ is the vector potential, and $\mathbf{k}_0$ is the initial crystal wavevector of the electron. After the pulse ends, the crystal momentum returns to its original value, $\mathbf{k}(t) \rightarrow \mathbf{k}_0$, and, consequently, there can be no interference of an electron wave with itself.

To deal with this fundamental problem, in Chapter 6 we have proposed a self-referenced interferometry in the reciprocal space of graphene. However, because the Berry phase is $\pm \pi$, the corresponding self-referenced interference term carries a double phase, $\pm 2\pi$, which is equivalent to zero and not observable directly. However, one can see an indirect effect of the Berry phase as an extra interference fringe typical for a vortex. Another, direct way of observing the reciprocal space Berry phase is the application of time-dependent and inhomogeneous magnetic field where electron wave packets with different spins move along different trajectories around a K-point and then are brought together to interfere [97]. However, such experiments are only possible on quantum lattice models because for real graphene the required magnetic fields would be too strong. Here we propose an approach to directly observe the Berry phase without a magnetic field. The idea is to use a superlattice superimposed on graphene to cause electron diffraction (Bragg reflection from the superlattice) in the reciprocal space. That causes the self-referenced phase to be different from $\pm 2\pi$ and, therefore, to be observable directly by the reciprocal space interferometry. In other terms, the diffraction from the superlattice creates a “which way” quantum mechanical uncertainty causing interference of the electron wave with
itself in the reciprocal space and making the Berry phase directly visible in discontinuities of the self-referenced interferograms.

To introduce our idea, we turn to Figure 7.1. The band structure including the highest valence band (VB) and the lowest conduction band (CB) and showing the Dirac K- and K'-points, is presented in panel (a). The geometry of the system in the real space is displayed in panel (b) where a graphene monolayer is superimposed on a periodic array of nanowires under electrostatic bias, which periodically modulates electron potential. Panel (c) shows an electron trajectory (the dashed red line) for an isolated monolayer of graphene in the reciprocal space caused by a single oscillation circularly polarized pulse.

Those initial points for which the corresponding trajectories pass precisely through the Dirac point constitute a curve that is called separatrix (shown by the solid blue line). The separatrix is, in fact, the mirror reflection in the x-axis of the electron trajectory originating at the K-point. If the initial point, k₀, is outside of the separatrix, as in panel (c), then the trajectory does not encircle the Dirac point, and the total Berry phase accumulated on such a trajectory is zero. In contrast, if k₀ is inside the separatrix, as in panel (d), then the trajectory does encircle the Dirac point and, consequently, the Berry phase is ±π for the K- and K' point, respectively.

Electron trajectories for graphene on a nanowire superlattice are illustrated in Figure 7.1(e). the red line shows the actual electron trajectory in the reciprocal space starting at a crystal momentum k₀, where the solid line corresponds to the electron in the VB and the dashed line in the CB. There are also two additional trajectories shown by the dash-dot blue and green lines that are obtained from the original (red) trajectory by shifting it by the superlattice reciprocal vectors, ±Q_y where Q_y = {0, 2π/L, 0}. The electron moving along the original (red) trajectory undergoes a Bragg reflection from the superlattice acquiring the wavevector −Q_y and jumping to the blue
trajectory, as shown by a vertical arrow. This jump is necessarily accompanied by a VB→CB transition to avoid the Pauli blocking due to the VB being fully occupied. Passing by the $K$-point, the electron undergoes the CB→VB transition and then another VB→CB transition at the point of the second Bragg reflection. The electron completes its trajectory at the initial $k_0$ point but in the CB state. Note that, the transitions “across” (i.e., close to) the $K$-point (between the red and blue trajectories in this case) are favored by the pseudospin selection rules [25] in comparison to transitions away from the $K$-point (between the red and green trajectories, not shown). We show in panel (e) only such favored transitions, which also are enhanced due to an increase of the interband dipole matrix element in the vicinity of $K$-point.
Figure 7.1 Schematic of the proposed graphene superlattice structure which enables the direct manifestation of the Berry phase without a magnetic field
(a) Electron dispersion of graphene monolayer obtained within tight-binding approximation. Energies of the highest valence band (π-band) and the lowest conduction band (π*-band) in the reciprocal space are displayed as functions of wavevector \( \mathbf{k} = \{k_x, k_y\} \). The two distinct Dirac points are labeled as \( K \) and \( K' \). (b) Schematic of the proposed structure. A graphene monolayer is positioned over a superlattice formed by nanowires with period \( L \) in the y-direction. Inset: Illustration of the electric field waveform \( \mathbf{F}(t) = \{F_x(t), F_y(t)\} \) as a function of time \( t \) for a single-oscillation circularly-polarized ultrashort pulse. (c) An illustration of an electron trajectory (dashed red line) in the reciprocal space, which starts and ends at a \( k_0 \)
-point outside the separatrix and passes close to the $K$-point without circling around it. The separatrix (solid blue line) separates the $k_0$ -points for those trajectories that circle the $K$-point and those that do not.

(d) The same as in panel (c) but for the $k_0$ point inside the separatrix. (e) Schematic of the reciprocal space trajectories and transitions caused by the Bragg reflections for the $k_0$-point outside of the separatrix, corresponding to the case of panel (c). The red line shows an electron trajectory where the solid and dashed segments correspond to the VB and CB, respectively, as indicated. The thin dash-dot green and blue lines are Bragg-shifted replicas of the original trajectory. See other details in the text. (f) The same as in panel (e) but for the $k_0$ -point inside the separatrix, corresponding to the case of panel (d).

Analogous arguments apply to the alternative case when the $k_0$ -point is inside the separatrix shown in Figure 7.1(f). However, in this case, the transitions across the $K$ -point, which are enhanced, are those between the original red trajectory and the Bragg-shifted green trajectory.

In both cases of the initial crystal moments inside and outside of the separatrix [Figure 7.1 (e)-(f)], the electron circles the $K$-point but only part of its trajectory. Therefore the Berry phase, $\phi$, accumulated due to such a passage is reduced with respect to the complete circling: $|\phi| < \pi$. (Note that the jumps due to the Bragg reflections do not contribute to the Berry phase.) Thus in a self-referenced interferometry, the phase will be observable since $2|\phi| < 2\pi$.

The CB population induced by the strong optical field is measurable in the reciprocal space by time- and angle- resolved photoemission spectroscopy (TR-ARPES) techniques [8, 107, 108]. Resolving the electrons originating from the CB after the pulse ends but before the electron collisions smear-out the distribution, one will register a self- referenced interferogram. Because $2|\phi| < 2\pi$, there will be discontinuities of the electron distribution on all three separatrices shown in Figure 7.1 (e) and (f).

7.2 Details of Solution

Assume a graphene monolayer positioned in the $xy$-plane with the radiation incident in the $z$ direction – see inset in Figure 7.1. A single oscillation pulse field is defined by its field vector $F_L = \{F_x, F_y, 0\}$ where
\[ F_x(t) = -F_0 e^{-u^2(1 - 2u^2)} , \quad F_y(t) = \pm 2F_0 u e^{-u^2} \]  

(2)

\pm \text{ signs correspond to opposite circularities, } F_0 \text{ is the amplitude, which is related to the pulse power } P = cF_0^2 / 4\pi , c \text{ is the speed of light, } u = t/\tau , \text{ and } \tau \approx 1 \text{ fs is approximately quarter optical oscillation period. Assuming vacuum wavelength of } 1.5 \text{ \(\mu\)m, the duration of the pulse is } T = 5 \text{ fs.}

Experimentally, the processes of energy-momentum relaxation in the photoexcited CB electron population occur during times ranging from \(\sim 10 - 20 \text{ fs}\) to \(\sim 200 - 800 \text{ fs}\) [49-57] where the shortest, \(\sim 10 \text{ fs}\), times are due to ultrafast electron-electron interactions while longer, \(\sim 1 \text{ ps}\), times are those of phonon-assisted cooling.

An advantage of ultrafast strong-field processes considered in this article is that the full cycle of optical excitation is completed within a few femtoseconds when the electron relaxation processes do not have enough time to occur. Therefore, the electron dynamics can be considered coherent, and one can describe it by the time-dependent Schrödinger equation (TDSE) with the Hamiltonian of the following form:

\[ \hat{H} = \hat{H}_0 + e\mathbf{F}(t) \cdot \mathbf{r} + \Delta(y) \]  

(3)

where \(\hat{H}_0\) is the field-free Hamiltonian, \(\mathbf{r} = \{x, y\}\) is a two-dimensional (2D) radius vector in the plane of graphene, \(\Delta(y) = V_0 \cos(Q_yy)\) is an electrostatic potential periodic in the \(y\)-direction with period \(L\), reciprocal lattice vector \(\mathbf{Q} = \{0, Q_y, 0\}, Q_y = 2\pi/L\), and amplitude \(V_0\). The dipole approximation used here is applicable since the unit cell is much smaller than the radiation wavelength and the electron velocities are much smaller than the speed of light.

The field-free electron Hamiltonian, \(\hat{H}_0\), is described by the tight-binding model (TB) with nearest neighbor hopping. We solve the TDSE using a basis of Houston functions [64] as has previously been described [92, 109, 110]. Some details of the solution are shown below in
this Section. We used realistic parameters: \( L = 10 \) nm, and \( V_0 = 0.05 \) eV. The parameters of the unperturbed Hamiltonian, \( \hat{H}_0 \), are the same as in Chapter 2.

We consider graphene at the point of neutrality where the Fermi surface is at the Dirac points. We solve the Schrödinger equation numerically in the representation of the Houston functions in a similar manner we described in Chapter 4.

### 7.3 Results and Discussion

The electric field of the optical pulse generates both interband and intraband electron quantum transitions. The interband transitions, \( \text{VB} \leftrightarrow \text{CB} \), cause a redistribution of the electron population between different bands. The dynamics in the reciprocal space is universally expressed by the Bloch acceleration theorem. Consequently, the states, which belong to different bands (VB and CB) but have the same initial crystal momentum, \( \textbf{k}_0 \), will have the same crystal momentum, \( \textbf{k}(t) \), at all moments of time \( t \). After the pulse ends, the crystal momentum returns to its initial value \( \textbf{k}_0 \). The periodic potential, \( \Delta(y) \), couples states within each band with crystal moments \( \textbf{k} \) and \( \textbf{k}' = \textbf{k} \pm n\textbf{Q} \), where \( n = \pm 1, \pm 3, \ldots \) is the order of the Bragg reflection from the underlying periodic array of the metal nanowires. Assuming potential \( \Delta(y) \) to be smooth and weak enough, we will only take into account \( n = \pm 1 \). This is illustrated by the three coupled trajectories in Figure 7.1.

Consider first the results obtained for a single-oscillation circularly polarized optical pulse illustrated in Figure 7.1. These are shown in Figure 7.2 where the electron population of the conduction band, \( N_c(\textbf{k},t) \), is displayed in the reciprocal space after the end of the excitation pulse whose amplitude is \( F_0 = 0.5 \) V/Å. As one can see, the distributions of the population in the vicinity of the \( K \) - vs. \( K' \) -point are different because the chirality of the circularly-polarized
pulse causes significantly different electron trajectories at the nonequivalent Dirac points, which are intrinsically chiral themselves. (Note that for linearly polarized pulses, there is no such a distinction: the distribution at the K- and K'-points are identical – Chapter 4, e.g., Figure 4.5 and Figure 4.6.) As expected [see Figure 7.1 (e)-(f) and the related discussion], there are discontinuities at the positions of all three separatrices due to the partial Berry phase $2|\phi| < 2\pi$, which are especially pronounced for the separatrices Bragg-shifted by $\pm Q$.

Figure 7.2 Conduction band population of graphene plotted (color coded) in the extended Brillouin zone scheme as a function of crystal momentum $k$ at the end of the optical pulse. The pulse has one optical oscillation with a circular polarization.

The duration of the circular pulse is 5 fs, and its amplitude $F_0 = 0.5$ V/Å, as shown in the inset. Magnified distributions around the two nonequivalent Dirac points, K and K', is shown in the right panels. The separatrix is indicated by the dashed green line superimposed on the population distribution. The three discontinuities are clearly seen at the separatrix and its replicas Bragg-shifted by $\pm Q$. 

To elucidate the phases of the electronic states in the presence of the topological $\pm \pi$ Berry fluxes at the Dirac points, we will use the idea of self-reference interferometry in the reciprocal space (refer to Chapter 6). Consider pulse with two oscillations with opposite circularity, as shown in the inset of Figure 7.3. The idea is that during such a pulse, an electron, which moves in the reciprocal space according to Eq.(1), passes twice, in the opposite directions, in the vicinity of the Dirac point where the VB↔CB transitions are likely to occur. After the pulse, the electron crystal momentum returns to its initial value $k_0$ irrespectively of the quantum transitions that has occurred. Consequently, the amplitudes corresponding to the VB↔CB transitions during these two passes interfere. Their phases differ by a dynamic phase, which is due to the energy difference between the VB and the CB and leads to the formation of interference fringes, and the Berry phase of $2\varphi$. In pure graphene, Berry phase $\varphi = \pm \pi$; this results in the phase of $2\varphi = \pm 2\pi$ in the self-referenced interferometry. Thus the Berry phase does not lead to discontinuities of the electron population fringes. In our case of a superlattice, $|2\varphi| < 2\pi$, and there will be both intensity discontinuities and fringe shifts on the separatrices and their Bragg images.

The resulting momentum distribution of electrons at the end of the two-oscillation chiral pulse is shown in Figure 7.3. It is an interferogram with many interference fringes, which is highly chiral in the vicinity of the Dirac points. There are bifurcations of fringes clearly present at the interferogram, which are characteristic of vertices. Interestingly enough, the number and density of fringes at the K′ point is appreciably greater than at the K - point. In fact, in one case, the Berry phase adds to the dynamic phase; in a pure graphene, the addition of the $2\varphi = 2\pi$ geometric phase to the self-referenced interferogram causes an appearance of an extra fringe. In the other case, it subtracts from the dynamic phase, which causes the disappearance of one fringe. An important peculiarity of these interferograms is their singularity: there are both
amplitude discontinuities and fringe shifts at the two separatrices (corresponding to the two optical peri-
ods) and their Bragg replicas.

Let us briefly discuss our predictions and ways to observe them experimentally. As we have already mentioned above in the introductory part of this Letter, the interferograms of Figure 7.2 and Figure 7.3 can be read out using TR-ARPES where an XUV pulse transfers the graphene electrons into the continuum. These electrons are analyzed in their energy and tangential momentum. The XUV pulse should have energy uncertainty less than the VB ↔ CB transition energy, which is needed to resolve the CB- from VB-originating electrons. Given that the shortest known electron-momentum relaxation times in graphene are $\tau_e > 10$ fs, the corresponding energy width of the XUV pulse in TR-ARPES should be $\Delta E \sim \hbar / \tau_e < 0.1$ eV, which will allow one to resolve the CB electrons for the most of the interferograms in Figure 7.2 and Figure 7.3.
Figure 7.3 Similar to Figure 7.2 but with a two-cycle pulse with opposite circularities (clockwise then counterclockwise) for the two periods. The amplitude ratio for the first and second periods is $\alpha = 0.75$. The expanded image of CB population near the K and K’ points are shown on the separate panels to the right. The dashed green lines indicate the two separatrices corresponding to the two optical-oscillation periods.

To better visualize the jump in CB population amplitude, we plot CB population amplitude across a vertical line in reciprocal space, i.e., for a fixed value of $q_x$ draw $|\beta_c(k, t)|^2$ with respect to $q_y$ in Figure 7.4. Panel (a) corresponds to one-cycle pulse, whereas panel (b) is related to the two-cycle field.
Figure 7.4 Residual CB population plotted as a function of \( q_y \) with a fixed value of \( q_x \).
Panel (a) corresponds to one-cycle pulse (Figure 7.2) with \( q_x = 0.1 \text{ Å}^{-1} \) (black) and \( q_x = 0.2 \text{ Å}^{-1} \) (red). The three jumps stemming from the nontrivial geometric (Berry) phase are evident. Panel (b) corresponds to two-cycle pulse (Figure 7.3) with the second cycle of the opposite rotation and amplitude ratio of \( \alpha = 0.75 \). For this plot, \( q_x = 0.1 \text{ Å}^{-1} \). There are six jumps visible originating from the nontrivial Berry phase.

The electron-electron collision dynamics will manifest itself by the smearing-out of the interferograms, which can also be traced by TR-ARPES with a temporal resolutions of a few fs and the momentum resolution defined by the ARPES setup, which is realistically \( \sim 1.5 \) percent of the Brillouin zone edge (\( \approx 1.6 \text{ Å} \)) that is \( \approx 0.025 \text{ Å} \) [107]; the momentum resolution can be as high as 0.005 Å for nano-ARPES [111]. Such resolutions are more than sufficient to observe the interference fringes predicted in this Letter and their evolution caused by electron collisions.

From fundamental symmetries, graphene possesses mirror (\( P \)-) symmetry with respect to reflection in the \( xz \)-plane and is invariant with respect to time reversal (\( T \)-symmetric). These symmetries imply, in particular, that the \( K \) - and \( K' \) -points have the same properties except their Berry curvatures are opposite leading to the opposite Berry phases of \( \pm \pi \). Related to these is the Chern number of zero and graphene is globally topologically trivial. In sharp contrast, the state, in which a strong (nonperturbative) ultrashort circularly-polarized pulse leaves graphene, has neither \( P \)- nor \( T \)- symmetry. It has the sense of rotation determined by the circular polarization of
the excitation pulse and is fundamentally optically-active. This and similar “topologically charged” states of matter created by intense, ultrafast, and chiral optical fields are of significant interest fundamentally and for applications in petahertz-bandwidth information processing.
In this dissertation, we theorize the fundamentals of an ultrafast and ultrastrong optical field interacting with graphene and graphene-like nanocrystals as a prototype of two-dimensional class of materials. It has long been anticipated that a laser with ultrashort pulse and at the same time very strong intensity, provides unique opportunity to explore exotic phenomena in materials, the key idea being that a sample can tolerate a stronger electric field if the duration of the interaction is shortened.

Graphene and graphene-like nanocrystals are ideal for light-driven applications due to:

- Excellent mobility coming from their Dirac-type band structure.
- Screening is negligible (low carrier concentration), and hence a strong optical field can be generated.
- Epitaxial graphene on SIC (1000) is very robust and can withstand high laser intensities.
- Optical response of graphene is ultrafast and broadband.

Below I have highlighted the most important contributions and results achieved in this dissertation:

- In Chapter 3, we study the dynamics of electrons in an ultra-strong static electric field (a few V/Å) and obtain an analytical solution for the Wannier-Stark (WS) states and corresponding energy spectrum of graphene within the two-band tight binding model.
- Electron states in graphene have a WS ladder structure with energy levels separated by the Bloch frequency, which is proportional to both the electric field and the lattice period of graphene in the direction of electric field.
The singular behavior of the dipole operator near the Dirac cones result in the redistribution of carrier density and very strong mixture of conduction and valence bands.

As a result of such mixing, the energy spectrum of graphene shows anticrossing points, which are characterized by the corresponding anticrossing gaps. It is shown that the anticrossing gaps are proportional to electric field at the corresponding anticrossing points with the calculated values $2.54/l$ (eV), where $l = 1, 2, \ldots$ is the order of the anticrossing point. The largest anticrossing gap $\sim 2.54$ eV corresponds to the anticrossing point $l = 1$ at the electric field $\sim 3.59$ V/Å.

We, further studied (Chapter 4) the interaction of graphene with ultrafast optical fields. We show that graphene subjected to an ultrafast (near-single-oscillation pulse) and strong (F $\sim 1-3$ V/Å) pulse exhibits behavior dramatically different from both insulators and metals.

Within the duration of a few femtosecond ($\sim 1-10$ fs) pulses with the frequency centered in the optical regime, the system is Hamiltonian and the coherent dynamics of electron is described by the time dependent Schrödinger equation.

This fully coherent dynamics of electron system evolves on a sub-fs time scale and is faster than electron-electron relaxation and other dephasing processes.

Graphene exhibits dramatically different behavior from both insulators and metals. Field-induced, Zener-type electron transfer from the valence band (VB) to the conduction band (CB) is deeply irreversible (nonadiabatic): the residual CB population is close to the maximum population.
The interference between the “paths” corresponding to different numbers of reflections at the Dirac point (which acts like a beam splitter in conventional interferometer) lead to a phenomenon similar to the Fabry-Perot interference found in optics. However, this time one has an electrical Fabry-Perot interferometer working on the basis of quantum interference.

Correspondingly, an ultrashort electronic current can be induced in graphene on a femtosecond timescale.

The ultrafast optically-induced currents and charge transfer in graphene may provide a fundamental basis for detection and calibration of ultrashort intense laser pulses and are promising for petahertz information processing.

In Chapter 5, we discuss the theoretical investigation of buckled Dirac materials (silicene and germanene) interacting with ultrashort and ultrastrong optical pulses.

The strong nonlinearity of the system for the fields applied (V/Å) will cause the violation of the charge (C), parity (P) and time reversal symmetries.

Such symmetry violations are related to the electron transfer between the sublattices produced by the normal field component and result in nonreciprocity, optical rectification and the appearance of a cross current.

We also note a direct resemblance between silicene and field-effect transistors (FET). In FETs, the (perpendicular) gate field changes the carrier concentration and thereby, controls its conductance. Analogously, in silicene, the normal field component of the pulse, transfers carriers between two sublattices, and consequently modulates the response function of silicene to the in-plane field.
We further studied and proposed techniques, which enabled the topological manifestation of graphene (Chapter 6 and 7). Singular nature of the Dirac cones and the chirality of graphene are encoded in the phase factor of electron wave function. The non-trivial Berry phase of $\pm \pi$ corresponding to electron trajectories involving the $K$- and $K'$- points is revealed using the few-cycle circularly polarized pulse. Below I have summarized the theory and the achievements:

- Circular polarization of the pulse causes electron to circle in the reciprocal space accumulating the dynamic phase along this closed trajectory.
- Circling around a Dirac ($K$ or $K'$) point adds also the Berry phase of $\pm \pi$, respectively.
- The quantum excitation amplitudes corresponding to different optical cycles then interfere, and their fringes reflect both the dynamic and Berry phases.
- A graphene superlattice is proposed by superimposing it on a periodic array of nanowires to cause electron diffraction (Bragg reflection from the superlattice) in the reciprocal space.
- The diffraction from the superlattice creates a “which way” quantum mechanical uncertainty causing interference of the electron wave with itself and making the Berry phase directly visible in discontinuities of the self-referenced interferograms.
- This dynamics of the interferograms formation provides an attosecond “clock”.
- The interference fringes carry rich information of the electronic spectra and interband dynamics near the Dirac points and the chirality of the pulse, and provide unique opportunity in fundamental study of two-dimensional (2D) graphene-like nanosystems and Topological Insulators (TI).
• It is an attosecond self-referenced interferometry in the reciprocal space of graphene, and does not need an external source for calibration.

• The interference fringes of population dynamics and the discontinuity corresponding to the topological Berry phase are fundamentally observable using *Time- and Angle Resolved Photoemission Spectroscopy* (Tr-ARPES).

The results of this work already present a big step towards the feasibility and understanding of optically induced currents in two-dimensional nanostructures, and will motivate further investigations hereafter. Below I outline some additional steps can be taken:

• Investigation of the High Harmonic Generation (HHG) as a consequence of the ultrafast induced current and finding a way to enhance the HHG in 2D crystals.

• Detailed analysis of the decoherence phenomena, in particular, electron-electron relaxation, and their time scale in 2D materials and employing it into the theory of ultrafast kinetics.

• Further exploration of the ultrafast ARPES (femtosecond time and nanometer length scale) is the key step in the experimentation and proof-of-principle of our theory as well as other studies involving coherent control and ultrafast optoelectronics (petahertz information processing).

Our results and achievements find applications in spectroscopy, imaging, laser technology, transmitting and processing information. We are dealing with the fastest phenomena in optics by which we can precisely control processes in-situ and switch the induced electric currents at a rate that is far beyond the capabilities of conventional electronics.
APPENDICES

Appendix A: graphene in external electric field: derivation of the expansion coefficients

Here we derive the expansion coefficient of graphene wave function in an external electric field which falls from the general form of the Hamiltonian in chapter 3. We express the general solution of the Schrödinger equations (3-1) and (3-2) in the form (3-7), i.e., in the basis of eigenfunctions of field-free Hamiltonian $H_0$. Substituting expression (3-7) for the wave function $\psi(\mathbf{r})$ into the Schrödinger equations (3-1) and (3-2), we obtain

$$E \sum_{k_1} \left[ \phi_e(k_1)\Psi_{k_1}^{(v)}(\mathbf{r}) + \phi_c(k_1)\Psi_{k_1}^{(c)}(\mathbf{r}) \right]$$

$$= (\mathcal{H}_0 + e\mathbf{F}\mathbf{r}) \sum_{k_1} \left[ \phi_e(k_1)\Psi_{k_1}^{(v)}(\mathbf{r}) + \phi_c(k_1)\Psi_{k_1}^{(c)}(\mathbf{r}) \right]$$

(A1)

We multiply both sides of Eq. (A1) by $\Psi_{k_1}^{(v)*}(\mathbf{r})$ and then integrate it by $\mathbf{r}$. taking into account that $\Psi_{k_1}^{(c)}(\mathbf{r})$ are eigenfunctions of Hamiltonian $H_0$, we obtain

$$E\phi_e(k) = E_v(k)\phi_e(k)$$

$$+ e \sum_{k_1} \phi_e(k_1) \int d\mathbf{r} \Psi_{k_1}^{(v)*}(\mathbf{r})(\mathbf{F}\mathbf{r})\Psi_{k_1}^{(c)}(\mathbf{r})$$

$$+ e \sum_{k_1} \phi_c(k_1) \int d\mathbf{r} \Psi_{k_1}^{(v)*}(\mathbf{r})(\mathbf{F}\mathbf{r})\Psi_{k_1}^{(c)}(\mathbf{r})$$

(A2)

Substituting explicit expression (3-6) for $\Psi_{k_1}^{(v)}(\mathbf{r})$, we rewrite the second term in the right-hand side of Eq. (A2) as follows:
\[ e \sum_{\mathbf{k}_1} \phi_{v}(\mathbf{k}_1) \int d\mathbf{r} \psi_{\mathbf{k}}^{(v)\ast}(\mathbf{r})(\mathbf{F}\mathbf{r})\Psi_{\mathbf{k}_1}^{(v)}(\mathbf{r}) \]

\[ = \frac{e}{2} \sum_{\mathbf{k}_1} \phi_{v}(\mathbf{k}_1)(1 + e^{i(\varphi_{\mathbf{k}} - \varphi_{\mathbf{k}_1})}) \int d\mathbf{r}(\mathbf{F}\mathbf{r})e^{i\mathbf{r}(\mathbf{k} - \mathbf{k}_1)} \]

\[ = \frac{e}{2} \sum_{\mathbf{k}_1} \phi_{v}(\mathbf{k}_1)(1 + e^{i(\varphi_{\mathbf{k}} - \varphi_{\mathbf{k}_1})}) \left( -i\mathbf{F} \frac{\partial}{\partial \mathbf{k}_1} \right) \delta(\mathbf{k} - \mathbf{k}_1) \]

\[ = i\mathbf{F} \frac{\partial \phi_{v}(\mathbf{k})}{\partial \mathbf{k}} + \frac{e}{2} \phi_{v}(\mathbf{k}) \mathbf{F} \frac{\partial \varphi_{\mathbf{k}}}{\partial \mathbf{k}}, \quad (A3) \]

where in the last line, in the sum (integral) over \( \mathbf{k}_1 \), we use integration by parts. The final expression contains an additional term \( \frac{e}{2} \phi_{v}(\mathbf{k}) \mathbf{F} \frac{\partial \varphi_{\mathbf{k}}}{\partial \mathbf{k}} \), which is not included in the system of equations (3-8) and (3-9) since this term can be eliminated by substitution \( \phi_{v}(\mathbf{k}) \rightarrow \phi_{v}(\mathbf{k})e^{(e/2c)\mathbf{k}} \) and does not affect the energy spectrum of the system.

The third term on the right-hand side of Eq. (A2) can be rewritten as

\[ e \sum_{\mathbf{k}_1} \phi_{c}(\mathbf{k}_1) \int d\mathbf{r} \psi_{\mathbf{k}}^{(c)\ast}(\mathbf{r})(\mathbf{F}\mathbf{r})\Psi_{\mathbf{k}_1}^{(c)}(\mathbf{r}) \]

\[ = \frac{e}{2} \sum_{\mathbf{k}_1} \phi_{c}(\mathbf{k}_1)(-1 + e^{i(\varphi_{\mathbf{k}} - \varphi_{\mathbf{k}_1})}) \int d\mathbf{r}(\mathbf{F}\mathbf{r})e^{i\mathbf{r}(\mathbf{k} - \mathbf{k}_1)} \]

\[ = \frac{e}{2} \sum_{\mathbf{k}_1} \phi_{c}(\mathbf{k}_1)(-1 + e^{i(\varphi_{\mathbf{k}} - \varphi_{\mathbf{k}_1})}) \left( -i\mathbf{F} \frac{\partial}{\partial \mathbf{k}_1} \right) \delta(\mathbf{k} - \mathbf{k}_1) \]

\[ = \frac{e}{2} \phi_{c}(\mathbf{k}) \mathbf{F} \frac{\partial \varphi_{\mathbf{k}}}{\partial \mathbf{k}} = \mathbf{F}\mathbf{D}(\mathbf{k})\phi_{c}(\mathbf{k}), \quad (A4) \]

where the term proportional to \( \frac{\partial \varphi_{\mathbf{k}}}{\partial \mathbf{k}} \) is zero due to the orthogonality of the conduction and valence band free-field functions:

\[ (-1 + e^{i(\varphi_{\mathbf{k}} - \varphi_{\mathbf{k}_1})}) \delta(\mathbf{k} - \mathbf{k}_1) = 0 \quad (A5) \]
Combining Eqs. (A2)–(A4), we obtain Eq. (8). Similarly, multiplying Eq. (A1) by $\Psi_{kr}^{(c^*)(r)}$ and integrating it by $r$, we can derive Eq. (3-9).
List of Publications

Journal Papers


Conference Proceedings


REFERENCES


