

# **Modeling Nonlinear Optical Response in 2D materials from Nonequilibrium Quantum Dynamics**

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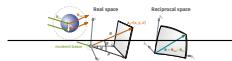
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Wenwen Mao  
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*To my*

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## **Summary**

Modeling Nonlinear Optical Response in 2D materials from Nonequilibrium

Quantum Dynamics

by

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Through the exploration of high-order harmonic generation, this research contributes to the broader scientific community's knowledge and paves the way for new discoveries and technological breakthroughs. The study of HHG not only deepens our comprehension of fundamental physics but also holds great promise for revolutionizing various fields, ranging from materials science and chemistry to biology and quantum technologies.

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# List of Abbreviations

- h-BN Hexagonal boron nitride. 8  
HHG High-Order Harmonic Generation. 1, 4  
QuI Quantum Interference. 3, 24  
QuIC Quantum Interference Control. 26, 27, 32–38  
TDSE Time-dependent Schrödinger equation. 12, 26

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# Chapter 1

## INTRODUCTION

In the conventional understanding of linear optics, the response of a material to an incident electromagnetic wave is linearly proportional to the strength of the electric field. However, when the intensity of the incident light exceeds a certain threshold, the nonlinear optical response becomes significant. This regime reveals a rich variety of phenomena, including the generation of new frequencies, phase modulation, and harmonic generation. Recent advancements in laser technology, driven by groundbreaking research in the field of nonlinear optics [1–3], have ushered in a new era of intense light generation. These developments have paved the way for in-depth exploration of light-matter interactions in highly nonlinear regimes. One of the most captivating nonlinear optical phenomena made accessible by these advances is High-order Harmonic Generation (**HHG**), a process characterized by its extreme photon upconversion and remarkable nonlinear characteristics.

### 1.1 Nonlinear Optical Response

Linear response theory is most applicable when the perturbations are small. In other words, the system's behavior is approximately linear in the vicinity of its equilibrium or initial state, the behavior of a system when it reacts proportionally to an applied perturbation. The system's behavior is described by linear

susceptibility ( $\chi^{(1)}$ ). Mathematically, if  $R$  is the response and  $P$  is the perturbation, linearity can be expressed as  $R = \alpha P$ , where  $\alpha$  is a constant. Nonlinear response extends the concept of linear response by considering the behavior of a system when the response is not directly proportional to the magnitude of the applied perturbation. In nonlinear systems, the response may involve higher-order terms, and the relationship between the perturbation and the response becomes more complex. Higher-order susceptibility terms are introduced, leading to nonlinear susceptibilities ( $\chi^{(2)}, \chi^{(3)}, \dots$ ). Nonlinear susceptibilities are coefficients that relate higher-order terms of the perturbing field to the response of the system. The response of a nonlinear system can often be expressed as a power series expansion, where the terms involve powers of the perturbing field. For example,  $R = \alpha P + \beta P^2 + \gamma P^3 + \dots$ . Nonlinear response often involves multiphoton processes, where multiple photons are absorbed simultaneously. The absorption of two or more photons can occur during a single interaction with the material. The probability of multiphoton absorption processes increases with the intensity of the incident light, making these processes more prominent at higher light intensities. Multiphoton absorption is often associated with higher harmonic generation, where the absorbed photons contribute to the generation of new frequencies that are integer multiples of the incident frequency. The absorption properties of a material can become intensity-dependent. This means that the absorption coefficient of the material varies with the intensity of the incident light. Intensity-dependent absorption is a key feature of nonlinear response and is often exploited in applications such as laser-induced material processing.

## 1.2 Photocarrier Effect

In the realm of photovoltaic effects, the second-order nonlinear optical effect, as explored in [4], has garnered considerable attention for its potential in achieving highly efficient light-to-current conversion. Investigations into shift-current, detailed in references [5–8], exemplify the significance of this phenomenon.

Another noteworthy aspect of second-order nonlinear current is the "injection current" [4, 9–12]. This current can be induced by the disruption of time-reversal symmetry through elliptically or circularly polarized light, in addition

to the breaking of intrinsic spatial inversion symmetry. The injection current results from the population imbalance induced by quantum interference (**QuI**) between various excitation paths, arising from the interference between absorption pathways associated with orthogonal components of polarization. Consequently, this leads to a polar distribution of electrons or holes in momentum space, generating a current injection that temporally aligns with optical intensity. Remarkably, the non-oscillating current induced by quantum interference may persist even after the perturbing laser irradiation ceases.

It is noteworthy that, unlike the shift-current, which occurs solely during laser irradiation, the injection current exhibits persistence even after the conclusion of laser irradiation. This enduring quality underscores the unique and sustained contribution of the injection current in the context of nonlinear optical effects.

Venturing beyond second-order nonlinear effects, researchers have delved into the realm of photovoltaic effects induced by intense few-cycle laser pulses [13–18]. Notably, such laser pulses possess the capability to extrinsically break spatial inversion symmetry. In addition to this, the presence of a strong field introduces highly nonlinear excitation channels, including pathways such as tunneling excitation. The amalgamation of extrinsic spatial inversion symmetry breaking and intense nonlinear interactions between light and matter opens the possibility for an intense few-cycle laser pulse to induce a direct current (dc-current) even in a material with intrinsic inversion symmetry.

The uniqueness of the photovoltaic effect with a few-cycle pulse lies in its dependence on breaking the inversion symmetry of the incident light fields. This intrinsic connection allows for the manipulation of the induced current by controlling both the intensity and carrier-envelope phase of the pulse [13, 16]. The exploration of these intense few-cycle laser pulses not only expands the understanding of nonlinear optical phenomena but also unveils avenues for precise control and manipulation of induced currents through tailored light-matter interactions.

In recent research, an effective method for manipulating valley population has surfaced, centered around the synergistic interplay of two circularly polarized lights with distinct frequencies, denoted as  $\omega$  and  $2\omega$ . This investigation is

particularly pertinent in the context of two-dimensional systems [19, 20]. Individually, each circularly polarized light disrupts time-reversal symmetry, and when combined, the fields exhibit the added capability of breaking spatial inversion symmetry. This dual infringement upon time-reversal and spatial inversion symmetries gives rise to a population imbalance in momentum space upon laser excitation. This, in turn, manifests as a sustained net charge flow persisting even after the cessation of laser irradiation. Notably, this methodology has extended beyond theoretical exploration, with numerical studies incorporating first-principles calculations applied to bulk solids [21]. The multifaceted approach of combining circularly polarized lights at different frequencies not only enriches our understanding of valley population dynamics but also holds promise for diverse applications in the realm of materials and quantum phenomena.

### 1.3 High-order Harmonic Generation

In the nonlinear optical process High-order Harmonic Generation (**HHG**), photons from the laser field are absorbed by the material, promoting electrons to higher energy states. These electrons then undergo complex dynamics, involving acceleration, coherent motion, and recombination with their parent ions. Through this intricate dance, the electrons emit high-energy photons with frequencies much higher than that of the incident laser, often extending into the extreme ultraviolet (XUV) and X-ray regions of the electromagnetic spectrum [22].

Since first observed in 1987 using rare gases as target specimens [23, 24], gas-phase HHG has been intensively utilized to generate ultrashort attosecond light pulses [25–27] for investigating ultrafast dynamics in matter in the time domain which is a typical time scale for the motion of electrons.[28–31]. HHG provides a unique window into electron dynamics and allows us to investigate processes occurring on attosecond timescales. The emitted harmonics carry valuable information about the electronic structure, band gaps, and transient states of the material, offering a powerful tool for probing and controlling ultrafast processes. In recent years, there have been significant advancements in experimental tech-

niques for studying high-order harmonic generation. The use of intense femtosecond laser pulses, pulse shaping methods, and advanced detection schemes have enabled precise control and characterization of the generated harmonics. These experimental advances have led to breakthroughs in attosecond science, providing tools for investigating ultrafast phenomena in a wide range of atoms [29, 32, 33], molecules [34–36], and solids [30, 31, 37–39]. The HHG in solid-state systems was first observed in ZnO in 2011 in mid-infrared (MIR) laser field [40], and it has since garnered significant attention, both from a fundamental research perspective and due to its technological potential, as evidenced by recent studies in solids [41–45].

## 1.4 Review on Numerical Methods

The generation of high-order harmonics involves complex quantum mechanical processes and intricate interplays between the laser field and the electronic structure of the material. The phenomenon can be understood within the framework of the three-step model [46, 47]. This semi-classical framework delineates the solid HHG process through three stages: 1. Ionization: Initially, an electron is ionized by the intense laser field and electron tunneling excitation from the valence band to the conduction band.

2. Acceleration: Subsequently, the strong laser field imparts energy to the liberated electron (holes), propelling its acceleration away from the ionized molecule.

3. Recombination: In the final step, the oscillatory force of the laser field drives the electron back toward the ionized parent molecule. During this process, the electron undergoes recombination with the molecule, releasing the surplus kinetic energy acquired in the second step in the form of a high-energy photon.

The understanding and control of HHG have been greatly advanced by the development of sophisticated theoretical models, such as the time-dependent Schrödinger equation and time-dependent density functional theory, enabling accurate predictions and interpretations of experimental observations.

## 1.5 Experiments and Thermodynamic model on graphene

## 1.6 Structure of the Thesis

This thesis aims to provide a comprehensive overview of the phenomenon of high-order harmonic generation in the context of nonlinear optics. We will explore the theoretical foundations of HHG, including the quantum mechanical description of the process and the role of electron dynamics. Additionally, we will delve into the experimental techniques and state-of-the-art advancements in generating and characterizing high-order harmonics. By investigating HHG, we seek to deepen our understanding of the nonlinear optical response of materials and unlock the potential for applications in fields such as ultrafast spectroscopy, attosecond science, and advanced imaging techniques.

This thesis is organized as follows: Chapter 2 first introduces the theoretical foundations to study the light-induced electron dynamics in graphene based on the tight-binding model and quantum master equation. In Chapter 3 we investigate the THz-induced HHG in graphene with the method described in Chapter 2. The microscopic mechanism of HHG with the quasi-static approximation and the population distribution in the Brillouin zone is described in detail together with its numerical implementation in Chapter 3. In Chapter 4, we elucidate the role of the nonequilibrium nature of THz-induced electron dynamics by comparing the nonequilibrium picture in the present work and the thermodynamic picture in the previous work [48]. Finally, our findings are summarized in Sec. ??.

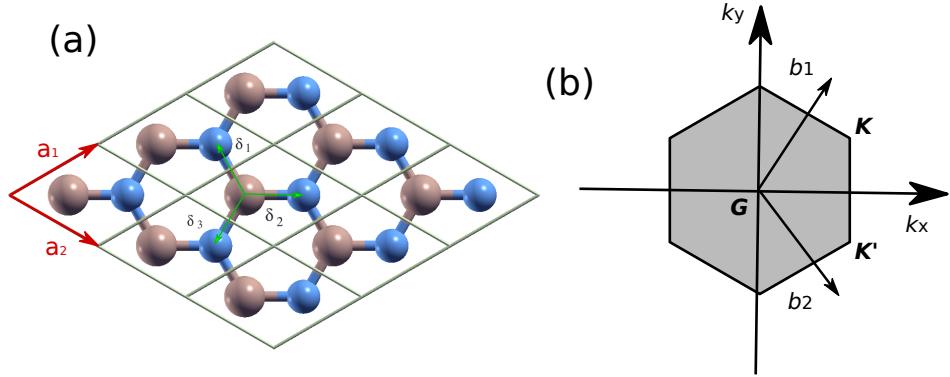
# Chapter 2

## THEORETICAL FOUNDATIONS

### 2.1 Crystallography Properties

The hexagonal lattice nanostructure, a fundamental Bravais lattice, manifests as a distinctive geometric arrangement prevalent across a spectrum of materials, owing to its highly efficient packing characteristics. This lattice's spatial configuration profoundly influences the mechanical, electrical, and thermal properties of materials. Understanding lattice structures is crucial for deciphering material behavior across diverse conditions, spanning from semimetals to topological insulators. This significance is particularly noteworthy in the realm of two-dimensional materials. We have selected graphene, exemplifying a semimetal, and hexagonal boron nitride (h-BN), recognized as an insulator, for our discussion on nonlinear optical response on 2d materials.

Graphene, an extraordinary carbon allotrope, showcases a captivating atomic arrangement within a hexagonal lattice nanostructure, depicted in Figure 2.1 (a). Carbon atoms meticulously align in a single layer, forming an exceptional two-dimensional material. The unique atomic-scale hexagonal lattice structure involves each carbon atom intricately bonding through  $\sigma$ -bonds with its three nearest neighbors and a delocalized  $\pi$ -bond. This precise arrangement plays a pivotal role in the formation of a valence band elegantly spanning the entirety of the graphene sheet, making monolayer graphene an outstanding conductor of electricity, and finding applications in electronic devices, sensors, and various fields.



**Figure 2.1:** (a) Hexagonal lattice showing in different colors the two triangular sublattices. (b) Brillouin zone in momentum space.

Similar to graphene, Hexagonal boron nitride (**h-BN**) also features a hexagonal lattice structure, but with alternating boron and nitrogen atoms forming the hexagons, making it a wide-gap insulator due to inversion symmetry breaking, which is used as a dielectric material in electronics, a substrate for graphene-based devices, and as a solid lubricant.

### 2.1.1 Structural Parameters

We define the basis of hexagonal lattice primitive vectors  $E = (\vec{a}_1, \vec{a}_2)$  as shown in Fig 2.1 (a):

$$\vec{a}_1 = a \begin{pmatrix} \frac{\sqrt{3}}{2} \\ \frac{1}{2} \end{pmatrix}, \vec{a}_2 = a \begin{pmatrix} \frac{\sqrt{3}}{2} \\ -\frac{1}{2} \end{pmatrix}$$

Where  $a$  is the lattice constant, for graphene  $a = 1.42\text{\AA}$  [49], and for **h-BN**  $a = 2.5\text{\AA}$  [50]. Generate only  $A$  sites while sites in  $B$  sublattice are generated by  $n_1\vec{a}_1 + n_2\vec{a}_2 + \vec{\delta}$ , where  $\vec{\delta}$  has to be chosen as one of the three nearest-neighbor vectors,

$$\vec{\delta}_1 = a \begin{pmatrix} -\frac{1}{2\sqrt{3}} \\ \frac{1}{2} \end{pmatrix}, \vec{\delta}_2 = a \begin{pmatrix} \frac{1}{\sqrt{3}} \\ 0 \end{pmatrix}, \vec{\delta}_3 = a \begin{pmatrix} -\frac{1}{2\sqrt{3}} \\ -\frac{1}{2} \end{pmatrix}$$

### 2.1.2 Reciprocal Space

The reciprocal basis  $B = (b_1, b_2, b_3)$  is generated using the formula:

$$\vec{b}_k = \frac{2\pi \cdot \vec{a}_i \times \vec{a}_j}{V}$$

$i, j, k$  are circular permutations,  $V$  the mix product between the three vectors, i.e. the volume of the unitary cell. Then we get the 2D reciprocal vectors as shown in Fig 2.1 (b):

$$\vec{b}_1 = k_D \begin{pmatrix} \frac{1}{2} \\ \frac{\sqrt{3}}{2} \end{pmatrix}, \vec{b}_2 = k_D \begin{pmatrix} \frac{1}{2} \\ -\frac{\sqrt{3}}{2} \end{pmatrix}$$

And with  $k_D = \frac{4\pi}{\sqrt{3}a}$ . The corresponding Brillouin zone is depicted together with the two high-symmetry points K and K' Fig 2.1 (b). Two inequivalent corners of the Brillouin zone  $K$  and  $K'$  can be chosen as follows:

$$K = k_D \left( \frac{1}{2}, \frac{1}{2\sqrt{3}} \right), \quad K' = k_D \left( \frac{1}{2}, -\frac{1}{2\sqrt{3}} \right)$$

## 2.2 Tight-binding Approach

In this section, we delve into the fundamental principles of the tight-binding approach, with a particular focus on the nearest neighbor tight-binding model. This approach is essential for understanding the electronic properties of materials and is a crucial component of graphene's electronic structure analysis.

The foundation of the tight-binding approach is rooted in the Bloch theorem, which is satisfied by the tight-binding function

$$\Phi_\alpha(\mathbf{r}, \mathbf{k}) = \frac{1}{\sqrt{N}} \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}} \phi_\alpha(\mathbf{r} - \mathbf{R}_\alpha), \alpha = A \text{ or } B \quad (2.1)$$

Here,  $N$  represents the number of unit cells, and  $\phi_\alpha(\mathbf{r} - \mathbf{R}_\alpha)$  denotes the orbital function of an electron at cell  $\mathbf{R}$  in sublattice  $\alpha$ . In the context of a honeycomb lattice, we focus on the nearest neighbor approximation. This approximation asserts that an atom in sublattice A only interacts with its three closest neighbor atoms in sublattice B. This simplification is particularly useful for understanding the interactions between electrons bound to non-equivalent atoms.

The Hamiltonian operator for this nearest-neighbor interaction is expressed as:

$$\hat{H}_{AB} = \frac{1}{N} \sum_{\mathbf{R}_A} \sum_{\mathbf{R}_B} e^{i\mathbf{k}(\mathbf{R}_B - \mathbf{R}_A)} \langle \phi_A(\mathbf{r} - \mathbf{R}_A) | \hat{H} | \phi_B(\mathbf{r} - \mathbf{R}_B) \rangle \quad (2.2)$$

Due to the translational invariance in a Bravais lattice, the summation over each atom in a sublattice occurs  $N$  times, simplifying the expression to:

$$\hat{H}_{AB} = \sum_{\mathbf{R}_A} e^{i\mathbf{k}(\mathbf{R}_B - \mathbf{R}_A)} \langle \phi_A(\mathbf{r} - \mathbf{R}_A) | \hat{H} | \phi_B(\mathbf{r} - \mathbf{R}_B) \rangle \quad (2.3)$$

To transition from real space to momentum space, we employ a Fourier transform, allowing us to represent the Hamiltonian in terms of momentum space. This transformation results in the tight-binding Hamiltonian under the momentum representation, as defined by:

$$c_{\mathbf{R}_\alpha, \sigma} = \frac{1}{\sqrt{N}} \sum_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{R}_\alpha} c_{\mathbf{k}, \sigma} \quad (2.4)$$

$$c_{\mathbf{R}_\alpha, \sigma}^\dagger = \frac{1}{\sqrt{N}} \sum_{\mathbf{k}} e^{-i\mathbf{k}\cdot\mathbf{R}_\alpha} c_{\mathbf{k}, \sigma}^+ \quad (2.5)$$

$\sigma = \uparrow, \downarrow$  presents the electron spin, With the orthogonal normalization conditions

$$\delta_{\mathbf{k}\mathbf{k}'} = \frac{1}{N} \sum_{\mathbf{k}} e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{R}_\alpha} \quad (2.6)$$

We transform the Hamiltonian of real space into the momentum space representation, and then the tight-binding Hamiltonian under the momentum representation is:

$$\hat{H} = \begin{pmatrix} \epsilon_A & t_0 f(\mathbf{k}) \\ t_0 f(\mathbf{k})^* & \epsilon_B \end{pmatrix} \quad (2.7)$$

Here  $\epsilon_A$  and  $\epsilon_B$  are the on-site energies of electrons on the nearest neighbor atoms,  $t_0$  presents the hopping parameter:

$$t_0 = \left\langle \phi_A(\mathbf{r} - \mathbf{R}_A) | \hat{H} | \phi_B(\mathbf{r} - \mathbf{R}_A - \vec{\delta}_i) \right\rangle \quad (i = 1, 2, 3)$$

For graphene, we set  $\epsilon_A$  and  $\epsilon_B$  to 0, and  $t_0 = 2.8 \text{ eV}$  in accordance with the pre-

vious work [49]. For h-BN  $\epsilon_B$  and  $\epsilon_N$  denote the on-site energies for boron and nitrogen sites, respectively.

$$\hat{H}(\mathbf{k}) = \begin{pmatrix} \epsilon_B & t_0 f(\mathbf{k}) \\ t_0 f(\mathbf{k})^* & \epsilon_N \end{pmatrix}, \quad (2.8)$$

We set  $\epsilon_B$  to 3.34 eV and  $\epsilon_N$  to  $-2.56$  eV and  $t_0$  to 2.6 eV computed with the first-principles calculations [51], the band gap  $E_g = \epsilon_b - \epsilon_n$  equals 5.9 eV.

The off-diagonal terms of the tight-binding Hamiltonian 2.7:

$$\begin{aligned} f(\mathbf{k}) &= e^{i\mathbf{k}\vec{\delta}_1} + e^{i\mathbf{k}\vec{\delta}_2} + e^{i\mathbf{k}\vec{\delta}_3} \\ &= e^{-\frac{ia k_x}{\sqrt{3}}} + 2e^{\frac{ia k_x}{2\sqrt{3}}} \cos\left(\frac{a}{2}k_y\right) \end{aligned} \quad (2.9)$$

Solving the stationary Schrödinger equation using matrix diagonalization:

$$\hat{H}_k |\phi_{bk}\rangle = \epsilon_{bk} |\phi_b\rangle, \quad (2.10)$$

We get the eigenenergy of Hamiltonian from 2.7, where  $b$  is a band index,  $|\phi_{bk}\rangle$  is an eigenstate, and  $\epsilon_{bk}$  corresponds to the eigenenergy. As the Hamiltonian is a 2-by-2 matrix in this work, the band index  $b$  denotes either a conduction ( $b = c$ ) or valence ( $b = v$ ) state.

$$\epsilon_{bk} = E_0 \pm \frac{1}{2} \sqrt{E_g^2 + 4t_0^2|f|^2} \quad (2.11)$$

$E_0 = \frac{\epsilon_A + \epsilon_B}{2}$  and  $E_g = \epsilon_b - \epsilon_n$  is the energy gap. For graphene,  $\epsilon_A = \epsilon_B = 0$  the band gap equals 0. Their corresponding eigenvectors are:

$$|\phi_b\rangle = \begin{pmatrix} \frac{E_g \pm \sqrt{E_g^2 + 4t_0^2|f|^2}}{2t_0 f^*} \\ 1 \end{pmatrix} \quad (2.12)$$

## 2.3 Electron Dynamics

Consider the crystal under the electric field  $E$ , to avoid that Bloch's theorem cannot be applied, let the electric field enter through a uniform vector potential  $A(t)$ .

The time-dependent Hamiltonian is written as

$$\hat{H}(t) = \frac{[\hat{p} + eA(t)]^2}{2m} + V(r) \quad (2.13)$$

Transforming to the  $k$ -space representation, we have

$$\hat{H}(k, t) = \hat{H}\left(k + \frac{e}{\hbar} A(t)\right) \quad (2.14)$$

where  $k$  denotes the Bloch wavevector, and  $|\psi_k(t)\rangle$  is a single-particle electroinc wavefunction at  $k$ . The vector potential  $A(t)$  is related to the applied electric field  $E(t)$  as  $E(t) = -dA(t)/dt$ , and it is included in the Hamiltonian as the wavevector shift  $k \rightarrow k + eA(t)/\hbar$  via the Peierls substitution [52].

### 2.3.1 Time-dependent Schrödinger Equation

The light-induced electron dynamics can be described by solving the following time-dependent Schrödinger equation (TDSE) at each  $k$ -point:

$$i\hbar \frac{d}{dt} |\psi_k(t)\rangle = \hat{H}\left(k + \frac{eA(t)}{\hbar}\right) |\psi_k(t)\rangle, \quad (2.15)$$

Solving this time-dependent Schrödinger equation (TDSE) is an initial value problem. In two-band systems, usually the ground state  $\psi_k(0)$  is used as the initial state occupied at the valence band with:

$$\psi_k(0) = \begin{pmatrix} 0 \\ 1 \end{pmatrix} \quad (2.16)$$

The adiabatic approximation is used almost all the time in solving time-propagation, which will be explained in more detail in the appendix A. Various numerical schemes can be chosen for doing the time propagation, here we split the propagation into short-time propagation using the composition property:

$$|\psi_k(t')\rangle = \exp\left[-i \int_t^{t'} d\tau \hat{H}(\tau)\right] |\psi_{k+A(t)}\rangle \quad (2.17)$$

In practice, simpler schemes are usually used and self-consistency is often neglected. Instead, we rely on a sufficiently small  $\Delta t$ ,  $t' = t + \Delta t$ , the exponential mid-point propagator is given by:

$$U(t + \Delta t, t) \approx U_{EM}(t + \Delta t, t) = \exp\{-i\Delta t \hat{H}(t + \Delta t/2)\} \quad (2.18)$$

We approximate the exponential using a Taylor expansion to fourth-order:

$$\exp\{A\} = \sum_{k=0}^{\infty} \frac{1}{k!} A^k \quad (2.19)$$

Once the time-evolution of the wavefunctions,  $|\psi_k(t)\rangle$  is computed, the current induced in the matter can be further evaluated with

$$J_k(t) = \frac{1}{(2\pi)^2} \int_{BZ} dk \langle \psi_k(t) | \hat{J}_k(t) | \psi_k(t) \rangle. \quad (2.20)$$

Here,  $\hat{J}_k(t)$  is the current operator, and it is defined as

$$\hat{J}_k(t) = \frac{\partial}{\partial k} \hat{H} \left( k + \frac{eA(t)}{\hbar} \right) = -t_0 \begin{pmatrix} 0 & \frac{\partial f(k+A)}{\partial A} \\ \frac{\partial f^*(k+A)}{\partial A} & 0 \end{pmatrix}, \quad (2.21)$$

where  $\frac{\partial f(k)}{\partial k}$  is given by

$$\frac{\partial f(k)}{\partial k} = i\delta_1 e^{ik\cdot\delta_1} + i\delta_2 e^{ik\cdot\delta_2} + i\delta_3 e^{ik\cdot\delta_3}. \quad (2.22)$$

Current 2.20 can be further decomposed into:

$$\begin{aligned} J_{b,k}(t) &= \langle \psi_{b,k}(t) | J(t) | \psi_{b,k}(t) \rangle \\ &= \sum_{b',b''} c_{b'k}(t) c_{b''k}^*(t) \langle \phi_{b''k}^H(t) | J(t) | \phi_{b'k}^H(t) \rangle + \sum_{b',b''} |c_{b'k}(t)|^2 \langle \phi_{b'k}^H(t) | J(t) | \phi_{b'k}^H(t) \rangle \end{aligned} \quad (2.23)$$

Here the off-diagonal terms contribute to the Interband current, and the diagonal terms contribute to the Intraband current.

$$J_{inter;b,k}(t) = \sum_{b',b''} c_{b'k}(t) c_{b''k}^*(t) \langle \phi_{b''k}^H(t) | J(t) | \phi_{b'k}^H(t) \rangle \quad (2.24)$$

$$J_{intra;b,k}(t) = \sum_{b',b''} |c_{b'k}(t)|^2 \langle \phi_{b'k}^H(t) | J(t) | \phi_{b'k}^H(t) \rangle \quad (2.25)$$

By combining time-dependent wavefunction  $\psi_k(t)$  solved from Eq. (2.7) and the eigenstates  $\phi_{ck}$  defined with Eq. (2.10), the conduction population distribution  $n_{ck}$  with the laser irradiation at instantaneous time  $t$  can be evaluated as:

$$n_{ck} = |\langle \phi_{ck} | \psi_k(t) \rangle|^2, \quad (2.26)$$

$\frac{\partial \epsilon_{b,k+A(t)}}{\partial k} = -\langle \phi_{b'k}^H(t) | J(t) | \phi_{b'k}^H(t) \rangle$  defines the band velocity. The eigenenergy of conduction band at time  $t$  is  $\epsilon_{c,k+A(t)} = E_0 + \frac{1}{2} \sqrt{E_g^2 + 4t_0^2 |f(k + A(t))|^2}$

$$\frac{\partial \epsilon_{v,k+A(t)}}{\partial k} = -\frac{t_0^2}{2\epsilon_{v,k+A(t)} - (\epsilon_b + \epsilon_n)} \cdot (f^*(k + A(t)) \frac{\partial f(k + A(t))}{\partial k} + c.c.) \quad (2.27)$$

$$\frac{\partial \epsilon_{c,k+A(t)}}{\partial k} = \frac{t_0^2}{2\epsilon_{c,k+A(t)} - (\epsilon_b + \epsilon_n)} \cdot (f^*(k + A(t)) \frac{\partial f(k + A(t))}{\partial k} + c.c.) \quad (2.28)$$

### 2.3.2 Quantum Master Equation

In contrast to closed quantum systems, which are entirely isolated from external influences and can be adequately described by the Schrödinger equation, the quantum master equation is typically used in the context of the time evolution of an open quantum system, where the system of interest is susceptible to exchanges of energy, particles, or information with its external environment. To expound processes such as relaxation, dephasing, and thermalization of the nonlinear response experiments, the quantum master equation is predominantly employed which is salient in the realm of open quantum systems.

We describe the light-induced electron dynamics in graphene with the following quantum master equation [53–56]:

$$\frac{d}{dt} \rho_k(t) = \frac{1}{i\hbar} [\hat{H}_{k+eA(t)/\hbar}, \rho_k(t)] + \hat{D}[\rho_k(t)], \quad (2.29)$$

$\rho_k(t)$  is the reduced density matrix at  $k$ . The quantum master equation delineates the dynamical evolution of the density matrix associated with the quantum system, which encompasses both pure and mixed quantum states. To elucidate the impact of dissipation, we formulate the relaxation operator, denoted as  $\hat{D}[\rho_k(t)]$ , within the framework of Eq.(2.29) employing the relaxation time approximation[57] and employing the Houston basis [58, 59]. The Houston states are characterized as eigenstates of the instantaneous Hamiltonian, expressed as:

$$\hat{H}_{k+eA(t)/\hbar}|u_{bk}^H(t)\rangle = \epsilon_{b,k+eA(t)/\hbar}|u_{bk}^H(t)\rangle \quad (2.30)$$

The expansion of the reduced density matrix can then be carried out using the Houston states.

$$\rho_k(t) = \sum_{bb'} \rho_{bb',k}(t)|u_{bk}^H(t)\rangle\langle u_{b'k}^H(t)|, \quad (2.31)$$

where  $\rho_{bb',k}(t)$  are the expansion coefficients. On the basis of the Houston state expansion, we define the relaxation operator [53, 54, 60] as

$$\hat{D}[\rho_k(t)] = - \sum_b \frac{\rho_{bb,k}(t) - f^{FD}(\epsilon_{b,k+eA(t)/\hbar}, T_e, \mu)}{T_1} |u_{bk}^H(t)\rangle\langle u_{bk}^H(t)| - \sum_{b \neq b'} \frac{\rho_{bb',k}(t)}{T_2} |u_{bk}^H(t)\rangle\langle u_{b'k}^H(t)|, \quad (2.32)$$

$T_1$  is the longitudinal relaxation time,  $T_2$  is the transverse relaxation time, and  $f^{FD}(\epsilon)$  is the Fermi–Dirac distribution

$$f^{FD}(\epsilon, T_e, \mu) = \frac{1}{e^{(\epsilon-\mu)/k_B T_e} + 1}. \quad (2.33)$$

$\mu$  is the chemical potential, and  $T_e$  is the electron temperature. In the following discussion, we set the longitudinal relaxation time  $T_1$  to 100 fs and the transverse relaxation time  $T_2$  to 20 fs in accordance with the previous works [53–56]. The electron temperature  $T_e$  is set to 300 K unless stated otherwise. The chemical potential  $\mu$  is treated as a tunable parameter to study the effect of doping.

We directly solve the quantum master equation, Eq. (2.29), in the time domain by employing the Runge-Kutta method without any approximation. The electric current is obtained by employing the time-dependent density matrix  $\rho_k(t)$ , which

evolves according to Eq. (2.29):

$$J(t) = \frac{2}{(2\pi)^2} \int dk \text{Tr} [\hat{J}_k(t) \rho_k(t)], \quad (2.34)$$

where  $\hat{J}_k(t)$  is the current operator defined as

$$\hat{J}_k(t) = -\frac{\partial H(k + eA(t)/\hbar)}{\partial A(t)}. \quad (2.35)$$

The intraband component of the current is

$$J_k^{\text{intra}}(t) = \sum_{b=v,c} \frac{(-2)}{(2\pi)^2} \frac{e}{\hbar} \times \int dk \frac{\partial \epsilon_{b,k+eA(t)/\hbar}}{\partial k} n_{b,k+eA(t)/\hbar},$$

where the band population  $n_{b,k+eA(t)/\hbar}$  is defined with the Houston states of the Hamiltonian  $|u_{b,k}^H(t)\rangle$  computed from Eq 2.30:

$$n_{b,k+eA(t)/\hbar}(t) = \langle u_{b,k}^H(t) | \rho_k(t) | u_{b,k}^H(t) \rangle \quad (2.36)$$

# Chapter 3

## CO-LINEAR POLARIZATION INDUCED PHOTOVOLTAIC EFFECT

Addressing the photovoltaic effect within the perturbative regime has garnered significant attention, particularly in the exploration of dc current injection using two-color linearly polarized light [61–67]. Early investigations have underscored the intricate interplay between a fundamental frequency, denoted as  $\omega$ , and its second harmonic,  $2\omega$  [61–63]. A notable study by Jimenez-Galan et al. [19] utilized deeply off-resonant bi-circular laser fields with frequencies  $\omega$  and  $2\omega$  to generate a substantial population imbalance in the Brillouin zone. However, it is worth noting that, in principle, the use of linearly polarized light with two frequencies is sufficient to break time-reversal symmetry.

In this Chapter, we first theoretically explore the phenomenon of dc-current injection and the generation of population imbalance through the application of two-color linearly polarized laser fields with frequencies  $\omega$  and  $2\omega$  based on time-dependent perturbation analysis. To ground our analysis, we scrutinize light-induced electron dynamics in a prototypical two-dimensional material, monolayer hexagonal boron-nitride (*h*-BN), leveraging a simple tight-binding approximation first in a perturbative resonant regime.

In our quantum dynamics simulations, we further uncover that ballistic current can be induced even in the deeply off-resonant regime with two-color linearly polarized light. Consequently, efficient injection of dc-current and the cre-

ation of a substantial population imbalance can be realized by employing two-color linearly polarized laser fields with frequencies  $\omega$  and  $2\omega$ , without relying on the ellipticity of light. These findings offer a potential pathway for achieving ultrafast and efficient control of electron population in matter using multi-color linearly polarized light, opening new avenues for exploring the frontiers of quantum dynamics and optoelectronic applications. This streamlined approach offers a promising avenue for achieving efficient and controlled current injection under conditions of deep off-resonance, potentially opening up new possibilities for nonlinear optoelectronic applications.

### 3.1 Time-dependent Perturbative Analysis on QuI

Time-dependent perturbation theory provides a formalism for describing the response of quantum systems to time-varying external fields, making it well-suited for analyzing the interaction of materials with intense electromagnetic radiation. It provides a formalism for describing the response of quantum systems to time-varying external fields, making it well-suited for analyzing the interaction of materials with intense electromagnetic radiation. Exploring the photovoltaic effect within the perturbative regime has led to a notable focus on elucidating the injection of direct current (dc) through the use of two-color linearly polarized light [61–67]. Here, we investigate the nonlinear photocarrier injection process via the time-dependent perturbation analysis. Under adiabatic basis representation described in Appendix A, one can rewrite the equation of motion for the coefficient vector as

$$\begin{aligned} i \frac{d}{dt} c_k(t) &= \\ iE(t) \cdot \left( \begin{array}{cc} 0 & e^{-i \int_0^t dt' \Delta \epsilon_{cv,k+A(t')} + i \Delta \phi_{cv,k}^g(t)} \left\langle u_{v,k+A(t)} \left| \frac{\partial u_{c,k+A(t)}}{\partial k} \right. \right\rangle \\ e^{-i \int_0^t dt' \Delta \epsilon_{vc,k+A(t')} + i \Delta \phi_{vc,k}^g(t)} \left\langle u_{c,k+A(t)} \left| \frac{\partial u_{v,k+A(t)}}{\partial k} \right. \right\rangle & 0 \end{array} \right) c_k(t) \\ &= \mathcal{H}(t) c_k(t). \end{aligned} \quad (3.1)$$

$c_k(t) = \begin{pmatrix} c_{v,k}(t) \\ c_{c,k}(t) \end{pmatrix}$  is the coefficient vector,  $\Delta \epsilon_{bb',k+A(t)}$  is defined by the difference of the single-particle energies as  $\epsilon_{b,k+A(t)} - \epsilon_{b',k+A(t)}$ . For simplicity, here

### 3.1. TIME-DEPENDENT PERTURBATIVE ANALYSIS ON QUI

assume that the contributions from the geometric phases,  $\Delta\phi_{cv,k}^g(t)$  are zero. Then expand the Hamiltonian in Eq. (A.10) up to the second order of the field  $A(t)$  as

$$\mathcal{H}(t) \approx \mathcal{H}^{(1)}(t) + \mathcal{H}_{dyn}^{(2)}(t) + \mathcal{H}_{dip}^{(2)}(t), \quad (3.2)$$

$$\mathcal{H}^{(1)}(t) = iE(t) \cdot \begin{pmatrix} 0 & e^{-i\Delta\epsilon_{cv,k}t} \left\langle u_{v,k} \middle| \frac{\partial u_{c,k}}{\partial k} \right\rangle \\ e^{-i\Delta\epsilon_{vc,k}t} \left\langle u_{c,k} \middle| \frac{\partial u_{v,k}}{\partial k} \right\rangle & 0 \end{pmatrix}, \quad (3.3)$$

$\mathcal{H}_{dyn}^{(2)}(t)$  and  $\mathcal{H}_{dip}^{(2)}(t)$ , are given by

$$\mathcal{H}_{dyn}^{(2)}(t) = E(t) \cdot \begin{pmatrix} 0 & \frac{\partial \Delta\epsilon_{cv,k}}{\partial k} \cdot \left( \int_0^t dt' A(t') \right) e^{-i\Delta\epsilon_{cv,k}t} \left\langle u_{v,k} \middle| \frac{\partial u_{c,k}}{\partial k} \right\rangle \\ \frac{\partial \Delta\epsilon_{vc,k}}{\partial k} \cdot \left( \int_0^t dt' A(t') \right) e^{-i\Delta\epsilon_{vc,k}t} \left\langle u_{c,k} \middle| \frac{\partial u_{v,k}}{\partial k} \right\rangle & 0 \end{pmatrix}, \quad (3.4)$$

and

$$\mathcal{H}_{dip}^{(2)}(t) = \begin{pmatrix} 0 & e^{-i\Delta\epsilon_{cv,k}t} A(t) \cdot \frac{\partial u_{v,k}}{\partial k} \Big|_{iE(t) \cdot \frac{\partial u_{c,k}}{\partial k}} \\ e^{-i\Delta\epsilon_{vc,k}t} A(t) \cdot \frac{\partial u_{c,k}}{\partial k} \Big|_{iE(t) \cdot \frac{\partial u_{v,k}}{\partial k}} & 0 \end{pmatrix}. \quad (3.5)$$

Here,  $\mathcal{H}_{dyn}^{(2)}(t)$  originates from the modification of the dynamical phase factor:

$$e^{-i \int_0^t dt' \Delta\epsilon_{vc,k+A(t')}} \quad (3.6)$$

while  $\mathcal{H}_{dip}^{(2)}(t)$  originates from the modification of the dipole matrix elements:

$$i \left\langle u_{v,k+A(t)} \middle| \frac{\partial u_{c,k+A(t)}}{\partial k} \right\rangle \quad (3.7)$$

Hereafter, we analyze the photocarrier injection process based on this perturba-

tive expansion of the Hamiltonian. Use perturbation expansion of Eq. (A.10):

$$i \frac{d}{dt} (c_k^{(0)}(t) + c_k^{(1)}(t) + c_k^{(2)}(t)) = (\mathcal{H}_k^{(0)} + \mathcal{H}_k^{(1)}(t) + \mathcal{H}_k^{(2)}(t))(c_k^{(0)}(t) + c_k^{(1)}(t) + c_k^{(2)}(t)) \quad (3.8)$$

Under initial condition  $\mathcal{H}_k^{(0)}(t=0) = 0$ ,  $c_k^{(0)}(t=0) = \begin{pmatrix} 1 \\ 0 \end{pmatrix}$ , the first and second-order coefficient vectors for the conduction band can be written as:

$$c_{c,k}^{(1)}(t) = \left\langle u_{c,k} \left| \frac{\partial u_{v,k}}{\partial k} \right. \right\rangle \int_0^t dt' e^{-i\Delta\epsilon_{vc,k} t'} E_1(t') \quad (3.9)$$

$$c_{c,k,dyn}^{(2)}(t) = \frac{1}{i} \frac{\partial \Delta\epsilon_{vc,k}}{\partial k} \left\langle u_{c,k} \left| \frac{\partial u_{v,k}}{\partial k} \right. \right\rangle \int_0^t dt' e^{-i\Delta\epsilon_{vc,k} t'} E_2(t') \int_0^{t'} dt'' A_2(t'') \quad (3.10)$$

$$c_{c,k,dip}^{(2)}(t) = \frac{\partial \left\langle u_{c,k} \left| \frac{\partial u_{v,k}}{\partial k} \right. \right\rangle}{\partial k} \int_0^t dt' e^{-i\Delta\epsilon_{vc,k} t'} E_2(t') A_2(t') \quad (3.11)$$

Under two-color linearly polarized light, here we consider the perturbation by the external linearly polarized vector potential for  $\vec{e}$ -direction, assuming that the perturbation only exists time between 0 and  $T_0$  under the Gaussian distribution:

$$f(t) = e^{-\frac{(t-T_0)^2}{2\sigma^2}} \quad (3.12)$$

$$A_1(t) = A_1 \vec{e} \cos[2w(t - T_0) + \phi] e^{-\frac{(t-T_0)^2}{2\sigma^2}}, \quad (3.13)$$

$$A_2(t) = A_2 \vec{e} \cos[w(t - T_0)] e^{-\frac{(t-T_0)^2}{2\sigma^2}} \quad (3.14)$$

$w$  is the carrier frequency of the field,  $\vec{e}$  represents a unit vector along the polarization direction of the laser field. We assume  $T_0 \gg 0$  and  $\sigma \gg 0$  to make the approximation:

$$\int_0^t A_2 \vec{e} \cos[w(t - T_0)] e^{-\frac{(t-T_0)^2}{2\sigma^2}} = \frac{A_2 \vec{e}}{w} \sin[w(t' - T_0)] e^{-\frac{(t'-T_0)^2}{2\sigma^2}} \quad (3.15)$$

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The corresponding external electric field  $E(t) = -dA(t)/dt$  can be written as the following pulsed form:

$$E_1(t) = 2wA_1 \vec{e} \sin[2w(t - T_0) + \phi] e^{-\frac{(t-T_0)^2}{2\sigma^2}}, \quad (3.16)$$

$$E_2(t) = wA_2 \vec{e} \sin[w(t - T_0)] e^{-\frac{(t-T_0)^2}{2\sigma^2}} \quad (3.17)$$

Now, let's express this in terms of the first-order coefficient vector is:

$$\begin{aligned} c_{c,k}^{(1)}(t) &= \left\langle u_{c,k} \left| \frac{\partial u_{v,k}}{\partial k} \right. \right\rangle \int_0^t dt' e^{-i\Delta\epsilon_{vc,k} t'} 2wA_1 \vec{e} \cdot \sin[2w(t' - T_0) + \phi] e^{-\frac{(t'-T_0)^2}{2\sigma^2}} \\ &= \frac{A_1 \vec{e} w}{i} \left\langle u_{c,k} \left| \frac{\partial u_{v,k}}{\partial k} \right. \right\rangle \int_0^t dt' e^{-i\Delta\epsilon_{vc,k} t' - \frac{(t'-T_0)^2}{2\sigma^2}} \cdot (e^{i[2w(t' - T_0) + \phi]} - e^{-i[2w(t' - T_0) + \phi]}) \end{aligned} \quad (3.18)$$

We consider the population distribution after the laser pulse, so we replace the integra  $\int_0^t$  by  $\int_\infty^\infty$ . Under the Gaussian integral,

$$\int_{-\infty}^\infty e^{-x^2} dx = \sqrt{\pi} \quad (3.19)$$

we get:

$$c_{c,k}^{(1)}(t) = \frac{A_1 \vec{e} w \cdot \sigma \sqrt{2\pi}}{i} \left\langle u_{c,k} \left| \frac{\partial u_{v,k}}{\partial k} \right. \right\rangle \cdot e^{-i\Delta\epsilon_{vc,k} T_0} [e^{-\frac{1}{2}(\Delta\epsilon_{vc,k} - 2w)^2 \sigma^2 - i\phi} - e^{-\frac{1}{2}(\Delta\epsilon_{vc,k} + 2w)^2 \sigma^2 + i\phi}] \quad (3.20)$$

Similarly to the first-order perturbation coefficient vector's derivation, the second-order coefficient  $c_{c,k}^{(2)}(t)$  can be written as:

$$c_{c,k,dyn}^{(2)}(t) = \frac{(A_2 \vec{e})^2 \cdot \sigma \sqrt{\pi}}{2i} \frac{\partial \Delta\epsilon_{vc,k}}{\partial k} \left\langle u_{c,k} \left| \frac{\partial u_{v,k}}{\partial k} \right. \right\rangle \cdot e^{-i\Delta\epsilon_{vc,k} T_0} \cdot [e^{-\frac{\sigma^2}{4} \Delta\epsilon_{vc,k}^2} - \frac{1}{2}(e^{-\frac{\sigma^2}{4} (\Delta\epsilon_{vc,k} - 2w)^2} + e^{-\frac{\sigma^2}{4} (\Delta\epsilon_{vc,k} + 2w)^2})] \quad (3.21)$$

$$c_{c,k,dip}^{(2)}(t) = \frac{(A_2 \vec{e})^2 w \cdot \sigma \sqrt{\pi}}{4i} \cdot \frac{\partial \left\langle u_{c,k} \left| \frac{\partial u_{v,k}}{\partial k} \right. \right\rangle}{\partial k} \cdot e^{-i\Delta\epsilon_{vc,k} T_0} [e^{-\frac{\sigma^2}{4} (\Delta\epsilon_{vc,k} - 2w)^2} - e^{-\frac{\sigma^2}{4} (\Delta\epsilon_{vc,k} + 2w)^2}] \quad (3.22)$$

This completes the derivation of the population of the conduction band after the

laser pulse:

$$\begin{aligned}
 |c_{c,k}(t)|^2 &= |c_{c,k}^{(1)}(t)|^2 + |c_{c,k,dyn}^{(2)}(t)|^2 + |c_{c,k,dip}^{(2)}(t)|^2 \\
 &\quad + c_{c,k}^{(1)*}(t) c_{c,k,dyn}^{(2)}(t) + c.c. \\
 &\quad + c_{c,k}^{(1)*}(t) c_{c,k,dip}^{(2)}(t) + c.c. \\
 &\quad + c_{c,k,dyn}^{(2)*}(t) c_{c,k,dip}^{(2)}(t) + c.c.
 \end{aligned} \tag{3.23}$$

We consider a prototypical two-dimensional insulator, monolayer hexagonal boron-nitride (*h*-BN). For the 2-band hBN-tight-binding model, the inversion symmetric is breaking:

$$u_k(-\vec{r}) \neq u_{-k}(\vec{r}) \tag{3.24}$$

We apply the time-reversal relation for the derivation:

$$u_k^*(\vec{r}) = u_{-k}(\vec{r}) \tag{3.25}$$

To compare the  $|c_{c,-k}(t)|^2$ , the absolute value of the coefficient becomes:

$$\begin{aligned}
 |c_{c,k}^{(1)}(t)|^2 &= \left| \frac{A_1 \vec{e} w \cdot \sigma \sqrt{2\pi}}{i} \left\langle u_{c,k} \left| \frac{\partial u_{v,k}}{\partial k} \right. \right\rangle \right|^2 \\
 &\quad \cdot [e^{-(\Delta\epsilon_{vc,k}-2w)^2\sigma^2} + e^{-(\Delta\epsilon_{vc,k}+2w)^2\sigma^2} - 2e^{-\frac{1}{2}((\Delta\epsilon_{vc,k}-2w)^2\sigma^2+(\Delta\epsilon_{vc,k}+2w)^2\sigma^2)} \cos(2\phi)] \\
 &= |c_{c,-k}^{(1)}(t)|^2
 \end{aligned} \tag{3.26}$$

$$\begin{aligned}
 |c_{c,k,dyn}^{(2)}(t)|^2 &= \left| \frac{(A_2 \vec{e})^2 \cdot \sigma \sqrt{\pi}}{2} \frac{\partial \Delta\epsilon_{vc,k}}{\partial k} \left\langle u_{c,k} \left| \frac{\partial u_{v,k}}{\partial k} \right. \right\rangle \cdot [e^{-\frac{\sigma^2}{4}\Delta\epsilon_{vc,k}^2} - \frac{1}{2}(e^{-\frac{\sigma^2}{4}(\Delta\epsilon_{vc,k}-2w)^2} + e^{-\frac{\sigma^2}{4}(\Delta\epsilon_{vc,k}+2w)^2})] \right|^2 \\
 &= |c_{c,-k,dyn}^{(2)}(t)|^2
 \end{aligned} \tag{3.27}$$

$$\begin{aligned}
 |c_{c,k,dip}^{(2)}(t)|^2 &= \left| \frac{(A_2 \vec{e})^2 w \cdot \sigma \sqrt{\pi}}{4} \cdot \frac{\partial \left\langle u_{c,k} \left| \frac{\partial u_{v,k}}{\partial k} \right. \right\rangle}{\partial k} [e^{-\frac{\sigma^2}{4}(\Delta\epsilon_{vc,k}-2w)^2} - e^{-\frac{\sigma^2}{4}(\Delta\epsilon_{vc,k}+2w)^2}] \right|^2 \\
 &= |c_{c,-k,dip}^{(2)}(t)|^2
 \end{aligned} \tag{3.28}$$

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The interference terms are:

$$\begin{aligned}
c_{c,k}^{(1)}(t)^* c_{c,k,dyn}^{(2)}(t) + c.c. &= \sqrt{2} A_1 A_2^2 \vec{e} w \cdot \sigma^2 \pi \frac{\partial \Delta \epsilon_{vc,k}}{\partial k} \left| \left\langle u_{c,k} \left| \frac{\partial u_{v,k}}{\partial k} \right. \right\rangle \right|^2 \\
&\cdot [e^{-\frac{\sigma^2}{4} \Delta \epsilon_{vc,k}^2} - \frac{1}{2} (e^{-\frac{\sigma^2}{4} (\Delta \epsilon_{vc,k} - 2w)^2} + e^{-\frac{\sigma^2}{4} (\Delta \epsilon_{vc,k} + 2w)^2})] \\
&\cdot [e^{-\frac{1}{2} (\Delta \epsilon_{vc,k} - 2w)^2 \sigma^2} - e^{-\frac{1}{2} (\Delta \epsilon_{vc,k} + 2w)^2 \sigma^2}] \cos \phi \\
&= -(c_{c,-k}^{(1)}(t)^* c_{c,-k,dyn}^{(2)}(t) + c.c.)
\end{aligned} \tag{3.29}$$

$$\begin{aligned}
c_{c,k}^{(1)}(t)^* c_{c,k,dip}^{(2)}(t) + c.c. &= \frac{\sqrt{2} A_1 A_2^2 \vec{e} w^2 \cdot \sigma^2 \pi}{4} \cdot (e^{-\frac{\sigma^2}{4} (\Delta \epsilon_{vc,k} - 2w)^2} - e^{-\frac{\sigma^2}{4} (\Delta \epsilon_{vc,k} + 2w)^2}) \\
&\cdot \left( \left\langle \frac{\partial u_{v,k}}{\partial k} \left| u_{c,k} \right. \right\rangle \frac{\partial \left\langle u_{c,k} \left| \frac{\partial u_{v,k}}{\partial k} \right. \right\rangle}{\partial k} [e^{-\frac{1}{2} (\Delta \epsilon_{vc,k} - 2w)^2 \sigma^2 + i\phi} - e^{-\frac{1}{2} (\Delta \epsilon_{vc,k} + 2w)^2 \sigma^2 - i\phi}] \right. \\
&\left. + \frac{\partial \left\langle \frac{\partial u_{v,k}}{\partial k} \left| u_{c,k} \right. \right\rangle}{\partial k} \left\langle u_{c,k} \left| \frac{\partial u_{v,k}}{\partial k} \right. \right\rangle [e^{-\frac{1}{2} (\Delta \epsilon_{vc,k} - 2w)^2 \sigma^2 - i\phi} - e^{-\frac{1}{2} (\Delta \epsilon_{vc,k} + 2w)^2 \sigma^2 + i\phi}] \right)
\end{aligned} \tag{3.30}$$

Here under the time-reversal relation,  $u_k^*(\vec{r}) = u_{-k}(\vec{r})$ , so for  $-k$ , we have:

$$\left\langle \frac{\partial u_{v,-k}}{\partial(-k)} \left| u_{c,-k} \right. \right\rangle \frac{\partial \left\langle u_{c,-k} \left| \frac{\partial u_{v,-k}}{\partial(-k)} \right. \right\rangle}{\partial(-k)} = \left\langle \frac{\partial u_{v,k}^*}{\partial(-k)} \left| u_{c,k}^* \right. \right\rangle \frac{\partial \left\langle u_{c,k}^* \left| \frac{\partial u_{v,k}^*}{\partial(-k)} \right. \right\rangle}{\partial(-k)} \tag{3.31}$$

$$= - \left\langle u_{c,k} \left| \frac{\partial u_{v,k}}{\partial k} \right. \right\rangle \frac{\partial \left\langle \frac{\partial u_{v,k}}{\partial k} \left| u_{c,k} \right. \right\rangle}{\partial k} \tag{3.32}$$

The interference terms for central symmetry point  $-k$  can be written as:

$$\begin{aligned}
c_{c,-k}^{(1)}(t)^* c_{c,-k,dip}^{(2)}(t) + c.c. &= \frac{\sqrt{2} A_1 A_2^2 \vec{e} w^2 \cdot \sigma^2 \pi}{4} \cdot (e^{-\frac{\sigma^2}{4} (\Delta \epsilon_{vc,k} - 2w)^2} - e^{-\frac{\sigma^2}{4} (\Delta \epsilon_{vc,k} + 2w)^2}) \\
&\cdot (- \left\langle u_{c,k} \left| \frac{\partial u_{v,k}}{\partial k} \right. \right\rangle \frac{\partial \left\langle \frac{\partial u_{v,k}}{\partial k} \left| u_{c,k} \right. \right\rangle}{\partial k} [e^{-\frac{1}{2} (\Delta \epsilon_{vc,k} - 2w)^2 \sigma^2 + i\phi} - e^{-\frac{1}{2} (\Delta \epsilon_{vc,k} + 2w)^2 \sigma^2 - i\phi}] \\
&- \frac{\partial \left\langle u_{c,k} \left| \frac{\partial u_{v,k}}{\partial k} \right. \right\rangle}{\partial k} \left\langle \frac{\partial u_{v,k}}{\partial k} \left| u_{c,k} \right. \right\rangle [e^{-\frac{1}{2} (\Delta \epsilon_{vc,k} - 2w)^2 \sigma^2 - i\phi} - e^{-\frac{1}{2} (\Delta \epsilon_{vc,k} + 2w)^2 \sigma^2 + i\phi}])
\end{aligned} \tag{3.33}$$

$$\begin{aligned}
 c_{c,k,dyn}^{(2)}(t)^* c_{c,k,dip}^{(2)}(t) + c.c. &= \frac{(A_2 \vec{e})^4 w \cdot \sigma^2 \pi}{8} \cdot [e^{-\frac{\sigma^2}{4}(\Delta\epsilon_{vc,k}-2w)^2} - e^{-\frac{\sigma^2}{4}(\Delta\epsilon_{vc,k}+2w)^2}] \\
 &\cdot [e^{-\frac{\sigma^2}{4}\Delta\epsilon_{vc,k}^2} - \frac{1}{2}(e^{-\frac{\sigma^2}{4}(\Delta\epsilon_{vc,k}-2w)^2} + e^{-\frac{\sigma^2}{4}(\Delta\epsilon_{vc,k}+2w)^2})] \\
 &\cdot \frac{\partial \Delta\epsilon_{vc,k}}{\partial k} \left( \left\langle u_{c,k} \left| \frac{\partial u_{v,k}}{\partial k} \right. \right\rangle \frac{\partial \left\langle u_{c,k} \left| \frac{\partial u_{v,k}}{\partial k} \right. \right\rangle}{\partial k} + \frac{\partial \left\langle \frac{\partial u_{v,k}}{\partial k} \left| u_{c,k} \right. \right\rangle}{\partial k} \left\langle u_{c,k} \left| \frac{\partial u_{v,k}}{\partial k} \right. \right\rangle \right) \tag{3.34}
 \end{aligned}$$

$$\begin{aligned}
 c_{c,-k,dyn}^{(2)}(t)^* c_{c,-k,dip}^{(2)}(t) + c.c. &= \frac{(A_2 \vec{e})^4 w \cdot \sigma^2 \pi}{8} \cdot [e^{-\frac{\sigma^2}{4}(\Delta\epsilon_{vc,k}-2w)^2} - e^{-\frac{\sigma^2}{4}(\Delta\epsilon_{vc,k}+2w)^2}] \\
 &\cdot [e^{-\frac{\sigma^2}{4}\Delta\epsilon_{vc,k}^2} - \frac{1}{2}(e^{-\frac{\sigma^2}{4}(\Delta\epsilon_{vc,k}-2w)^2} + e^{-\frac{\sigma^2}{4}(\Delta\epsilon_{vc,k}+2w)^2})] \\
 &\cdot \frac{\partial \Delta\epsilon_{vc,k}}{\partial k} \left( \left\langle u_{c,k} \left| \frac{\partial u_{v,k}}{\partial k} \right. \right\rangle \frac{\partial \left\langle \frac{\partial u_{v,k}}{\partial k} \left| u_{c,k} \right. \right\rangle}{\partial k} + \frac{\partial \left\langle u_{c,k} \left| \frac{\partial u_{v,k}}{\partial k} \right. \right\rangle}{\partial k} \left\langle \frac{\partial u_{v,k}}{\partial k} \left| u_{c,k} \right. \right\rangle \right) \\
 &= c_{c,k,dyn}^{(2)}(t)^* c_{c,k,dip}^{(2)}(t) + c.c. \tag{3.35}
 \end{aligned}$$

To summarize the steps, the asymmetric population distribution between  $k$  and  $-k$  can be understood by the quantum interference (**Qui**) of different excitation paths:

### 3.1. TIME-DEPENDENT PERTURBATIVE ANALYSIS ON QUI

$$\begin{aligned}
|c_{c,k}(t)|^2 - |c_{c,-k}(t)|^2 &= 2c_{c,k}^{(1)}(t)^* c_{c,k,dyn}^{(2)}(t) + c_{c,k}^{(1)}(t)^* c_{c,k,dip}^{(2)}(t) - c_{c,-k}^{(1)}(t)^* c_{c,-k,dip}^{(2)}(t) + c.c. \\
&= 2\sqrt{2}A_1 A_2^2 \vec{e}w \cdot \sigma^2 \pi \frac{\partial \Delta \epsilon_{vc,k}}{\partial k} \left| \left\langle u_{c,k} \left| \frac{\partial u_{v,k}}{\partial k} \right. \right\rangle \right|^2 \\
&\quad \cdot [e^{-\frac{\sigma^2}{4}(\Delta \epsilon_{vc,k} - 2w)^2} - \frac{1}{2}(e^{-\frac{\sigma^2}{4}(\Delta \epsilon_{vc,k} - 2w)^2} + e^{-\frac{\sigma^2}{4}(\Delta \epsilon_{vc,k} + 2w)^2})] \\
&\quad \cdot [e^{-\frac{1}{2}(\Delta \epsilon_{vc,k} - 2w)^2 \sigma^2} - e^{-\frac{1}{2}(\Delta \epsilon_{vc,k} + 2w)^2 \sigma^2}] \cos \phi \\
&\quad + \frac{\sqrt{2}A_1 A_2^2 \vec{e}w^2 \cdot \sigma^2 \pi}{2} \cdot (e^{-\frac{\sigma^2}{4}(\Delta \epsilon_{vc,k} - 2w)^2} - e^{-\frac{\sigma^2}{4}(\Delta \epsilon_{vc,k} + 2w)^2}) \\
&\quad \cdot (\left\langle u_{c,k} \left| \frac{\partial u_{v,k}}{\partial k} \right. \right\rangle \frac{\partial \left\langle \frac{\partial u_{v,k}}{\partial k} \middle| u_{c,k} \right\rangle}{\partial k} + \frac{\partial \left\langle u_{c,k} \left| \frac{\partial u_{v,k}}{\partial k} \right. \right\rangle}{\partial k} \left\langle \frac{\partial u_{v,k}}{\partial k} \middle| u_{c,k} \right\rangle) \\
&\quad \cdot [e^{-\frac{1}{2}(\Delta \epsilon_{vc,k} - 2w)^2 \sigma^2} - e^{-\frac{1}{2}(\Delta \epsilon_{vc,k} + 2w)^2 \sigma^2}] \cos \phi \\
&= \sqrt{2}A_1 A_2^2 \vec{e}w \cdot \sigma^2 \pi [e^{-\frac{1}{2}(\Delta \epsilon_{vc,k} - 2w)^2 \sigma^2} - e^{-\frac{1}{2}(\Delta \epsilon_{vc,k} + 2w)^2 \sigma^2}] \\
&\quad \cdot [\frac{\partial \Delta \epsilon_{vc,k}}{\partial k} \left| \left\langle u_{c,k} \left| \frac{\partial u_{v,k}}{\partial k} \right. \right\rangle \right|^2 (2e^{-\frac{\sigma^2}{4}(\Delta \epsilon_{vc,k} - 2w)^2} - e^{-\frac{\sigma^2}{4}(\Delta \epsilon_{vc,k} - 2w)^2} - e^{-\frac{\sigma^2}{4}(\Delta \epsilon_{vc,k} + 2w)^2}) \\
&\quad + \frac{w}{2} (\left\langle u_{c,k} \left| \frac{\partial u_{v,k}}{\partial k} \right. \right\rangle \frac{\partial \left\langle \frac{\partial u_{v,k}}{\partial k} \middle| u_{c,k} \right\rangle}{\partial k} + \frac{\partial \left\langle u_{c,k} \left| \frac{\partial u_{v,k}}{\partial k} \right. \right\rangle}{\partial k} \left\langle \frac{\partial u_{v,k}}{\partial k} \middle| u_{c,k} \right\rangle) \\
&\quad \cdot (e^{-\frac{1}{4}(\Delta \epsilon_{vc,k} - 2w)^2 \sigma^2} - e^{-\frac{1}{4}(\Delta \epsilon_{vc,k} + 2w)^2 \sigma^2})] \cos \phi
\end{aligned} \tag{3.36}$$

We consider the band gap between valence and conduction bands close to twice the field's frequency:

$$\Delta \epsilon_{vc,k} + 2w \approx 0 \tag{3.37}$$

Because  $\sigma \gg 0$ . In a nutshell, the population imbalance becomes:

$$\begin{aligned}
|c_{c,k}(t)|^2 - |c_{c,-k}(t)|^2 &\approx \sqrt{2}A_1 A_2^2 \vec{e}w \cdot \sigma^2 \pi e^{-\frac{3}{4}(\Delta \epsilon_{vc,k} + 2w)^2 \sigma^2} [\frac{\partial \Delta \epsilon_{vc,k}}{\partial k} \left| \left\langle u_{c,k} \left| \frac{\partial u_{v,k}}{\partial k} \right. \right\rangle \right|^2 \\
&\quad + \frac{w}{2} (\left\langle u_{c,k} \left| \frac{\partial u_{v,k}}{\partial k} \right. \right\rangle \frac{\partial \left\langle \frac{\partial u_{v,k}}{\partial k} \middle| u_{c,k} \right\rangle}{\partial k} + \frac{\partial \left\langle u_{c,k} \left| \frac{\partial u_{v,k}}{\partial k} \right. \right\rangle}{\partial k} \left\langle \frac{\partial u_{v,k}}{\partial k} \middle| u_{c,k} \right\rangle)] \cos \phi
\end{aligned} \tag{3.38}$$

The utilization of two-color fields, such as  $\omega$  and  $2\omega$ , has opened a potential to break the time-reversal symmetry of the systems, even when the combined field is linearly polarized. This symmetry breaking leads to a population imbalance

induced by laser irradiation, consequently resulting in dc-current injection. The population imbalance in this scheme is caused by quantum interference between two excitation paths: One is the two-photon absorption process with photons at the frequency  $\omega$ , while the other is the one-photon absorption process with photons at the frequency  $2\omega$ . Hence, this protocol for dc-current injection is known as quantum interference control (**QuIC**). By manipulating the relative phase of the optical fields at frequencies  $\omega$  and  $2\omega$ , **QuIC** can be applied to achieve control over one- and two-photon absorption processes, often referred to as (1 + 2 **QuIC**).

### 3.2 Third-order Nonlinear Regime: 1 + 2 QuIC

From perturbation analysis in Sec 3.1, the disruption of time-reversal symmetry can be achieved through the use of linearly polarized light featuring two distinct frequencies. This implies that the injection of dc-current and the generation of a substantial population imbalance can be efficiently realized without relying on the ellipticity of light. This principle is exemplified by employing two-color linearly polarized laser fields with frequencies  $\omega$  and  $2\omega$ . In this configuration, the intrinsic properties of linear polarization and the dual frequencies are sufficient to break time-reversal symmetry, facilitating the desired outcomes of dc-current injection and the establishment of a pronounced population imbalance. This approach provides a versatile and simplified means to manipulate quantum interference and achieve specific optical responses in the system without the need for elliptically polarized light. This protocol for dc-current injection is also known as quantum interference control (**QuIC**). By manipulating the relative phase of the optical fields at frequencies  $\omega$  and  $2\omega$ , **QuIC** can be applied to achieve control over one- and two-photon absorption processes, often referred to as (1 + 2 **QuIC**).

For practical simulation, we examine the light-induced electron dynamics in a prototypical two-dimensional insulator, monolayer hexagonal boron-nitride (*h*-BN), using a simple tight-binding approximation and **TDSEs** introduced in Chapter 2. In the quantum dynamics simulation, we employ the following expression for the vector potential of the applied two-color fields within the interval

$-\frac{\tau}{2} < t < \frac{\tau}{2}$  and zero outside this range:

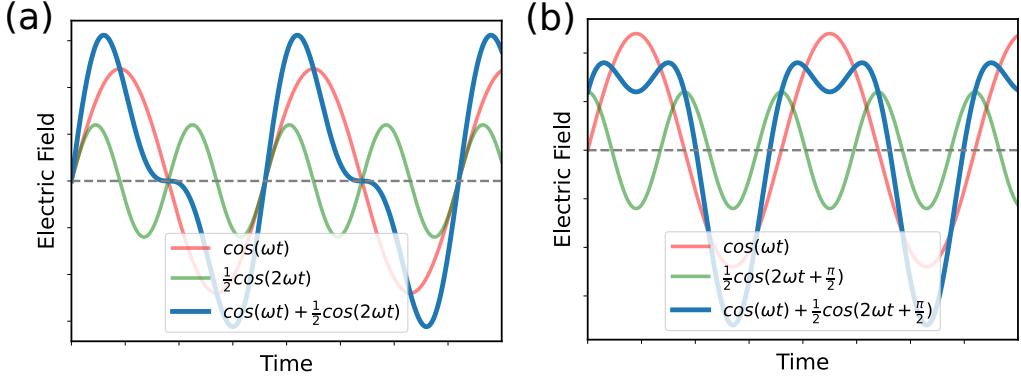
$$A(t) = -e_p \frac{E_0}{\omega} \left[ \cos(\omega t) + \frac{1}{4} \cos(2\omega t + \phi) \right] \times \cos^4\left(\frac{\pi}{\tau}t\right)$$

$e_p$  represents a unit vector along the polarization direction of the laser field,  $E_0$  denotes the peak field strength,  $\omega$  is the fundamental frequency, and  $\tau$  is the duration of the laser field pulse. To illustrate dc current injection according to perturbation derivation in Section 3.1, we simulate electron dynamics using the vector potential from Eq. (3.40) with  $\omega$  set to 3 eV for practical calculations. Note that the photon energy satisfies the condition ( $\omega \leq E_g \leq 2\hbar\omega$ ) for the 1+2 QuIC process [62]. Furthermore, we set the laser polarization direction,  $e_p$ , with the  $\Gamma-K$  direction, the pulse duration,  $\tau$ , is set to 40 fs. We introduce a relative phase  $\phi$  between the two-color fields. The relative phase governs quantum interferences among different excitation paths induced via  $\omega$  and  $2\omega$  laser fields, while the global phase is utilized to extract a dc-like response from the quantum dynamics. By manipulating the relative phase  $\phi$  in the electric field described in Eq. (3.39):

$$E(t) = -e_p E_0 \left[ \cos(\omega t) + \frac{1}{2} \cos(2\omega t + \phi) \right]$$

one can induce a population imbalance and, consequently, a dc-current by extrinsically breaking the time-reversal symmetry by utilizing two-color fields with frequencies  $\omega$  and  $2\omega$ . Figure 3.1 (a) illustrates the electric field generated by the vector potential with a relative phase of  $\phi = 0$ , while Figure 3.1 (b) presents the field with a relative phase of  $\phi = \pi/2$ . It is evident that the field with  $\phi = 0$  in Fig. 3.1 (a) breaks the time-reversal symmetry, as  $E(t) \neq E(-t)$ , while the field with  $\phi = \pi/2$  in Fig. 3.1 (b) maintains the symmetry  $E(t) = E(-t)$ . Hence, the time-reversal symmetry of the Hamiltonian is broken when  $\phi = 0$  and preserved when  $\phi = \pi/2$ . Consequently, a population imbalance and resulting dc current injection are expected when  $\phi = 0$ , while symmetric excitation population and the absence of net residual current are anticipated when  $\phi = \pi/2$ .

To comprehensively assess the persistent dc-current following laser irradiation, we conduct an in-depth analysis utilizing the photo-excited conduction population  $n_{ck}$  computed from Eq. (2.26). Employing a weak enough laser field in the perturbation region with a strength of  $E_0 = 2.57$  MV/cm and fixing the relative

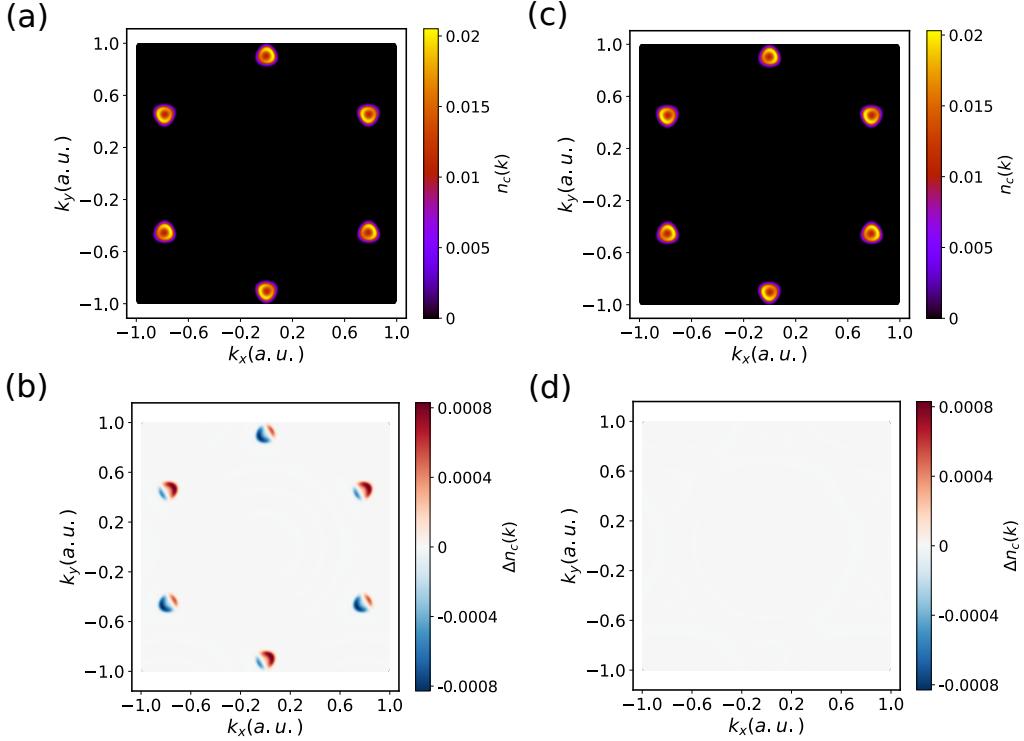


**Figure 3.1:** The time profiles of the electric field given by Eq. (3.39) are shown for (a)  $\phi = 0$  and (b)  $\phi = \pi/2$ .

phase at  $\phi = 0$ , the resulting conduction population is illustrated in Fig. 3.2 (a). For comparative purposes, Fig. 3.2 (b) presents the conduction population  $n_{ck}$  computed under the same field strength ( $E_0 = 2.57$  MV/cm) but with a distinct relative phase ( $\phi = 0$ ). In both instances, the conduction populations exhibit notable excitations centered around the  $K$ - and  $K'$ -points. This observation implies that the photo-absorption process is primarily governed by a one-photon absorption at the photon energy of  $2\hbar\omega$  and a two-photon absorption at the photon energy of  $\hbar\omega$ . The consistency in the excitation patterns further underscores the dominance of these absorption mechanisms in the system under the specified laser conditions.

While the population distributions in Fig. 3.2(a) and (b) may initially appear similar, a closer examination reveals nuanced distinctions. In the scenario of the time-reversal symmetry-broken field ( $\phi = 0$ ) illustrated in Fig. 3.2(a), the population distribution must manifest an imbalance between time-reversal Kramers pairs (e.g.,  $k$  and  $-k$ , or  $K$  and  $K'$ ). On the contrary, in the case of the time-reversal field ( $\phi = \pi/2$ ) showcased in Fig. 3.2(b), the population distribution  $n_{ck}$  is anticipated to lack such a population imbalance. This discrepancy arises from the absence of a persistent current under these conditions. This nuanced analysis deepens our understanding of the intricate relationship between population distributions and the underlying time-reversal symmetry characteristics, providing crucial insights into the dynamic behavior of the system.

To delineate the population imbalance across the Brillouin zone, we introduce the population imbalance distribution  $\Delta n_{c\bar{k}}$ , defined as the disparity in popula-



**Figure 3.2:** (a, b) The conduction population distribution  $n_c(k)$  computed with (a)  $\phi = 0$  and (b)  $\phi = \pi/2$ . (c, d) The population imbalance distribution  $\Delta n_c(k)$  computed with (c)  $\phi = 0$  and (d)  $\phi = \pi/2$ .

tion between the time-reversal pair  $k$ -points, expressed as:

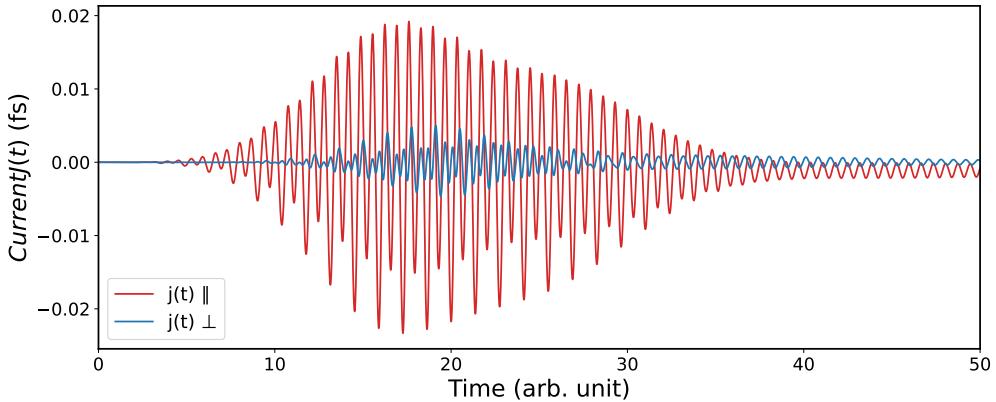
$$\Delta n_{ck} = n_{ck} - n_{c,-k} \quad (3.39)$$

Given the constraint  $0 \leq n_{ck} \leq 1$ , the population imbalance distribution is bounded by  $-1 \leq \Delta n_{ck} \leq 1$ . In scenarios where external fields maintain time-reversal symmetry, the populations at  $k$  and  $-k$  are equivalent, resulting in a population imbalance distribution of zero. Conversely, in instances where time-reversal symmetry is broken, non-equivalent populations can be induced at  $k$  and  $-k$ , giving rise to a finite population imbalance distribution  $\Delta n_{ck}$ . Figures 3.2(c) and (d) depict the population imbalance distribution,  $\Delta n_{ck}$ , derived from the population distributions presented in Figs. 3.2 (a) and (b), respectively. The figures clearly illustrate that when the external field disrupts time-reversal symmetry ( $\phi = 0$ ), a discernible finite population imbalance is induced. In contrast, when the field preserves time-reversal symmetry ( $\phi = \pi/2$ ), the population imbalance diminishes entirely. This comprehensive analysis of the population imbalance distri-

bution provides a detailed insight into the intricate interplay between external field characteristics and the resulting population asymmetry within the Brillouin zone.

The temporal evolution of the corresponding electric current, denoted as  $J_{total}(t)$ , can be computed using Eq.(2.20). This equation represents a functional dependence on the vector potential  $A(t)$ , as depicted in Fig.3.3. The total current encompasses multiple components and noises, often overshadowing the relatively small value of the dc-component following the laser pulse. To pragmatically examine and isolate the dc-current generated by the fields, we introduce the global phase  $\theta$  into the fields as described by the Eq.(3.40), as done in our prior study[68].

$$A(t) = -e_p \frac{E_0}{\omega} \left[ \cos(\omega t + \theta) + \frac{1}{4} \cos(2\omega t + 2\theta + \phi) \right] \times \cos^4\left(\frac{\pi}{\tau} t\right)$$



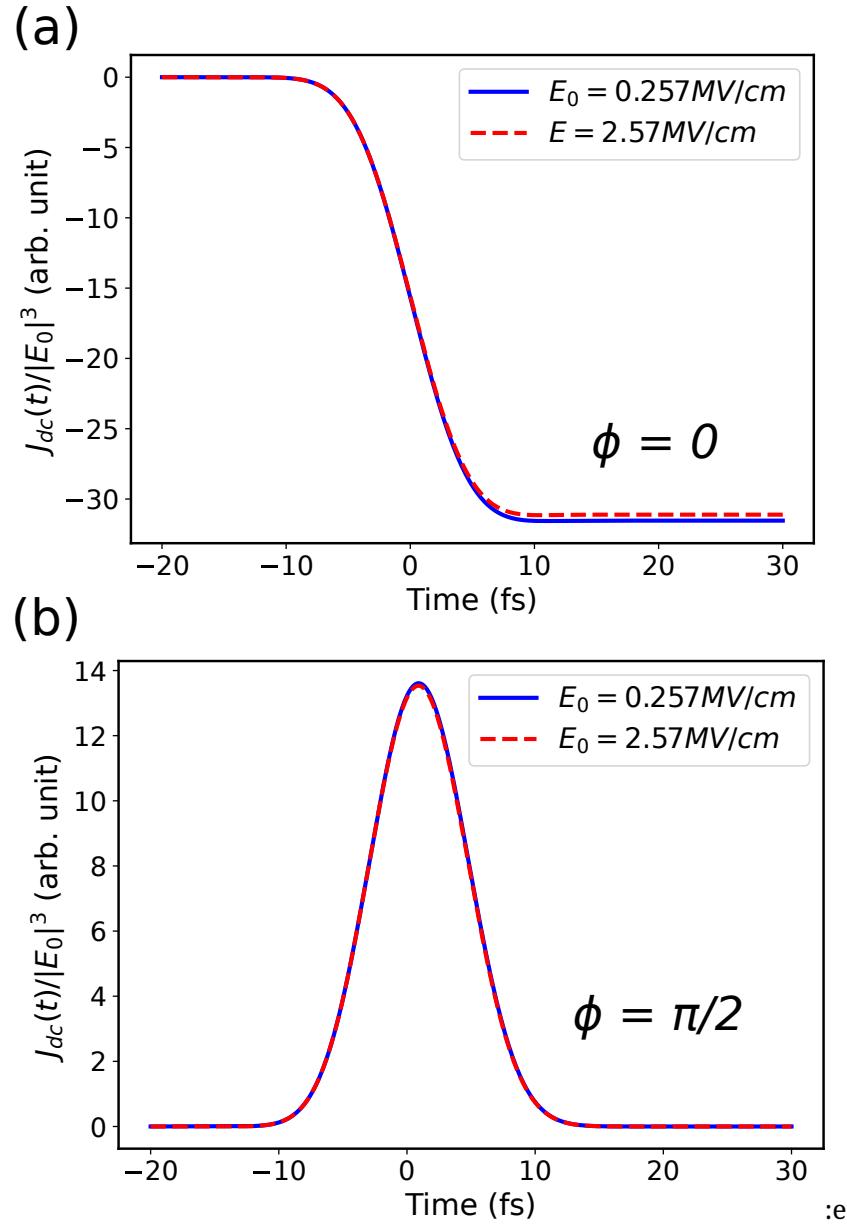
**Figure 3.3**

The time profiles of the current computed from Eq. (2.20) induced by the electric field given by Eq. (3.39) as shown in Fig. 3.1(a) with relative phase  $\phi = 0$ .

The current, expressed as a function of the global phase  $\theta$  in accordance with the vector potential given by Eq.(3.40), is explicitly denoted as  $J(t, \theta)$ . By maintaining all laser parameters constant in Eq.(3.40) except for the global phase  $\theta$ , we can isolate the direct current (dc)-like component of the induced current through the following integral:

$$J_{dc}(t) = \frac{1}{2\pi} \int_0^{2\pi} d\theta, J(t, \theta). \quad (3.40)$$

In this formulation, the integral averages out the higher-frequency components, enabling the extraction of the clean dc-like slow-frequency component of the induced current.



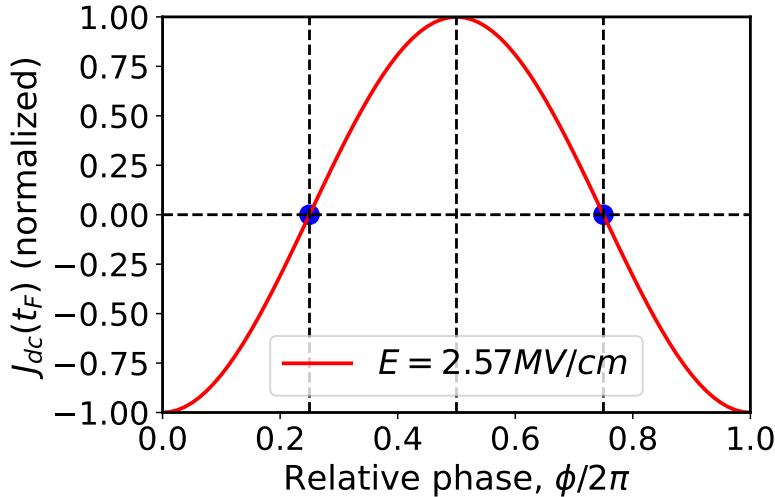
**Figure 3.4:** The dc components of the currents  $J_{dc}(t)$  computed from Eq. (3.40) are shown as a function of time. The results using the relative phase of  $\phi = 0$  are shown in panel (a), while those using  $\phi = \pi/2$  are shown in (b)

In Figure 3.4(a), the calculated direct current (dc) component of the scaled current,  $J_{\text{dc}}(t)/E_0^3$ , is presented for a relative phase of  $\phi = 0$ , encompassing results for various field strengths,  $E_0$ . Remarkably, the residual dc-current persists beyond the conclusion of the laser fields ( $t > \tau/2$ ). Notably, the scaled quantity,  $J_{\text{dc}}(t)/E_0^3$ , maintains identical behavior across different field strengths. This consistency suggests that the dc component of the induced current can be interpreted as a third-order nonlinear optical effect. This interpretation aligns with the inherent nature of the 1+2 QuIC process, which involves interference between one- and two-photon absorption processes, categorizing it as a third-order nonlinear optical phenomenon. The presented results shed light on the robust and field-independent nature of the observed third-order nonlinear optical effects in the system.

In Figure 3.4(b), the dc-current component of the scaled current,  $J_{\text{dc}}(t)/E_0^3$ , is depicted with a relative phase of  $\phi = \pi/2$ . In stark contrast to the results with  $\phi = 0$  shown in Fig.3.4(a), the currents in Fig.3.4 (b) do not manifest a persistent dc component after the conclusion of the laser irradiation. This outcome signifies that the applied field with a relative phase of  $\phi = \pi/2$  does not disrupt time-reversal symmetry, and consequently, no population imbalance is induced, resulting in the absence of a sustained current. It is noteworthy that, even in the case of  $\phi = \pi/2$ , the dc-component of the current is induced solely during the laser irradiation, highlighting yet another instance of a third-order nonlinear optical process. This observation provides further insight into the nuanced interplay between field characteristics and the resulting dynamical responses in the system.

By manipulating the relative phase  $\phi$ , one gains control over the extent of time-reversal symmetry breaking, thereby influencing the resulting population imbalance and dc- current injection [61]. For subsequent analysis, we systematically explore the persistent dc current by varying the relative phase  $\phi$ . Figure 3.5 illustrates the dependence of the dc-current on the relative phase  $\phi$  after laser irradiation, computed using a field with a strength of  $E_0 = 2.57$  MV/cm. The amplitude of the induced dc current reaches its maximum when  $\phi = 0$  and  $\phi = \pi$ , with opposite signs for these two phases. Moreover, the induced dc current exhibits continuous variation as the phase  $\phi$  is manipulated, attaining zero when  $\phi = \pi/2$ .

and  $\phi = 3\pi/2$ , corresponding to the points where the applied fields restore time-reversal symmetry. This straightforward phase dependence aligns with findings from prior works[61, 63], providing further validation of the controllable nature of the induced dc current through manipulation of the relative phase.

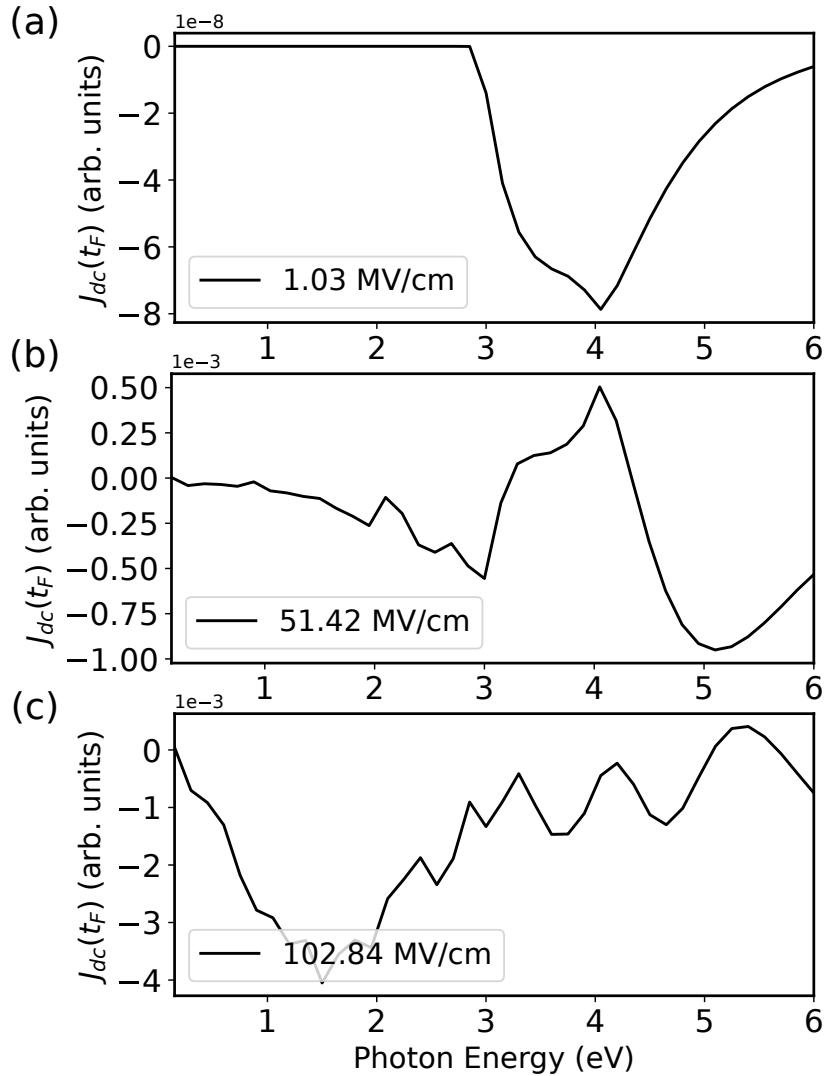


**Figure 3.5:** The persistent current  $J_{dc}(t_f)$  as a function of the relative phase,  $\phi$ . The results are computed by setting  $E_0$  to 2.57 MV/cm and  $\hbar\omega$  to 3 eV.

QuIC processes often exhibit resonance conditions at specific photon energies. By systematically investigating the photon-energy dependence, we can identify resonant regions where the interference effects are significantly enhanced. Investigating these dependencies aids in identifying the primary mechanisms at play. To scrutinize this phenomenon within our theoretical framework, we systematically evaluate the direct current (dc) after laser irradiation by varying the fundamental frequency  $\omega$  in Eq.(3.40). Figure 3.6 (a) illustrates the resulting dc current following laser irradiation with a field strength of  $E_0 = 1.03$  MV/m.

In line with the anticipated behavior of the  $1 + 2$  QuIC process, the residual dc-current diminishes when the fundamental photon energy falls below half of the band gap, i.e.,  $\hbar\omega \leq E_g/2 = 2.95$  eV, since the fundamental photon energy  $\hbar\omega$  must adhere to the condition  $\hbar\omega \geq E_g/2$ , where  $E_g$  signifies the band gap. In instances where the fundamental photon energy  $\hbar\omega$  falls below the gap, both the  $1 + 2$  QuIC process and the resultant direct current (dc) vanish. This exploration not only elucidates the pivotal role of photon energy in the manifestation of the  $1 + 2$  QuIC process but also underscores the significance of satisfying specific conditions for

its occurrence and subsequent dc-current induction. This behavior aligns with the expected characteristics of the  $1 + 2$  QuIC process and provides valuable insights into the influence of the fundamental frequency on the induced dc-current in our theoretical framework.



**Figure 3.6:** The current after the laser irradiation is shown as a function of the fundamental photon energy  $\hbar\omega$ . The results computed different field strengths: (a)  $E_0 = 1.03 \text{ MV/cm}$ , (b)  $51.43 \text{ MV/cm}$ , and (c)  $E_0 = 102.84 \text{ MV/cm}$ .

The investigation aids in comprehending the intricate relationship between photon energy, field strength, and the ensuing nonlinear processes. It is imperative to investigate the photon energy dependence of the direct current (dc) after laser irradiation while systematically varying the field strength,  $E_0$ , to unravel the intricacies of this highly nonlinear optical phenomenon. Figures 3.6 (b)

and (c) meticulously depict the photon-energy dependence of the persistent current following laser irradiation, calculated for two distinct field strengths: (b)  $E_0 = 51.42 \text{ MV/cm}$  and (c)  $E_0 = 102.84 \text{ MV/cm}$ . In stark contrast to the weak field regime typified by the 1 + 2 QuIC, the direct current (dc) can be induced even under deeply off-resonant conditions, where the photon energy is smaller than half of the band gap ( $\hbar\omega \leq E_g/2$ ), as evident in Figure 3.6(b). This compelling observation suggests that potent laser fields introduce additional pathways for electron excitation that extend beyond the realm of two-photon absorption. These additional processes, involving multiple photons, contribute to the creation of a population imbalance and a residual dc current, even in the deeply off-resonant regime. The nuanced interplay between laser field strength and photon energy unveiled in these results provides invaluable insights into the complex dynamics governing persistent currents in strong-field regimes.

Illustrated in Figure 3.6 (c), a noteworthy observation emerges: the magnitude of the direct current (dc) after laser irradiation in the deeply off-resonant regime ( $\hbar\omega \leq E_g/2$ ) surpasses that in the 1 + 2 QuIC regime ( $\hbar\omega \geq E_g/2$ ) as the applied field strength reaches exceptionally large values. This intriguing behavior finds its explanation in the ponderomotive energy, denoted as:

$$U_p = \frac{e^2 E_0^2}{4m\pi\omega_0^2} \quad (3.41)$$

The associated light-induced intraband transitions, both of which are more substantial for lower frequency driving[69]. Consequently, the ensuing nonlinear effects and the injection of dc current become more pronounced in the deeply off-resonant regime compared to the resonant condition. Our initial investigation focused on analyzing the electric current induced by these two-color laser fields within the weak field regime. We confirmed that the dc-component of the induced current persists even after laser irradiation when the fundamental photon energy  $\hbar\omega$  exceeds the optical gap,  $E_g/2$ . This ballistic current phenomenon originates from a population imbalance in the Brillouin zone, arising from quantum interference between two distinct excitation paths: one involving one-photon absorption at the photon energy of  $2\hbar\omega$ , and the other involving a two-photon absorption path at the photon energy of  $\hbar\omega$  [61–63].

This discovery sets the stage for a more in-depth exploration in the subsequent section, where we will delve into the intricacies of efficiently inducing DC current through highly nonlinear optical processes in the deeply off-resonant regime.

### 3.3 Deeply Off-resonant Highly-nonlinear Regime

Despite the significant interest in the nonlinear photovoltaic effect, there has been limited exploration of efficient current injection in the deeply off-resonant regime with multi-cycle light pulses, particularly using linearly polarized light. Subsequently, the scope of QuIC can be broadened to involve general integer combinations, denoted as  $M + N$  QuIC [65, 67]. In this extended scheme, two-color laser fields operating at frequencies  $\omega$  and  $\omega'$  induce  $M$ - and  $N$ -photon absorption processes, respectively. To investigate the mechanism of dc-current injection in the deeply off-resonant regime, as demonstrated in the previous section, we fix the fundamental photon energy  $\hbar\omega$  in Eq. (3.40) at 1 eV. Notably, this value is much smaller than half of the band gap,  $E_g/2 = 2.95$  eV, for this section.

Similarly, we start with evaluating the population imbalance induced by a strong field in the deeply off-resonant regime, we calculate the population distribution  $n_{c\vec{k}}$  after irradiating the laser field with a strength of 100 MV/cm. A distinct pattern emerges in the excited carrier population distribution around the  $K$  and  $K'$  points. This pattern can be understood through the multi-photon absorption resonances of the light-induced Floquet states[70]. In Fig.3.7(a), we present the computed population distribution in the conduction band. As anticipated from the preceding discussion, the photo-carrier distribution reveals a significant population imbalance between  $k$  and  $-k$  points. To enhance clarity in visualizing the population imbalance, we compute the population imbalance distribution  $\Delta n_{ck} = n_{ck} - n_{c,-k}$ . Figure 3.7(b) displays the resulting population imbalance distribution  $\Delta n_{ck}$ . Since  $\Delta n_{ck}$  is constrained by  $-1 \leq \Delta n_{ck} \leq 1$ , the population imbalance between  $k$  and  $-k$  is maximized when  $|\Delta n_{ck}| = 1$ . As observed in Fig.3.7 (b), the population imbalance distribution takes significantly large values, comparable to the maximum values ( $\pm 1$ ), across a wide range of the Brillouin zone.

### 3.3. DEEPLY OFF-RESONANT HIGHLY-NONLINEAR REGIME

We calculate the population imbalance ratio  $r_{im}$  defined as the maximum absolute value of the population imbalance distribution  $\Delta n_{ck}$  across the Brillouin zone for further qualification. Mathematically, it is expressed as:

$$r_{im} = \frac{\int_{BZ} dk |\Delta n_{ck}|}{\int_{BZ} dk (n_{ck} + n_{c,-k})} = \frac{\int_{BZ} dk |\Delta n_{ck}|}{2 \int_{BZ} dk n_{ck}}. \quad (3.42)$$

The computed imbalance ratio,  $r_{im}$ , from Figs. 3.7(a) and (b) is about 0.307. Hence, more than 30% of the excited electrons contribute to the population imbalance. This implies the potential for realizing a significant population imbalance through the use of linearly polarized light alone.

In an earlier study [19], significant control over valley population was proposed using bi-circular fields with counter-rotating  $\omega$  and  $2\omega$  two-color laser fields. In contrast, in this work, we demonstrate that significant valley population can be induced without relying on circular or elliptically polarized light; rather, bi-color linearly polarized light alone can break the time-reversal symmetry and cause such population control.

We commence our analysis of population imbalance by examining the light-induced current in the time domain within the deeply off-resonant regime. In Figure 3.8, we present the dc component of the current,  $J_{dc}(t)/E_0^3$ , computed with varying field strengths,  $E_0$ . For this analysis, the relative phase  $\phi$  is set to 0. Evidently, a third-order nonlinear response dominates the induced current in the case of weak field strength. Given that the photon energy of the second harmonic is smaller than the band-gap ( $2\hbar\omega < E_g$ ) and the QuIC process is forbidden, the third-order current returns to zero after the laser irradiation.

However, as the field strength becomes sufficiently strong, the dc-component remains finite even after laser irradiation, as depicted in Fig. 3.8. This observation suggests that a higher-order nonlinear process contributes to the ballistic dc-current injection beyond the third-order nonlinear effect.

Next, we explore the dependence of the ballistic current induced by deeply off-resonant light on the relative phase,  $\phi$ . Figure 3.9 illustrates the computed current as a function of the relative phase,  $\phi$ , with calculations conducted at a field strength of  $E_0 = 2 \times 10$  MV/cm. In accordance with the QuIC case shown in

Fig.3.5, the persistent current is maximized when the relative phase is  $\phi = 0$  or  $\phi = \pi$ , and it vanishes when the applied field exhibits time-reversal symmetry ( $\phi = \pi/2$  or  $\phi = 3\pi/2$ ). Therefore, even in the deeply off-resonant regime, the direction and magnitude of the persistent current can be controlled by manipulating the relative phase  $\phi$  between the two-color fields at frequencies  $\omega$  and  $2\omega$ .

To gain a more detailed understanding of the intricate mechanism behind dc current injection in the deeply off-resonant regime, we delve into an analysis of how the injected current scales with the applied field strength  $E_0$ . As depicted in Figure 3.10, the current amplitude after laser irradiation is plotted against the varying field strength. Notably, a reference line representing  $|E_0|^7$  is included for comparison.

The compelling observation from the figure is that the induced current exhibits a clear proportionality to  $|E_0|^7$  in the weak field regime. This insightful finding suggests that the seventh-order nonlinear process takes precedence in governing the dynamics of dc current injection under these conditions. This nuanced understanding provides a comprehensive insight into the intricate nonlinear optical processes that contribute to the observed dc current phenomena in the deeply off-resonant regime.

The observed scaling law of the induced dc current with the applied field strength might initially seem inconsistent with the expected behavior of a straightforward  $M + N$  QuIC process. In the conventional  $M + N$  QuIC scenario, the  $M$ -photon absorption process is initiated by light with frequency  $\omega$ , and the  $N$ -photon absorption process is triggered by light with frequency  $2\omega$ , resulting in an overall  $(M + N)$ -th order nonlinear process. For instance, if we consider a six-photon process for multi-photon absorption with light of frequency  $\omega$  and a three-photon process for light of frequency  $2\omega$ , the anticipated simple  $M+N$  QuIC process corresponds to the ninth-order nonlinear process ( $M + N = 6 + 3 = 9$ ).

However, our experimental observations reveal a scaling that indicates seventh-order nonlinearity instead. This apparent discrepancy in the observed and expected nonlinearities of the injected dc current can be rationalized by the presence of an additional excitation channel involving a four-photon absorption process. In this scenario, two photons at frequency  $\omega$  and the other two photons

### 3.3. DEEPLY OFF-RESONANT HIGHLY-NONLINEAR REGIME

at frequency  $2\omega$  combine to excite electrons. This additional four-photon excitation channel interferes with the three-photon absorption process at the photon energy of  $2\hbar\omega$ , resulting in seventh-order ( $7 = 3 + 4$ ) nonlinear current injection.

To delve deeper into the nonlinearity of the light-induced electron dynamics, we performed computations to determine the number of photo-excited carriers after laser irradiation using the expression:

$$N_{ex} = \frac{2}{A_{BZ}} \int_{BZ} dk n_{c,k}, \quad (3.43)$$

where  $A_{BZ} = \int_{BZ} dk$  represents the area of the Brillouin zone.

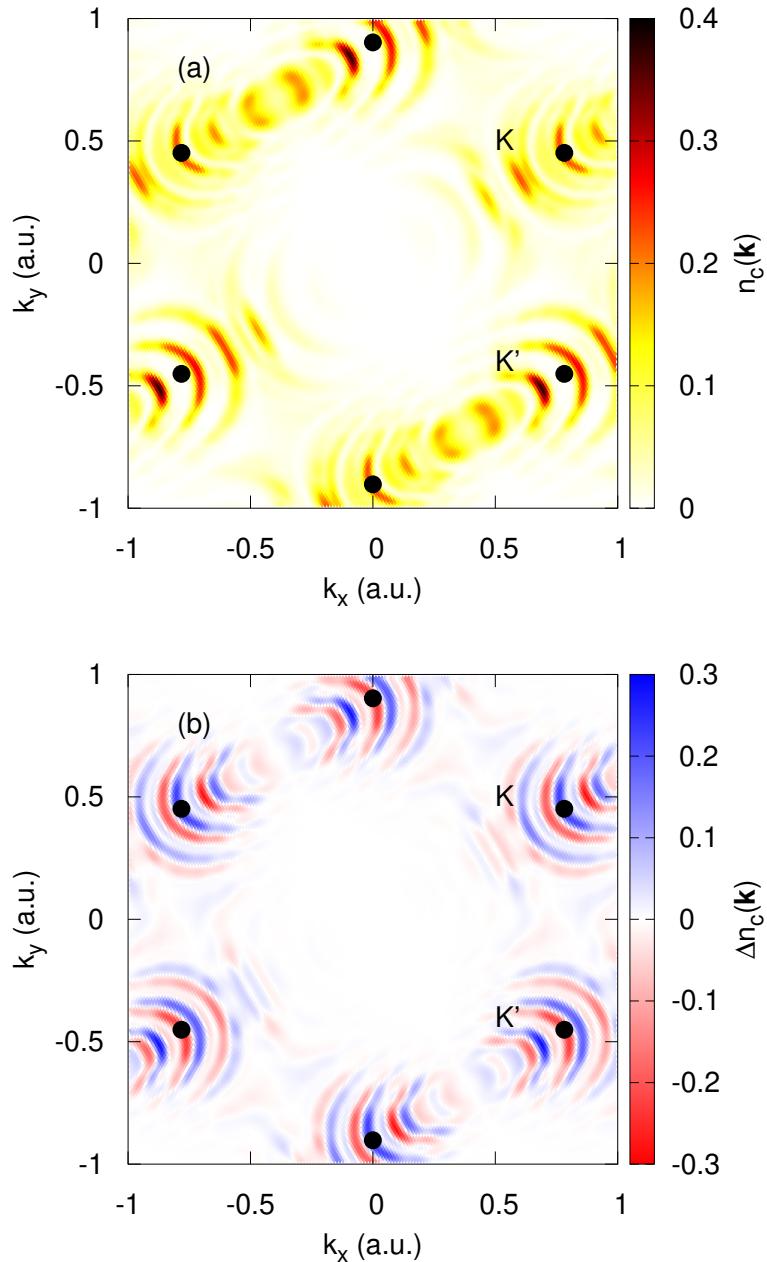
Figure 3.10 (b) presents the number of excited electrons as a function of the field strength,  $E_0$ , alongside a reference line proportional to  $|E_0|^6$ . In the weak field regime, the number of excited electrons exhibits proportionality to  $|E_0|^6$ , highlighting the dominance of the three-photon absorption process in the excitation mechanism. However, as the field strength increases, the deviation from the three-photon absorption line suggests the initiation of a nonperturbative mechanism in the excitation process.

In contrast to the  $|E_0|^6$ -dependence of the number of photo-excited carriers in the weak field regime, the injected current and the corresponding population imbalance follow a  $|E_0|^7$  scaling, as depicted in Figure 3.10 (a). The difference in nonlinearities between the absolute photo-carrier population and the population imbalance implies that the population imbalance is negligible concerning the absolute photo-carrier population in the weak field regime. However, in a strong field regime, the relative significance of the population imbalance becomes substantial as it grows more rapidly than the absolute photo-carrier population. Therefore, the distinction in nonlinearities between the total photocarrier population and the population imbalance indicates the potential for large-amplitude valley carrier population control.

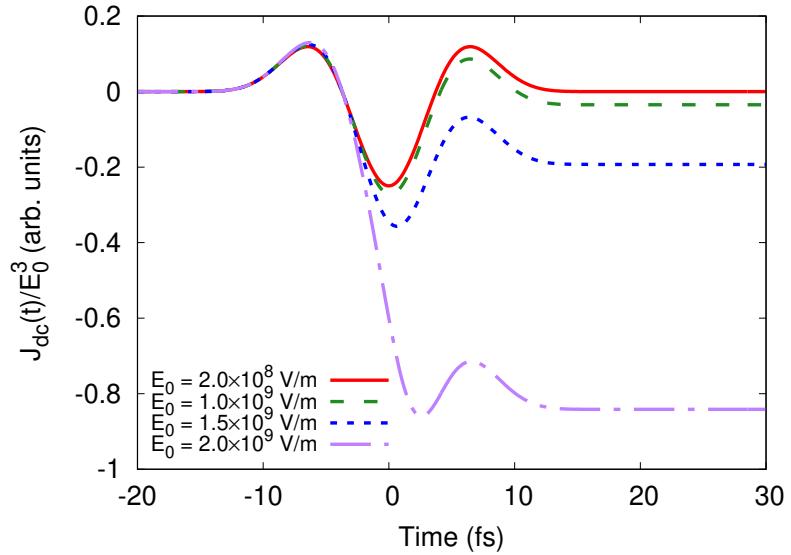
Expanding our analysis to the deeply off-resonant regime, where  $\hbar\omega \ll E_g/2$ , we observed an absence of population imbalance under weak applied field strength. However, as the field strength increased, a population imbalance in the Brillouin zone is formed, leading to the injection of the persistent dc-current after the laser

irradiation. Scaling analysis of the ballistic current injection with respect to the applied field strength  $E_0$  revealed that the population imbalance and the ballistic current result from an interference between three-photon absorption process with three photons of energy  $2\hbar\omega$  and a four-photon absorption process with two photons of energy  $2\hbar\omega$  and two photons of energy  $\hbar\omega$ . Consequently, we demonstrated that a multi-photon absorption process, incorporating photons with different energies, plays a pivotal role in addition to the multi-photon absorption process involving single-color photons.

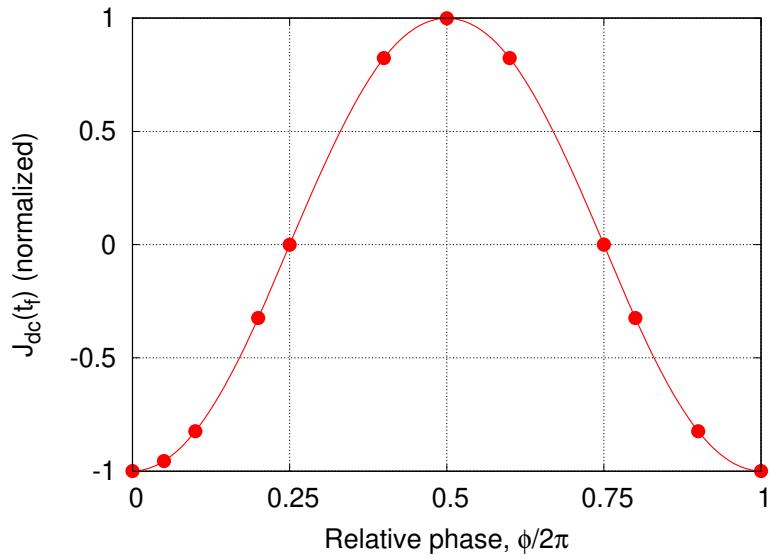
In previous works [19–21], the formation of substantial population imbalance and valley-population control has been discussed in monolayer systems such as monolayer *h*-BN and graphene, using bi-circular laser fields with frequencies  $\omega$  and  $2\omega$ . Recently, valley-population control with bi-circular fields has been extended to multi-layer and bulk systems [71] without relying on intrinsic inversion symmetry breaking and the Berry curvature at the valleys. In contrast to these works, our study demonstrates the induction of a large population imbalance and ballistic current injection without relying on the ellipticity of light. Instead, we rely on time-reversal symmetry breaking achieved through relative phase control between two-color linearly-polarized fields at frequencies  $\omega$  and  $2\omega$ . Furthermore, similar to Ref. [71], the injection mechanism with bi-color linearly polarized light does not rely on intrinsic inversion symmetry breaking, indicating an efficient dc current injection and population control with the scheme using linearly-polarized light. The potential of population control and the photovoltaic effect with linearly polarized light, in addition to circularly/elliptically polarized light, unveils novel avenues for realizing ultrafast opto-electronics, marked by precise control of current and population dynamics on the femtosecond time scale.



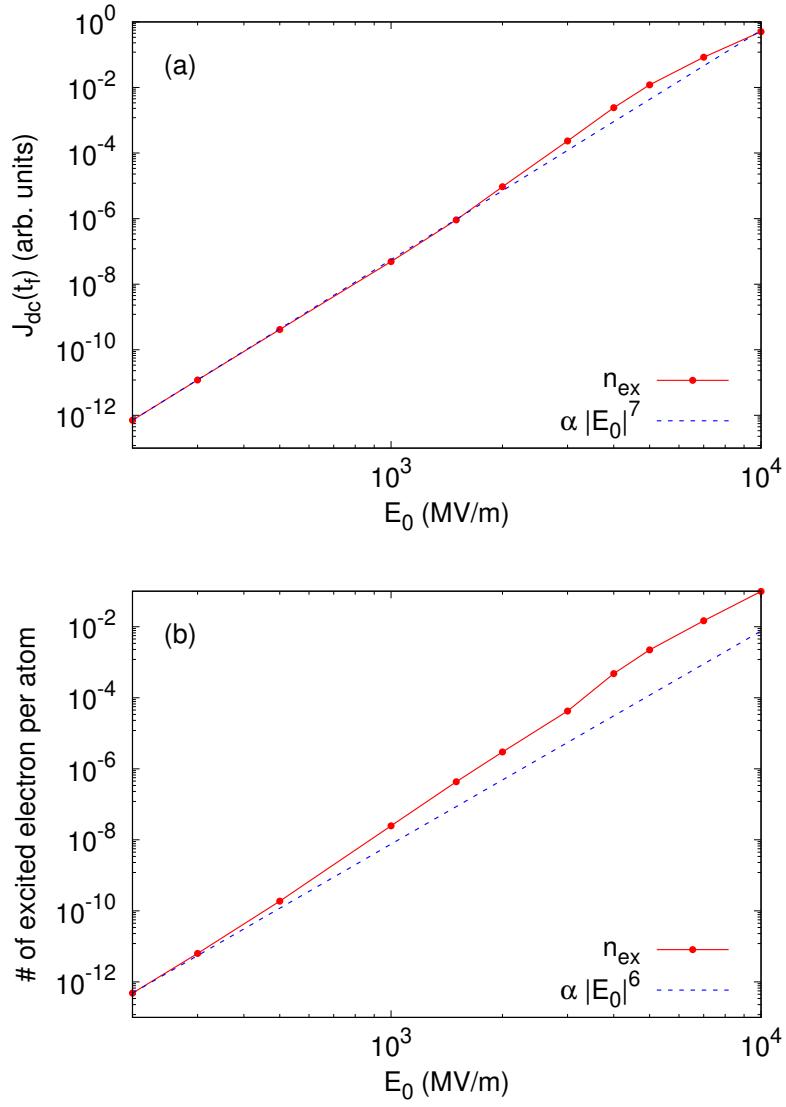
**Figure 3.7:** (a) The conduction population distribution  $n_c(\mathbf{k})$  after the irradiation of the laser field, and (b) the population imbalance distribution  $\Delta n_c(\mathbf{k})$  are shown. The results are computed by setting  $E_0$  to  $10^{10}$  V/m.



**Figure 3.8:** The dc components of the currents,  $J_{dc}(t)$ , are shown as a function of time. The results are computed with the deeply off-resonant condition,  $\hbar\omega = 1.0 \text{ eV}$ .



**Figure 3.9:** The persistent current,  $J_{dc}(t_f)$ , is shown as a function of the relative phase  $\phi$ . The results are computed with the deeply off-resonant condition,  $\hbar\omega = 1.0 \text{ eV}$ .



**Figure 3.10:** (a) The persistent current,  $|J_{dc}(t_f)|$ , is shown as a function of the field strength,  $E_0$ . (b) The number of conduction population after the laser irradiation is shown as a function of the field strength  $E_0$ .

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# Chapter 4

## THZ-INDUCED HHG AND NONLINEAR CHARGE TRANSPORT

Researchers have probed HHG in graphene particularly within the terahertz (THz) regime [72, 73]. THz-induced transparency of graphene, an intriguing nonlinear optical effect, has been explored [74–76], often analyzed through a thermodynamic model emphasizing the reduction of electric conductivity [48, 73]. Despite these advancements, a comprehensive understanding of the microscopic mechanisms governing these nonlinear effects remains elusive. The existing studies predominantly rely on thermodynamic models, lacking a thorough exploration of nonequilibrium quantum dynamics under dissipation. This research gap highlights the need for a deeper exploration of the underlying microscopic processes to unravel the intricacies of HHG and related nonlinear optical effects in graphene.

In this chapter, we delve into the intricate details of terahertz (THz)-induced high-order harmonic generation (HHG) and nonlinear electric transport in graphene. Our approach involves utilizing the quantum master equation with the relaxation time approximation to provide a comprehensive understanding of the underlying phenomena. To gain microscopic insights, we meticulously compare the outcomes of fully dynamic calculations with those obtained through a quasi-static approximation, wherein the electronic system is treated as a nonequilibrium steady state.

The key revelation from our investigation is that the THz-induced electron dynamics in graphene can be accurately represented by the nonequilibrium steady-state approach at each moment in time. Through a thorough population distribution analysis, we elucidate that THz-induced HHG in graphene stems from the reduction of effective conductivity, attributed to a significant displacement of electrons in the Brillouin zone.

To deepen our understanding, we draw comparisons between the nonequilibrium picture presented here and a thermodynamic perspective. This comparative analysis allows us to unravel the pivotal role of the nonequilibrium nature of electron dynamics in driving the extremely nonlinear optical and transport phenomena observed in graphene. Our study contributes valuable insights into the intricate interplay between THz fields, electron dynamics, and nonlinear behavior in graphene systems.

The comprehensive dynamical analysis derived from the quantum master equation provides a natural framework for understanding the intricate nonequilibrium features inherent in field-induced phenomena. Specifically, it allows for the exploration of phenomena characterized by symmetry breaking and delayed responses, unveiling the nuanced dynamics of the system under the influence of external fields. Ongoing theoretical investigations aim to delve deeper into these aspects, unraveling the subtleties of nonequilibrium behavior induced by light-matter interactions.

## 4.1 Fully Dynamical Simulations for THz Field

In this section, we first give a brief introduction of recent Experiments and Thermodynamic model on graphene. Next we delve into the microscopic intricacies governing the THz-induced high-order harmonic generation (HHG) in graphene, the electronic structure is described by the tight-binding model in Chapter 2. We initiate our investigation by conducting a detailed electron dynamics simulation using Eq. (2.29). The focus of this simulation is to analyze the high-order harmonic generation (HHG) in graphene under the influence of a linearly polarized

#### 4.1. FULLY DYNAMICAL SIMULATIONS FOR THZ FIELD

laser pulse. To facilitate this analysis, we adopt a specific form for the applied vector potential, described by the equation:

$$A(t) = -\frac{E_0}{\omega_0} e_x \sin(\omega_0 t) \cos^4 \left( \frac{\pi}{T_{\text{full}}} t \right), \quad (4.1)$$

where the simulation is conducted in the domain  $-T_{\text{full}}/2 < t < T_{\text{full}}/2$  and is zero outside this interval. Aligning with a previous experimental setup [72], we set specific parameters for the pulse: the peak field strength  $E_0$  is chosen as 8.5 MV/m, the mean photon energy  $\hbar\omega_0$  is set to 1.2407 meV, and the pulse duration  $T_{\text{full}}$  is established as 40 ps. Notably, the direction of the electric field  $e_x$  is defined along the  $\Gamma$ - $M$  direction.

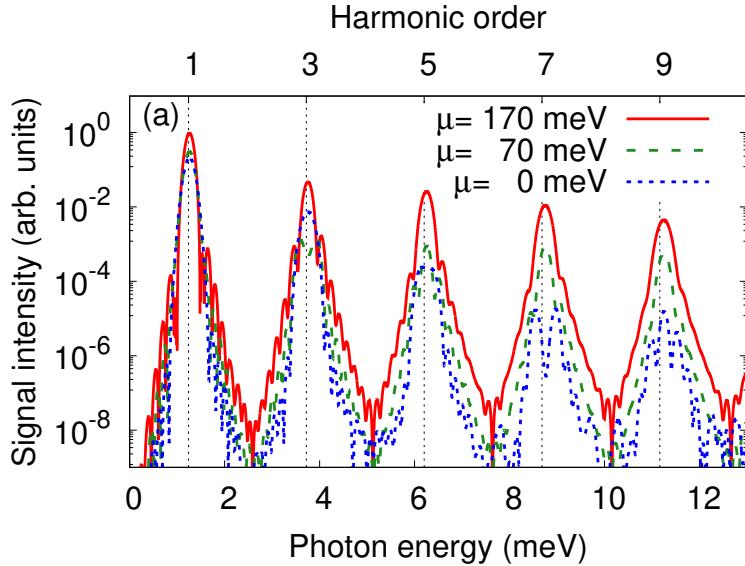
This detailed setup enables a thorough exploration of the electron dynamics under the influence of the specified laser pulse parameters, laying the groundwork for a comprehensive analysis of high-order harmonic generation in graphene.

Following the electron dynamics simulation governed by the field in Eq. (4.1), we proceed to compute the induced electric current, denoted as  $J(t)$ . To unveil the frequency content embedded within the current dynamics, we employ a Fourier transform applied to the current, yielding the high-order harmonics spectrum described by the expression:

$$I_{\text{HHG}}(\omega) \sim \omega^2 \left| \int_{-\infty}^{\infty} dt, J(t), e^{i\omega t} \right|^2. \quad (4.2)$$

Here,  $I_{\text{HHG}}(\omega)$  encapsulates the contribution of high-order harmonics, and the spectrum is determined by the square of the magnitude of the Fourier transform of the induced current. This approach enables us to discern and analyze the harmonic content within the electric current, providing valuable insights into the high-order harmonic generation phenomenon induced by the specified laser pulse.

In Figure 4.1, we present the computed HHG spectra, denoted as  $I_{\text{HHG}}(\omega)$ , corresponding to different chemical potentials  $\mu$ . Each chemical potential yields



**Figure 4.1:** Computed harmonic spectra  $I_{\text{HHG}}(\omega)$  with Eq. (4.2) for different chemical potentials,  $\mu = 0, 70$  and  $170$  meV.

distinct harmonic peaks, and a noticeable trend emerges: the intensities of the emitted harmonics systematically increase with the rise in the chemical potential. This observation aligns with findings from a recent experiment [73], where an analogous increase in emitted harmonic intensity was noted with an elevation in gate voltage.

The results presented here echo the interpretations from prior research, such as [48], where THz-induced high-order harmonic generation in graphene was elucidated through a thermodynamic framework. In contrast, our current study aims to advance the understanding of these THz-induced nonlinear phenomena by incorporating a comprehensive microscopic perspective. Specifically, we delve into the nonequilibrium nature of electron dynamics to refine our description of light-matter interactions and provide a more nuanced interpretation of the observed trends in high-order harmonic spectra with varying chemical potentials.

Following the electron dynamics calculations under THz fields, our findings reveal that the emitted harmonics experience enhancement with an increase in chemical potential. This theoretical insight aligns with recent experimental observations, where high-order harmonic generation is similarly enhanced through the application of a gate bias voltage [73].

## 4.2 Quasi-static Approximation

Subsequently, we introduce a quasi-static approximation to dissect the THz-induced electron dynamics, facilitating a reexamination of the nonlinear electric transport and the field-induced transparency phenomena inherent to graphene [56]. In our analysis, we make the assumption that the variation of the THz field is sufficiently slow, allowing the electronic system to be effectively characterized by a nonequilibrium steady state at each point in time. This assumption holds true under the equilibrium established between the field-induced excitation and relaxation processes. Its accuracy is particularly pronounced when the mean frequency of the THz field is significantly smaller than the intrinsic relaxation rates, denoted as  $1/T_1$  and  $1/T_2$ .

For practical considerations within the quasi-static approximation, we initiate our analysis by evaluating the electric current of a nonequilibrium steady state under a static electric field, represented as  $E(t) = E_0 e_x$ . The corresponding expression is given by:

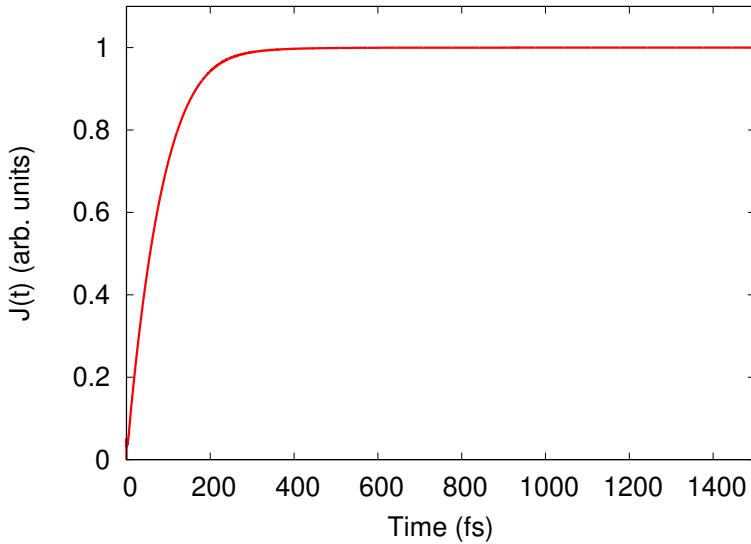
$$J_S(E_0) = \lim_{t \rightarrow \infty} \frac{2}{(2\pi)^2} \int dk \text{Tr} [\hat{J}k(t)\rho k(t)] . \quad (4.3)$$

In this equation, the electron dynamics are computed under a static field,  $A(t) = -E_0 e_x t$ . Over time, the electronic system attains a nonequilibrium steady state as a result of the equilibrium between field-induced excitation and relaxation processes.

Within the quasi-static approximation, we substitute the instantaneous electric field in the induced current  $J(t)$  with the steady current  $J_S(E_0)$  from Eq. (4.3), resulting in the approximation:

$$J(t) \approx J_S(E(t)) . \quad (4.4)$$

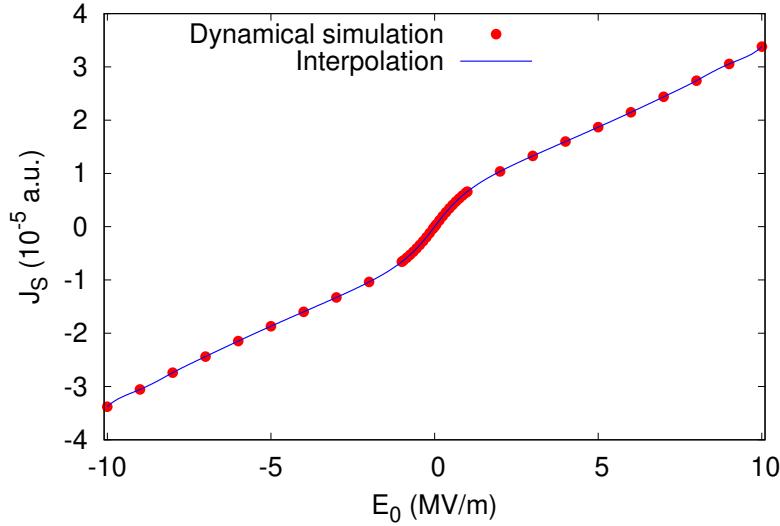
To assess the validity of this approximation, we first evaluate the steady current in Eq.(4.3) for various field strengths. For practical computations, we analyze the electron dynamics under a static electric field, denoted as  $E_0 = E_0 e_x$ . Figure 4.2 depicts the computed current as a function of time under a static field. In this simulation, the chemical potential  $\mu$  is set to 170 meV, and the field strength  $E_0$  is established at 8.5 MV/m. The initial state at  $t = 0$  corresponds to the thermal equilibrium state.



**Figure 4.2:** Electric current in graphene under a static electric field,  $E_0 = 8.5$  MV/m.

As observed in Fig.4.2, the application of the electric field induces an electric current at  $t = 0$ , and it steadily approaches the steady-state value, denoted as  $J_S(E_0)$ . This observation confirms that the electronic system, evolving under Eq.(2.29) with a static electric field, eventually reaches a nonequilibrium steady state after a sufficiently extended period of time propagation. This validation supports the reliability of the quasi-static approximation in capturing the nonequilibrium dynamics induced by a slowly varying electric field.

In our iterative simulations, we systematically vary the field strength  $E_0$  and assess the resulting values of the steady current. Denoting the  $k$ th set of employed field strength and evaluated current as  $E_k$  and  $J_k$  respectively, we represent the computed steady current  $J_k$  as red points in Figure 4.3 against the applied field strength  $E_k$ . To construct a continuous function  $J_S(E_0)$  from the discrete data



**Figure 4.3:** Steady current  $J_S(E_0)$  as a function of field strength  $E_0$ . The results of the fully dynamical calculation are shown as the red points, while the interpolated result is shown as the blue-solid line.

points  $E_k, J_k$  in Figure 4.3, we adopt a two-step interpolation procedure.

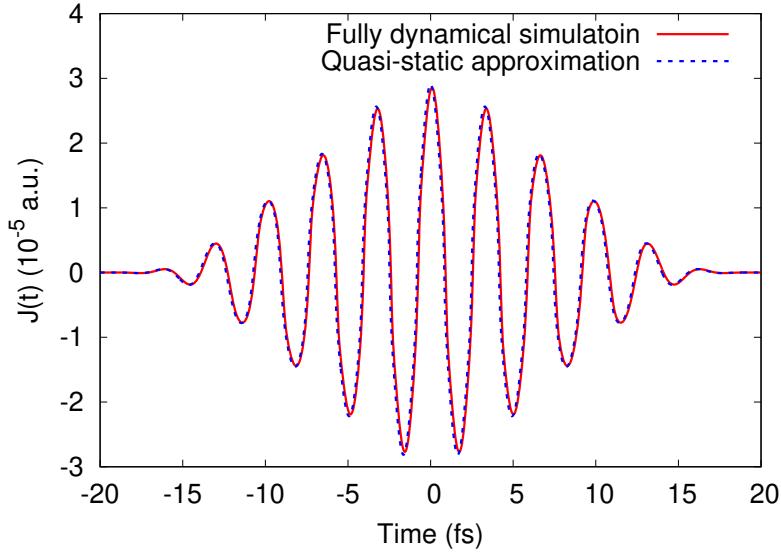
In the initial step of constructing the continuous function, we employ a polynomial regression with the following odd function:

$$J_{\text{polynomials}}(E_0) = \sum j = 0^4 e_x \alpha^{(2j+1)} E_0^{2j+1}, \quad (4.5)$$

where  $\alpha^{(j)}$  represents optimization parameters. These parameters are fine-tuned to ensure that the polynomial function  $J_{\text{polynomials}}(E_0)$  effectively reproduces the discrete points  $E_k, J_k$  in Figure 4.3.

Moving on to the second step, we aim to refine the discrepancy between the discrete points in Figure 4.3 and the polynomial function  $J_{\text{polynomials}}(E_0)$ . To achieve this, we define the residual error of the polynomial regression as:

$$\Delta J_k = J_k - J_{\text{polynomials}}(E_k). \quad (4.6)$$



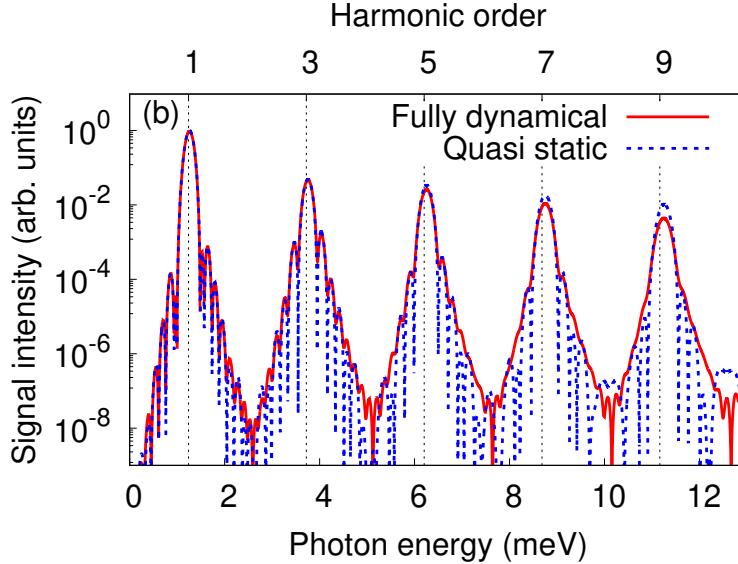
**Figure 4.4:** Comparison of the THz-induced current computed with the fully dynamical calculation and the quasi-static approximation.

Subsequently, we apply spline interpolation to the data points  $E_k, \Delta J_k$ , denoting the interpolated function as  $\Delta J_{\text{spline}}(E_0)$ . Finally, we approximate the continuous function,  $J_S(E_0)$ , as:

$$J_S(E_0) \approx J_{\text{polynomials}}(E_0) + \Delta J_{\text{spline}}(E_0). \quad (4.7)$$

Utilizing the approximated function in Eq.(4.7), we evaluate the THz-induced electric current with the quasi-static approximation, Eq.(4.4). The relationship between current and field as expressed in Eq. (4.3), we approximate the field-induced current  $J(t)$  by the steady-state current, where the instantaneous electric field is denoted as  $E(t)$ , leading to the approximation  $J(t) \approx J_S(E(t))$ . Figure 4.4 showcases the computed current as a function of time with the quasi-static approximation. To facilitate comparison, the result of the fully dynamical calculation is also presented. Applying a Fourier transform to the obtained current in Figure 4.4 yields the high-order harmonic generation (HHG) spectra depicted in Figure 4.5.

To gauge the accuracy of the quasi-static approximation, we computed the high-order harmonic generation spectrum  $I_{\text{HHG}}(\omega)$  using the approximated current,  $J_S(E(t))$ . Figure 4.5 illustrates the computed spectrum  $I_{\text{HHG}}(\omega)$  with the



**Figure 4.5:** Comparison of the HHG spectra computed with the fully dynamical simulations in Sec. ?? and the quasi-static approximation Sec. ?? . Here, the chemical potential is set to  $\mu = 170$  meV.

quasi-static approximation, with  $\mu$  set to 170 meV. For reference, the corresponding result from the fully dynamical calculation is also presented. As evident from the figure, the quasi-static approximation faithfully reproduces the results obtained from the fully dynamical calculation. Thus, we confirm that the quasi-static approximation adeptly captures the electron dynamics in graphene under THz fields. This observation suggests that the microscopic mechanism of THz-induced high-order harmonic generation (HHG) in graphene can be effectively elucidated based on the nonequilibrium steady state, considering the delicate balance between field-induced excitation and relaxation. It is worth noting that the accuracy of the quasi-static approximation diminishes for higher-order harmonics due to the rapid dynamics that cannot be adequately captured by the quasi-static picture.

We have validated that the THz-induced high-order harmonic generation in graphene is effectively captured by the quasi-static approximation, highlighting the relevance of the nonequilibrium steady-state in portraying essential aspects of THz-induced electron dynamics. A detailed microscopic analysis has been conducted to examine the significance of the intraband current and the population distribution within the Brillouin zone in this steady-state.

## 4.3 Nonlinear Charge Transport in Nonequilibrium Steady-state

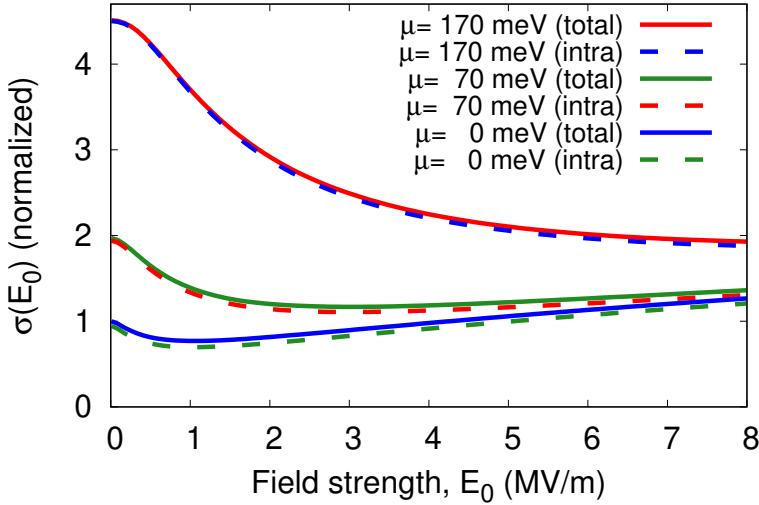
To provide a broader context, we juxtapose the nonequilibrium steady-state achieved within the quasi-static framework with insights garnered from a recently developed thermodynamic model [48]. This comparative analysis aims to elucidate the nonequilibrium mechanisms governing nonlinear optical and transport phenomena within graphene in the THz regime. By contrasting the quasi-static nonequilibrium picture with the thermodynamic model, we endeavor to unravel the underlying dynamics driving the intricate interplay between electron behavior and external THz fields in graphene systems. We then study the nonlinear electric conductivity in a static regime in order to develop microscopic insight into the THz-induced HHG. For this purpose, we first define the intraband component of the steady-state current in Eq. (4.3).

Next, we proceed to evaluate the effective conductivities using both the total steady current  $J_S(E_0)$  and the intraband component  $J_S^{\text{intra}}(E_0)$ . The effective total and intraband conductivities are computed as follows:

$$\sigma(E_0) = \frac{e_x \cdot J_S(E_0)}{E_0} , \quad (4.8)$$

$$\sigma^{\text{intra}}(E_0) = \frac{e_x \cdot J_S^{\text{intra}}(E_0)}{E_0} . \quad (4.9)$$

Figure 4.6 illustrates the computed effective conductivities,  $\sigma(E_0)$  and  $\sigma^{\text{intra}}(E_0)$ , as a function of the applied field strength  $E_0$  for different chemical potentials  $\mu$ . In this figure, the conductivities  $\sigma(E_0)$  obtained from the total steady current  $J_S(E_0)$  align well with those derived from the intraband current  $J_S^{\text{intra}}(E_0)$  across all investigated field strengths  $E_0$  and chemical potentials  $\mu$ . This observation implies that the charge transport in graphene under static and THz fields is predominantly governed by the intraband current. The intraband current is described by the product of the band group velocity and the band population in the Brillouin zone.



**Figure 4.6:** Nonlinear effective conductivities of graphene as a function of the static field strength  $E_0$  evaluated with the total currents (solid lines) and intra-band currents (dashed lines) for different values of the chemical potential,  $\mu = 0$ , 70 and 170 meV.

In Fig. 4.6, the effective conductivities,  $\sigma(E_0)$ , exhibit an initial reduction across all investigated chemical potentials  $\mu$  as the field strength increases from zero. This reduction in conductivity aligns with the field-induced transparency phenomenon observed in graphene [56], as the conductivity  $\sigma(E_0)$  is directly related to photoabsorption via Joule heating, given by:

$$E_{\text{Joule}} = E_0 \cdot J_S(E_0) = \sigma(E_0)E_0^2 \quad (4.10)$$

As the field strength continues to increase, graphene with relatively small chemical potentials (e.g.,  $\mu = 0$  or 70 meV) exhibits an increase in conductivity, while graphene with a relatively large chemical potential (e.g.,  $\mu = 170$  meV) continues to show a reduction in conductivity. These trends are consistent with a previous theoretical study on nonlinear transport in graphene using the linear band approximation [56]:

$$H_k = v_F (\sigma_x k_x + \sigma_y k_y) \quad (4.11)$$

Given that the present work employs a more comprehensive electronic structure throughout the full Brillouin zone based on the tight-binding model, it serves as a

validation of the low-energy Hamiltonian approximation for the graphene band-structure used in the previous work. In the previous study [56], the decrease in effective conductivity was attributed to the dispersion of the population imbalance in the Brillouin zone, while the increase in conductivity was linked to additional carrier injection through the Zener tunneling mechanism. These interpretations naturally apply to the results obtained in the present study, further confirming the robustness and applicability of the previously proposed mechanisms.

Given the aptitude of the quasi-static approximation in accurately delineating THz-induced electron dynamics, the interpretation of THz-induced High-Order Harmonic Generation (HHG) finds its foundation in the effective conductivities, as portrayed in Fig. 4.6. Should the conductivity  $\sigma(E_0)$  remain unswayed by the field strength  $E_0$ , the induced current maintains linear proportionality to the field strength, thereby precluding the generation of harmonics. Consequently, within the quasi-static framework, the emergence of harmonics stems from the nonlinearity inherent in the current  $J_S(E_0)$  and the field-strength-dependent conductivity  $\sigma(E_0)$ .

Examining Fig.4.6, it becomes evident that the conductivity exhibits heightened sensitivity to the field strength, particularly accentuated for larger chemical potentials. This accentuated dependence manifests as a pronounced reduction in conductivity with increasing field strength. This observation underpins the elucidation of the heightened HHG in Fig.4.1 accompanying a shift in chemical potential—attributed to the significant reduction in conductivity coincident with the amplified field strength.

In prior investigations [72, 73], the interpretation of THz-induced HHG in graphene was anchored in the reduction of conductivity, albeit within the framework of the thermodynamic model [48]. To unravel the influence of nonequilibrium dynamics in the steady state, we shall delve into the interrelation between the two models—the nonequilibrium steady-state model and the thermodynamic model—in the forthcoming section, Sec. 4.4.

Moving to the intraband current articulated in Eq.(2.36), it is crucial to recognize its composition—encompassing the product of band velocity and population. Given the inherent invariance of band velocity under the presence of

### 4.3. NONLINEAR CHARGE TRANSPORT IN NONEQUILIBRIUM STEADY-STATE

electric fields as an intrinsic material property, the crux of THz-induced current generation lies in the field-induced modulation of population. Furthermore, as expounded earlier, the THz-induced current is predominantly governed by the intraband component. For an intricate understanding of the THz-induced current at a microscopic level, we shall undertake an analysis of the population distribution within the Brillouin zone under the influence of the field. Figure 4.7 (a) delineates the equilibrium population distribution in the conduction band, denoted as  $f^{FD}(\epsilon_{c,k})$ , around a Dirac point (K point) in graphene, specifically at  $k = \frac{2\pi}{\sqrt{3}a} \left(1, \frac{1}{\sqrt{3}}\right)$ . Here, the chemical potential  $\mu$  is established at 170 meV. The equilibrium population exhibits a circular symmetry around the Dirac point, reflecting the partial filling of the Dirac cone by doped electrons.

We define the field-induced alteration in conduction population within a nonequilibrium steady state as:

$$\Delta n_{c,k} = \left[ n_{c,k'+eA(t)/\hbar}(t) - f^{FD}(\epsilon_{c,k'+eA(t)/\hbar}) \right]_{k'+eA(t)/\hbar=k} \quad (4.12)$$

Figures 4.7 (b-d) showcase the field-induced conduction population  $\Delta n_{c,k}$  for varying field strengths: (b) 0.01 MV/m, (c) 3 MV/m, and (d) 10 MV/m.

As illustrated in Fig. 4.7(b), the field-induced population modulation emerges along the ring-shaped contour defined by the single-particle energy  $\epsilon_{bk}$  and the Fermi energy  $\epsilon_F = \mu|_{T_e=0}$  as  $\epsilon_{bk} = \epsilon_F$ , specifically where  $\epsilon_{bk} = \epsilon_F$ . The modulation occurs in proximity to the Fermi energy due to the mild field excitation, and the ring structure derives from the circular symmetry inherent in the Dirac cone. In the weak field regime, the augmentation and reduction in conduction population  $\Delta n_{c,k}$  exhibit symmetric distribution along the field direction ( $x$ -axis). Conversely, in the strong-field regime, the distribution becomes non-symmetric, as evident in Figs. 4.7(c) and (d). Here, the red-colored region signifies an expanded range on the left side of the Dirac point, where population increase occurs, while the blue-colored region indicates a more confined area on the right side marked by population decrease. The pronounced elongation of the population increase along the field direction may be construed as a consequence of the field-induced intraband acceleration within the Brillouin zone. Simultaneously, the localized population decrease around the Dirac point, as observed in Fig. 4.7(a), can be at-

tributed to the field-induced displacement of initially localized electrons encircling the Dirac point.

In the preceding study [56], the decrease in conductivity was elucidated as the saturation of population imbalance surrounding the Dirac point. To scrutinize this interpretation, we present the conduction population distribution:

$$n_{c,k' + eA(t)/\hbar} \Big|_{k' + eA(t)/\hbar = k} \quad (4.13)$$

in lieu of the population change  $\Delta n_{c,k}$  in Fig.4.7(e), with the field strength  $E_0$  set to 10MV/m. It is noteworthy that the summation of the density in Fig.4.7(a) and the density change in Fig.4.7(d) corresponds to the density in Fig.4.7 (e).

Examining Fig.4.7(e), a discernible shift in the conduction population from the right to the left side of the Dirac cone is evident. This observation indicates that the population imbalance encircling the Dirac cone is already near its maximum saturation point, where no further population can be transferred from the right side to the left side. Consequently, the population imbalance, a pivotal determinant of the intraband current, reaches saturation in the strong-field regime, precluding any substantial increase. This saturation, in turn, leads to the saturation of the intraband current—predominant in the nonequilibrium steady state—ultimately culminating in the observed reduction in conductivity within the strong-field regime.

Our investigation reveals a substantial decrease in the effective conductivity of graphene in the strong-field regime, attributed to the saturation of population imbalance within the Brillouin zone. This reduction aligns with the observed THz-induced transparency in graphene, as reported experimentally [74–76] and theoretically investigated in prior studies [56]. Furthermore, we establish that this diminished conductivity leads to nonlinear current behavior in the strong-field regime, culminating in high-order harmonic generation in graphene. Thus, the origin of high-order harmonic generation can be comprehended through the lens of saturation of population displacement within the Brillouin zone in the context of nonequilibrium electron dynamics.

## 4.4 Comparison with Thermodynamic Model

Having elucidated the microscopic intricacies of THz-induced High-Order Harmonic Generation (HHG) in graphene within the framework of the nonequilibrium steady-state, our focus now shifts to investigating the distinctive role played by the nonequilibrium nature of THz-induced electron dynamics. To accomplish this, we undertake a comparative analysis with the previously formulated thermodynamic model [48]. In contrast to the present nonequilibrium model, the thermodynamic model relies on the utilization of the thermal Fermi–Dirac distribution to delineate laser-excited electronic systems. This model operates under the assumption that electrons swiftly undergo thermalization, allowing them to be effectively treated as an equilibrium state characterized by a notably high electron temperature  $T_e$ .

Within the thermodynamic model, equilibrium states find characterization through the electron temperature  $T_e$ , while in the developed nonequilibrium model, nonequilibrium steady-states are intrinsically defined by the applied field strength  $E_0$ , devoid of any reliance on temperature considerations. To ensure a equitable comparison between the two models, it becomes imperative to establish a connection between the electron temperature  $T_e$  and the field strength  $E_0$ . This connection is facilitated by the introduction of the field-induced excess energy for each model.

The total energy of the electronic system is formulated as:

$$E_{\text{tot}}(t) = \frac{2}{(2\pi)^2} \int dk \text{Tr} \left[ H_{k+eA(t)/\hbar} \rho_k(t) \right]. \quad (4.14)$$

Subsequently, the field-induced excess energy of the nonequilibrium steady-state is defined as

$$\Delta E_{\text{excess}}^{\text{NEQ}}(E_0) = \lim_{t \rightarrow \infty} [E_{\text{tot}}(t) - E_{\text{tot}}(-t)], \quad (4.15)$$

Here,  $\lim_{t \rightarrow \infty} E_{\text{tot}}(t)$  corresponds to the total energy in the nonequilibrium steady-state under the presence of the field  $E_0$ , while  $\lim_{t \rightarrow \infty} E_{\text{tot}}(-t)$  corresponds

to that of the equilibrium state without the field. Thus, the field-induced excess energy of the nonequilibrium model captures the energy difference between the nonequilibrium steady-state under an external field  $E_0$  and the field-free equilibrium state.

In contrast, the field-induced excess energy of the thermodynamic model is defined as the energy difference between finite temperature states at  $T_e$  and 300K, the initial temperature of the present nonequilibrium model:

$$\Delta E_{\text{excess}}^{\text{TM}} = \sum_{b=v,c} \frac{2}{(2\pi)^2} \int dk \epsilon_{bk} \times [f^{\text{FD}}(\epsilon_{bk}, T_e, \mu) - f^{\text{FD}}(\epsilon_{bk}, T_e = 300 \text{ K}, \mu)]. \quad (4.16)$$

Therefore,  $\Delta E_{\text{excess}}^{\text{TM}}$  is expressed as a function of the electron temperature  $T_e$ .

By employing Eq.(4.15) and Eq.(4.16), we establish a link between the applied field strength  $E_0$  characterizing the nonequilibrium steady-state and the electron temperature  $T_e$  inherent to the thermodynamic model through the concept of excess energy. This connection enables a comparative analysis of the effective conductivity  $\sigma(E_0)$  in the nonequilibrium steady-state and the linear conductivity of the thermodynamic model.

Figure 4.8 presents the conductivities of the nonequilibrium steady-state (depicted by the red-solid line) and the thermodynamic model (represented by the green-dashed line). The computations for the nonequilibrium steady-state consider a chemical potential  $\mu$  set to 170 meV and an electron temperature  $T_e$  in the relaxation operator set to 300 K. In contrast, the linear conductivity of the thermodynamic model is evaluated under the influence of a weak field, ensuring the induced current aligns with a linear response. The results for the thermodynamic model involve varying the electron temperature  $T_e$  while maintaining the total population constant, as expressed by:

$$N_{\text{tot}} = \frac{2}{(2\pi)^2} \sum_{b=v,c} \int dk f^{\text{FD}}(\epsilon_{bk}, T_e, \mu), \quad (4.17)$$

to the value at  $T_e = 300 \text{ K}$  and  $\mu = 170 \text{ meV}$ . Consequently, the chemical potential undergoes adjustments with changes in the electron temperature.

#### 4.4. COMPARISON WITH THERMODYNAMIC MODEL

Figure 4.8 illustrates that the conductivity of the thermodynamic model (depicted by the green-dashed line) initially experiences a decline with an increase in the excess energy, followed by a notable upturn once the excess energy reaches a moderately large value. In contrast, the conductivity of the nonequilibrium steady-state (represented by the red-solid line) consistently diminishes with the escalation of the excess energy across the entire explored range. It's important to note that the conductivity of the nonequilibrium steady-state in Fig.4.8 aligns with that in Fig.4.6 when considering the converted  $x$ -axis. The fundamental contrast between the conductivities of the nonequilibrium steady-state and the thermodynamic model arises from the interband excitation influenced by temperature. In the thermodynamic model, thermal excitation propels electrons from the valence band to the conduction band, augmenting the effective carrier population and subsequently enhancing conductivity with elevated electron temperatures. In contrast, the nonequilibrium steady-state experiences a significant suppression of field-induced interband excitation due to Pauli blocking, mitigating the artificial rise in effective carrier population and the resultant boost in conductivity.

In their previous study [48], the authors delved into the microscopic intricacies of THz-induced high-order harmonic generation and field-induced transparency in graphene using the thermodynamic model. Notably, the investigation adopted a single-band approximation in which only the conduction band was considered, while the valence band remained frozen. Surprisingly, this single-band approximation yielded better agreement with experimental results than the two-band approximation, where both valence and conduction bands were considered [73]. Despite the intuitive expectation that the two-band approximation would offer greater accuracy, the results indicated that the single-band approximation provided a more accurate depiction within the thermodynamic model.

To elucidate the role of the single-band approximation in the thermodynamic model, we extended our comparison between the thermodynamic model and the nonequilibrium steady-state by incorporating the single-band approximation into our analysis. In this adaptation, we phenomenologically constrained the population in the valence band, while maintaining the use of the Fermi–Dirac

distribution for the conduction band. This modification involved transforming the Fermi–Dirac distribution as follows:

$$\tilde{f}^{\text{MFD}}(\epsilon, T_e, \mu) = f^{\text{FD}}(\epsilon, T_e, \mu)\Theta(\epsilon) + \Theta(-\epsilon), \quad (4.18)$$

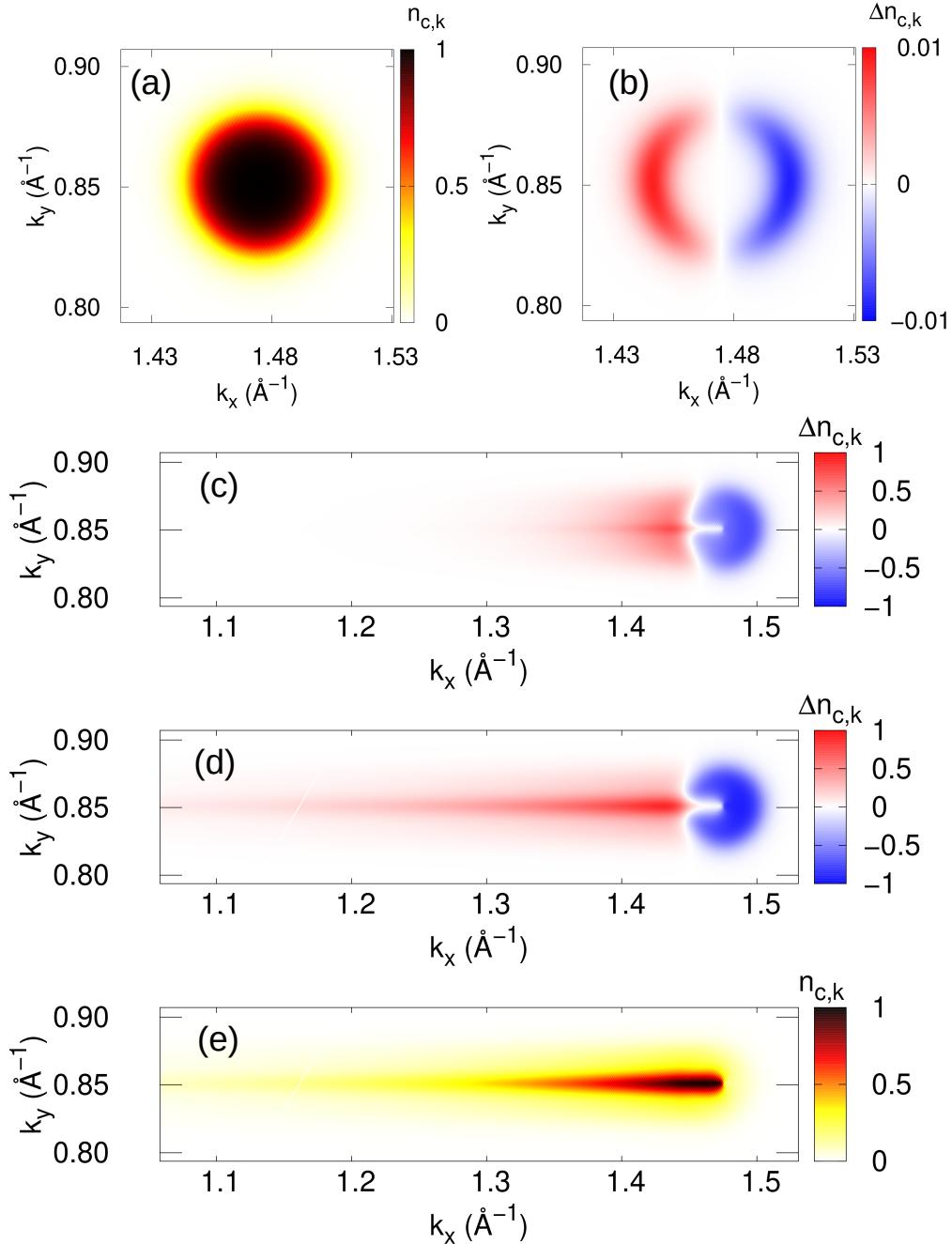
where  $\Theta(\epsilon)$  represents the Heaviside step function. By replacing the original Fermi–Dirac distribution (Eq.(2.33)) with the modified version (Eq.(4.18)), we conducted a comparative analysis of conductivity with the thermodynamic model. The results of the thermodynamic model incorporating the single-band approximation are depicted by the blue-dotted line in Fig. 4.8. Remarkably, this modified thermodynamic model effectively reproduces the conductivity trend observed in the nonequilibrium steady-state, showcasing a consistent monotonic decrease with an increase in excess energy.

This intriguing outcome suggests that the phenomenological freezing of the valence band in the single-band approximation curtails the artificial interband excitation in the thermodynamic model, leading to a more accurate portrayal of conductivity. In contrast, the nonequilibrium steady-state, based on a fully dynamical model, naturally captures the suppression of interband excitation, providing an accurate representation of electron dynamics in graphene under THz fields without resorting to the phenomenological freezing of the valence band.

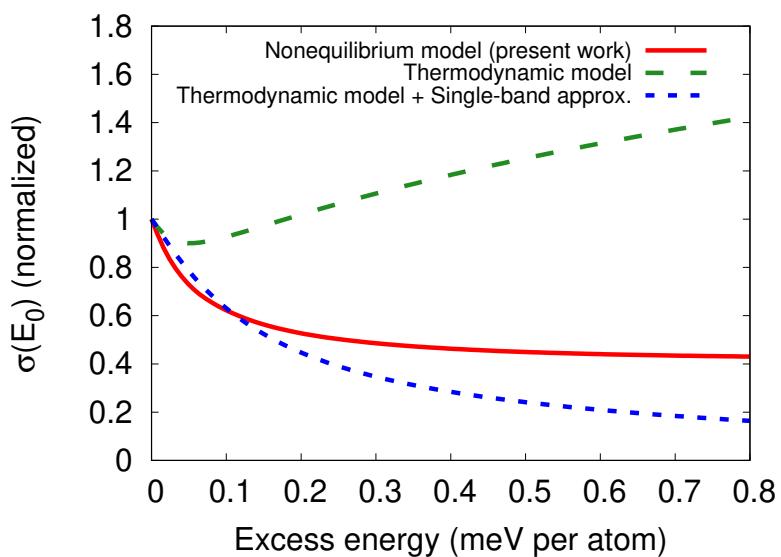
Consequently, our findings indicate that the thermodynamic model exhibits an artificial augmentation of electric conductivity when subjected to intense THz fields, stemming from pronounced interband transitions between the valence and conduction bands. In alignment with prior work [73], we introduced a single-band approximation, freezing the valence band to mitigate this spurious interband excitation. Correspondingly, the computed conductivity in the thermodynamic framework, employing this single-band approximation, accurately reflects the anticipated decreasing trend under field irradiation. This trend aligns with experimental observations of the field-induced transparency of graphene [74–76]. In contrast, the nonequilibrium model developed in this study effectively captures the diminishing trend in conductivity under field irradiation without the need for artificially freezing the valence band. This underscores the essential role of the nonequilibrium nature of electron dynamics in describing conductiv-

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ity reduction under field irradiation and preventing spurious interband excitation, as evidenced in the comparison with the thermodynamic model.



**Figure 4.7:** (a) The equilibrium population distribution in the conduction band  $f^{\text{FD}}(\epsilon_{c,k})$ . (b-d) The field induced conduction population change for different field strengths, (b) 0.01 MV/m, (c) 3 MV/m, and (d) 10 MV/m. (e) The population distribution in the conduction band in the nonequilibrium steady-state under a static field,  $E_0 = 10 \text{ MV/m}$ .



**Figure 4.8:** Computed effective conductivities are shown as a function of the excess energy. The results for the nonequilibrium steady-state (red-solid), the thermodynamic model (green-dashed), and the thermodynamic model plus the single-band approximation (blue-dotted) are shown.

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# Appendix A

## ADIABATIC BASIS REPRESENTATION

To analytically investigate nonlinear photocarrier injection in solids, we first introduce the equation of motion in the adiabatic basis representation. In this representation, we can naturally separate the interband transitions, the dynamical phase factor, and the geometric phase factor. To introduce the representation, we consider the following one-body Schrödinger equation for a  $k$ -point,

$$i \frac{d}{dt} |\psi_k(t)\rangle = H [k + A(t)] |\psi_k(t)\rangle, \quad (\text{A.1})$$

where  $A(t)$  is an external vector potential, which is related to the external electric field as  $E(t) = -dA(t)/dt$ . In this note, we assume that the vector potential is zero for the negative time;  $A(t \leq 0) = 0$ .

To introduce the adiabatic basis representation, we introduce the instantaneous eigenstates of the Hamiltonian as

$$H [k + A(t)] |u_{b,k+A(t)}\rangle = \epsilon_{b,k+A(t)} |u_{b,k+A(t)}\rangle, \quad (\text{A.2})$$

where  $b$  is the band index. Hereafter, we assume the two-band system, which has the valence band ( $b = v$ ) and the conduction band ( $b = c$ ). However, we can straightforwardly extend it to general systems.

On the basis of the instantaneous eigenstates defined by Eq. (A.2), we consider

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the following expansion of the wavefunction

$$|\psi_k(t)\rangle = c_{v,k}(t)e^{-i\int_0^t dt' \epsilon_{v,k+A(t')} e^{i\phi_{v,k}^g(t)}}|u_{v,k+A(t)}\rangle + c_{c,k}(t)e^{-i\int_0^t dt' \epsilon_{c,k+A(t')} e^{i\phi_{c,k}^g(t)}}|u_{c,k+A(t)}\rangle, \quad (\text{A.3})$$

where  $c_{b,k}(t)$  are the expansion coefficients. In the expansion, we explicitly include the dynamical phase factor,  $e^{-i\int_0^t dt' \epsilon_{v,k+A(t')}}$ , and the additional phase factor,  $e^{i\phi_{b,k}^g(t)}$ . The latter one will be defined later as the geometric phase factor.

Inserting Eq. (A.3) into Eq. (??), one obtains

$$\begin{aligned} \left[ i\frac{d}{dt} - H[k + A(t)] \right] |\psi_k(t)\rangle &= i\dot{c}_{v,k}(t)e^{-i\int_0^t dt' \epsilon_{v,k+A(t')} e^{i\phi_{v,k}^g(t)}}|u_{v,k+A(t)}\rangle \\ &\quad + i\dot{c}_{c,k}(t)e^{-i\int_0^t dt' \epsilon_{c,k+A(t')} e^{i\phi_{c,k}^g(t)}}|u_{c,k+A(t)}\rangle \\ &\quad - \dot{\phi}_{v,k}^g(t)c_{v,k}(t)e^{-i\int_0^t dt' \epsilon_{v,k+A(t')} e^{i\phi_{v,k}^g(t)}}|u_{v,k+A(t)}\rangle \\ &\quad - \dot{\phi}_{c,k}^g(t)c_{c,k}(t)e^{-i\int_0^t dt' \epsilon_{c,k+A(t')} e^{i\phi_{c,k}^g(t)}}|u_{c,k+A(t)}\rangle \\ &\quad - ic_{v,k}(t)e^{-i\int_0^t dt' \epsilon_{v,k+A(t')} e^{i\phi_{v,k}^g(t)}}E(t) \cdot \frac{\partial|u_{v,k+A(t)}\rangle}{\partial k} \\ &\quad - ic_{c,k}(t)e^{-i\int_0^t dt' \epsilon_{c,k+A(t')} e^{i\phi_{c,k}^g(t)}}E(t) \cdot \frac{\partial|u_{c,k+A(t)}\rangle}{\partial k} = 0. \end{aligned} \quad (\text{A.4})$$

By multiplying  $e^{+i\int_0^t dt' \epsilon_{v,k+A(t')} e^{-i\phi_{v,k}^g(t)}}\langle u_{v,k+A(t)}$  to Eq. (A.4), one obtains

$$\begin{aligned} &i\dot{c}_{v,k}(t) - \dot{\phi}_{v,k}^g(t)c_{v,k}(t) - ic_{v,k}(t)E(t) \cdot \left\langle u_{v,k+A(t)} \middle| \frac{\partial u_{v,k+A(t)}}{\partial k} \right\rangle \\ &- ic_{c,k}(t)e^{-i\int_0^t dt' \epsilon_{c,k+A(t')} - \epsilon_{v,k+A(t')} e^{i(\phi_{c,k}^g(t) - \phi_{v,k}^g(t))}}E(t) \cdot \left\langle u_{v,k+A(t)} \middle| \frac{\partial u_{c,k+A(t)}}{\partial k} \right\rangle = 0. \end{aligned} \quad (\text{A.5})$$

Likewise, by multiplying  $e^{+i\int_0^t dt' \epsilon_{c,k+A(t')} e^{-i\phi_{c,k}^g(t)}}\langle u_{c,k+A(t)}$  to Eq. (A.4), one obtains

$$\begin{aligned} &i\dot{c}_{c,k}(t) - \dot{\phi}_{c,k}^g(t)c_{c,k}(t) - ic_{c,k}(t)E(t) \cdot \left\langle u_{c,k+A(t)} \middle| \frac{\partial u_{c,k+A(t)}}{\partial k} \right\rangle \\ &- ic_{v,k}(t)e^{-i\int_0^t dt' \epsilon_{v,k+A(t')} - \epsilon_{c,k+A(t')} e^{i(\phi_{v,k}^g(t) - \phi_{c,k}^g(t))}}E(t) \cdot \left\langle u_{c,k+A(t)} \middle| \frac{\partial u_{v,k+A(t)}}{\partial k} \right\rangle = 0. \end{aligned} \quad (\text{A.6})$$

Combining Eq. (A.5) and Eq. (A.6), one can obtain the following matrix form,

$$i\frac{d}{dt}c_k(t) = \begin{pmatrix} \dot{\phi}_{v,k}^g(t) & 0 \\ 0 & \dot{\phi}_{c,k}^g(t) \end{pmatrix} c_k(t) + iE(t) \cdot \begin{pmatrix} \left\langle u_{v,k+A(t)} \left| \frac{\partial u_{v,k+A(t)}}{\partial k} \right. \right\rangle & e^{-i \int_0^t dt' \Delta \epsilon_{cv,k+A(t')} + i \Delta \phi_{cv,k}^g(t)} \left\langle u_{v,k+A(t)} \left| \frac{\partial u_{c,k+A(t)}}{\partial k} \right. \right\rangle \\ e^{-i \int_0^t dt' \Delta \epsilon_{vc,k+A(t')} + i \Delta \phi_{vc,k}^g(t)} \left\langle u_{c,k+A(t)} \left| \frac{\partial u_{v,k+A(t)}}{\partial k} \right. \right\rangle & \left\langle u_{v,k+A(t)} \left| \frac{\partial u_{v,k+A(t)}}{\partial k} \right. \right\rangle \end{pmatrix} c_k(t) \quad (\text{A.7})$$

where  $\Delta \epsilon_{bb',k+A(t)}$  is defined by the difference of the single particle energies as  $\epsilon_{b,k+A(t)} - \epsilon_{b',k+A(t)}$ , and  $\Delta \phi_{bb',k}^g(t)$  is defined by the difference of the geometric phases as  $\phi_{b,k}^g(t) - \phi_{b',k}^g(t)$ . Here, the coefficient vector was introduced as

$$c_k(t) = \begin{pmatrix} c_{v,k}(t) \\ c_{c,k}(t) \end{pmatrix}. \quad (\text{A.8})$$

Here, we define the geometric phases as

$$\begin{aligned} \phi_{b,k}^g(t) &= -i \int_0^t dt' E(t') \cdot \left\langle u_{b,k+A(t')} \left| \frac{\partial u_{b,k+A(t')}}{\partial k} \right. \right\rangle = i \int_0^t dt' \frac{dA(t')}{dt'} \cdot \left\langle u_{b,k+A(t')} \left| \frac{\partial u_{b,k+A(t')}}{\partial k} \right. \right\rangle \\ &= i \oint_{A(0)}^{A(t)} dA \cdot \left\langle u_{b,k+A} \left| \frac{\partial u_{b,k+A}}{\partial k} \right. \right\rangle. \end{aligned} \quad (\text{A.9})$$

As seen from the last expression in Eq. (A.9), the phase  $\phi_{b,k}^g$  depends only on the geometry of the path of the integral.

With the expression of the geometric phases in Eq. (A.9), one can rewrite the equation of motion for the coefficient vector as

$$\begin{aligned} i\frac{d}{dt}c_k(t) &= \\ iE(t) \cdot &\begin{pmatrix} 0 & e^{-i \int_0^t dt' \Delta \epsilon_{cv,k+A(t')} + i \Delta \phi_{cv,k}^g(t)} \left\langle u_{v,k+A(t)} \left| \frac{\partial u_{c,k+A(t)}}{\partial k} \right. \right\rangle \\ e^{-i \int_0^t dt' \Delta \epsilon_{vc,k+A(t')} + i \Delta \phi_{vc,k}^g(t)} \left\langle u_{c,k+A(t)} \left| \frac{\partial u_{v,k+A(t)}}{\partial k} \right. \right\rangle & 0 \end{pmatrix} c_k(t) \\ &= \mathcal{H}(t)c_k(t). \end{aligned} \quad (\text{A.10})$$

This is nothing but the time-dependent Schrödinger equation on the adiabatic basis, and it is closely related to the Houston basis expansion [58, 59].

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