FULL-BAND STRUCTURE CALCULATIONS OF OPTICAL INJECTION IN SEMICONDUCTORS: INVESTIGATIONS OF ONE-COLOR, TWO-COLOR, AND PUMP-PROBE SCENARIOS

by

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Abstract

Full-band structure calculations of optical injection in semiconductors: Investigations of one-color, two-color, and pump-probe scenarios

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Carrier, spin, charge current, and spin current injection by one- and two-color optical schemes are investigated within 30-band $k \cdot p$ theory. Parameters of the band model are optimized to give full-Brillouin zone band structures for GaAs and Ge that give accurate $\Gamma$-point effective masses and gyromagnetic factors and give access to the L valley, and to the $E_1$ and $E_1 + \Delta_1$ critical points in the linear optical absorption. Calculations of one- and two-photon carrier and spin injection and two-color current injection are performed for excitation energies in the range of 0–4 eV in GaAs and 0–3.5 eV in Ge. Significant spin and spin current injection occurs with 30% spin polarization in GaAs and Ge at photon energy matching the $E_1$ critical point. Further, the anisotropy and disparity of the current injection between parallel and perpendicular linearly-polarized beam configurations are calculated. For light propagating along a ⟨111⟩ crystal axis, anisotropic contributions in coherent current control and two-photon spin injection give rise to normal current components and in-plane spin components. In Ge, contributions from the holes to spin, electrical current, and spin current injection are investigated. Optical orientation results in 83% spin-polarized holes at the band edge. The effects of carrier dynamics in Ge are treated within a rate-equation model. The detection of spin dynamics in a pump-probe setup is considered, and the Fermi-factor approach is justified for electrons but not for holes. Carrier and current injection are further investigated in single-layer and bilayer graphene within the tight-binding model. In single-layer graphene, the linear-circular
dichroism in two-photon absorption yields an absorption coefficient that is twice as large for circularly polarized light compared to linearly polarized light. Coherent current injection is largest for co-circularly polarized beams and zero for cross-circularly polarized beams. For linearly polarized beams, the magnitude of the injected current is independent of beam polarizations. In contrast, the injected current in bilayer graphene shows disparity between parallel and perpendicular configurations of the beams. The resulting angular dependence of the current is a macroscopic, measurable consequence of interlayer coupling in the bilayer.
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Chapter 1

Introduction

The optical injection of carriers in semiconductors and the control of their velocity and spin is interesting from the point of view of both fundamental physics and potential technological applications. Optical methods allow the injection of carrier populations and currents without contacts, an initial step to further study electronic properties in a nonequilibrium regime. Potential technological applications of optical spin and current injection and control reside at the interface between optical and electrical processing. Electronics uses the current densities in semiconducting materials to carry information, while spintronics seeks to use the spin degree of freedom of carriers to the same effect [1]. Techniques allowing the manipulation of carrier motion and spin in nonmagnetic semiconductors are prerequisites to any advances in these fields. The optical control of carrier motion in bulk semiconductors is achieved by irradiation with a coherent optical field: “coherent control” [2]. The optical preparation of a spin-polarized population of carriers is accomplished by irradiation with a field carrying angular momentum: “optical orientation” [3].

Coherent control is the manipulation of the final state of a system upon excitation using coherent optical fields. The basic principle is illustrated in Figure 1.1. The transition from the initial state $|\psi_i\rangle$ to the final state $|\psi_f\rangle$ through two independent pathways, A and B, is considered. Quantum-mechanically, the transition probability is obtained by adding the transition amplitudes for pathways A and B and taking the absolute value squared. The cross-terms of A and B amplitudes yield an interference term that contributes constructively or destructively to the total transition probability. Changes in parameters of the pathways A and B allow one to control the transition probability and thus the final state of the excitation process [4].
Optical spin injection, or optical orientation, is the spin alignment of a carrier distribution due to an external electromagnetic field. Absorption of light carrying angular momentum induces a nonzero net spin polarization of the injected carriers in semiconductors with spin-orbit coupling [3]. The injection of a spin polarization relies on a lifting of the valence-band degeneracy at the band edge, a splitting induced by the spin-orbit interaction. Spin injection occurs for a range of excitation energy above the semiconducting band gap but below the energy necessary to connect the conduction band and the spin-orbit split-off band. At these energies, transitions into the conduction band originate from only a subset of the $p$-like valence bands. Transition probabilities for excitation by circularly-polarized light are dictated by selection rules. Investigation of the selection rules reveal that the optical injection of one spin orientation occurs in excess of the other, yielding a net spin population.

Coherent control and optical orientation are of fundamental interest as macroscopic manifestations of the quantum nature of electrons. They are also at the forefront of optical techniques with important potential applications in semiconductor technology. Optical processes offer the possibility to inject populations, polarizations, and currents with high carrier velocities, all without contacts or direct-current fields. Optically injected currents have research applications ranging from the study of Hall and spin Hall effects [5], charge density gratings [6], and out-of-equilibrium dynamics [7, 8], to the measurement and engineering of a carrier-envelope phase [9] and the emission of THz radiation with controllable polarization [10].

The use of $m$- and $n$-photon absorption to achieve coherent control originates from progress in the study of molecular processes [11]. As early as 1967, Manykin and Afanas’ev theoretically studied the suppression of transition rates by quantum interference of multiple-photon transitions [12, references therein]. In 1986, Brumer and Shapiro proposed a scheme involving the preparation of an initial superposition state and the subsequent excitation by phase-coherent optical fields to yield a controlled final state [13, 14]. In 1989, Kurizki et al. suggested to use the same idea for the excitation of donor states in semiconductors and offered the first proposal for photocurrent generation without a
bias voltage [15]. The quantum interference process applied to semiconductors affects the distribution of optically injected carriers in reciprocal space, resulting in a nonzero average velocity and thus the injection of an electrical current. In 1988, Shapiro et al. proposed a simplified coherent control scheme that does not rely on the preparation of a superposition state [16]. Phase-coherent laser beams of frequencies $\omega$ and $3\omega$ were suggested to excite and coherently control the final state of atoms or molecules. This interference of one- and three-photon processes was demonstrated by Chen et al. in 1990 [17]. The same year, Baranova et al. independently developed the coherent control technique using harmonically-related beams and applied it to photoionization of continuum states in a photomultiplier [18]. Using a two-color, $\omega$ and $2\omega$ field for the excitation, they reported the experimental observation of asymmetric photoionized carrier distributions. In 1995, Dupont et al. reported asymmetric distributions of carriers photoejected from a semiconductor quantum well using a similar technique [19].

In 1996, Atanasov et al. calculated the photocurrent injection rate in GaAs upon excitation across the band gap by the two-color, $\omega$ and $2\omega$ scheme and predicted it sufficiently large to be measurable [20]. The two equivalent pathways consist of two-photon absorption of the fundamental, $\omega$, and one-photon absorption of the second harmonic, $2\omega$. The cross-term of the transition amplitudes contributes to an asymmetrical distribution of injected carriers through reciprocal space, yielding a nonzero average velocity. The reciprocal-space distribution and the resulting electrical current are controlled by attributes of the two coherent components of the light field: their polarization and a relative phase parameter [20]. The first convincing experimental evidence of coherent current control was observed in GaAs in 1997 by Haché et al. using electrodes to collect the accumulated charge displacement [21, 22], and in 1999 by Côté et al. through emitted THz radiation [23]. The two-color, $\omega$ and $2\omega$ scheme has since become an often-studied method for optical current injection [2, 8, 9, 24–30].

Optical orientation has been observed from one-photon absorption across the band gap [31–34] and two-photon absorption with a sum photon energy greater than the band gap [35]. Selection rules differ in each case, but both one- and two-photon processes yield comparable degrees of spin polarization. While optical spin injection due to linear absorption has garnered the most attention in the literature [32–34, 36–38], significant spin injection also occurs beyond linear absorption [35].

Optical orientation of a spin polarization has also been studied in the two-color, $\omega$ and $2\omega$ scheme [39]. In 2000, Bhat and Sipe studied angular momentum transfer between
the coherent optical fields and the injected carriers, noticing spin-polarized carriers and currents. They predicted that specific polarizations of the $\omega$ and $2\omega$ fields yield spin current generation without accompanying electrical currents: pure spin currents [39]. Pure spin currents follow from the complete correlation of charge motion with spin polarization. In 2002, Stevens et al. reported the observation of currents injected in GaAs with circularly-polarized beams [27]. Although their detection technique using electrodes was not sensitive to spin, the currents behaved in accordance with the predicted spin-polarized currents [39]. In 2003, pure spin currents were reported in GaAs by Stevens et al. using a pump-probe technique and in ZnSe by Hübner et al. using the detection of circularly-polarized photoluminescence [40, 41].

Coherent current control has first been experimentally observed in GaAs [21–23]. By taking advantage of spin-orbit splitting in the valence bands, optical orientation [31, 32, 34] and spin-polarized and pure spin currents injection [27, 40, 42] have also been observed in GaAs. Calculations of these one- and two-color optical effects, optical orientation and coherent control, have been performed within the Kane model [43], the 14-band $k \cdot p$ model [35, 44–47], and the local-density approximation of density-functional theory [20, 36]. Thus far, only the approach based on density-functional theory gave access to the full band structure. The remaining models have truncated bases that limit the accurate description of the band structure to a region near the center of the Brillouin zone. This limited extent reduces their application to excitation near the band edge. For example, the 14-band model gives accurate band dispersion in a range of roughly 0.5 eV above and below the semiconducting band gap.

Recently, optical injection of charge currents [30, 48], spin currents [49], and spin polarizations [50] have also been observed in germanium. Ge is between gallium and arsenide in the periodic table, and so the properties of Ge and GaAs naturally exhibit many similarities. Indeed, in simple models of the band structure of GaAs near the center of the Brillouin zone the difference between the Ga and As atoms is neglected, in which case the lattice structure of GaAs (zinc-blende) is identical to that of Ge (diamond), and there is no qualitative difference between the band structures of the two semiconductors. Of course, more accurate models and calculations show crucial differences. GaAs has no center-of-inversion symmetry and thus can exhibit even-order nonlinear optical effects, while Ge cannot. GaAs is a direct band-gap semiconductor, while Ge has an indirect gap. The conduction-band minimum in Ge occurs at the L point rather than at the center of the Brillouin zone. For electrons injected near the $\Gamma$ point in Ge, the scattering to the
sidevalley at the L point is an effective relaxation process that does not exist in GaAs. For this reason, it is expected that hole dynamics play an important role in Ge, while in GaAs the spin-relaxation times for holes are typically much shorter than those for electrons and hole dynamics is often neglected [51, 52].

Germanium has potential applications in spintronics due to its long electron spin lifetime. Electron spin decoherence is dominated by hyperfine interaction with nuclear spins. This is reduced in Ge by the fact that the three most abundant isotopes, $^{74}\text{Ge}$, $^{72}\text{Ge}$, and $^{70}\text{Ge}$, have spinless nuclei [53]. Moreover, the hole contribution to optical response is of interest in Ge. In a pump-probe setup, the loss of injected electrons from the $\Gamma$ region leaves the probe sensitive to hole population and dynamics. The direct-gap energy of Ge, $E_{\text{dg}} = 0.805 \text{ eV}$ at 293 K [54], lies within the optical regime, providing a viable experimental scenario to study such dynamics optically.

The all-optical injection of currents using coherent control has also been studied in materials of reduced dimensionality. In quantum wells, the technique was first used to control the direction of photoexcited electrons [19]. Theoretically, the optical injection [55] and subsequent dynamics [56] of in-plane spin and electrical currents have been studied; to date, only the charge currents have been observed experimentally [28, 57, 58]. Spin currents ejected out of quantum well samples [59] and charge currents optically injected in quantum wires [60] are also predicted. The interest in studying coherent control in these structures lies in the achievement of greater spin polarization, better directional control, and device applications.

The successful isolation of a single graphene sheet in 2004 [61, 62] has sparked an intense research area around its unusual electronic and optical properties. Carriers in single-layer graphene obey Dirac’s equation and have a linear electronic energy-momentum dispersion with intersecting electron and hole bands [63–65]. At optical frequencies, the absorption per layer through a graphene stack is quantized in terms of universal constants [66]. Bilayer graphene has different but equivalently interesting electronic properties. The carriers in clean, unbiased bilayer graphene obey a massive Dirac equation; their band dispersion is gapless, quadratic at low energy and linear at high energy [67–69].

Both single and bilayer graphene are characterized by carrier mobilities that are unconventionally high [61, 70]. Their high optical conductivity and high carrier mobilities suggest potential applications as optically-controlled transport devices. Mele et al. have predicted that optical current injection by irradiation with a linearly-polarized, two-color, $\omega$ and $2\omega$ light field is significantly stronger in graphene than in conventional
Chapter 1. Introduction

semiconductors [71]. Coherent current control has been demonstrated experimentally in multilayer epitaxial graphene [72], carbon nanotubes, and graphite [73].

In this thesis, I present calculations of one- and two-color optical injection processes: carrier, spin, current, and spin current injection in GaAs and Ge within a full-Brillouin zone $k \cdot p$ model, carrier dynamics in Ge within a rate-equation model, and carrier and current injection in graphene and bilayer graphene within a tight-binding model. Chapters are organized as follows.

The description and optimization of band parameters of the full-Brillouin zone, 30-band $k \cdot p$ model are presented in Chapter 2. Material parameters that satisfy full-Brillouin zone coverage and accurate $\Gamma$-point effective masses and $g$ factors are presented for GaAs and Ge. The $k \cdot p$ parameters are obtained in a consistent way by least-square fitting quantities evaluated from the band-structure model to experimental data. Band energies are fitted at high-symmetry points and energy differences are minimized at symmetrically-equivalent and degeneracy points at the Brillouin-zone edges. Effective mass and gyromagnetic tensors are calculated numerically following the exact diagonalization of the Hamiltonian, including spin-orbit coupling.

Microscopic theory and 30-band $k \cdot p$ calculations of the optical charge, spin, current, and spin current injection for GaAs are presented in Chapter 3. One- and two-color injection processes are considered. The full-band structure calculations allow the prediction of optical responses at photon energies well above the 0.5 eV window; excitation energies in the range 0–4 eV are considered. A number of band structure features evidenced by experimental data become available, such as anisotropy or the high joint density of states responsible for the $E_1$ critical point in optical absorption.

The electron and hole contributions to one- and two-color injection processes in Ge are presented in Chapter 4. Carrier, spin, current, and spin current response tensors for injection across the direct gap are calculated within the 30-band $k \cdot p$ model. Results for Ge and GaAs are compared, addressing the similarity of optical injection responses between these two cubic crystals. I present the contributions of the hole spin and spin current injection. Anisotropy, dichroism, and injection at the $E_1$ resonance are considered.

The effects of electron and hole populations and dynamics in Ge on the absorption of a probe beam are presented in Chapter 5. An expression is given for the dielectric function in terms of the density matrix describing the population. Within the relaxation-time approximation, electron and hole density matrices are governed by a rate-equation model,
including electron scattering to the sidevalley at the L point. I calculate the contributions of phase-space filling and interconduction-band absorption to the differential absorption of a probe pulse. Further, I discuss how to extend this treatment to the hole bands in order to identify the contributions from both electron and hole spin dynamics.

Carrier and current injection in graphene and bilayer graphene are presented in Chapter 6. I present calculations of the two-photon absorption coefficient and extend the work of Mele et al. to consider circularly-polarized two-color injection and interlayer coupling effects. In two-photon absorption, graphene presents a strong and frequency-independent linear-circular dichroism. In the two-color, $\omega$ and $2\omega$ scheme, the current response is maximal for co-circularly polarized beams and vanish for opposite-circularly polarized beams. Further, the magnitude of the injected current is independent of the angle between polarization axes for linearly polarized beams. Calculations employ the tight-binding model, and results for single-layer and bilayer graphene are contrasted. Interlayer coupling in bilayer graphene has a distinct qualitative effect on the polarization dependence of two-photon absorption and coherent current control.

All calculations of this thesis employ the independent-particle approximation, associating the perturbing electric field used in the response calculations with the Maxwell field in the medium. The electron-hole interaction and other many-body effects are neglected throughout. The electron-hole interaction induces exciton formation and makes important contributions near the onset of absorption. However, the exciton binding energy is typically on the order of 10 meV, much smaller than the range of energies considered in this work. Only direct-gap optical injection is calculated; optical absorption across the indirect gap of Ge is accessible only with the contribution of crystal momentum from phonon scattering, and is neglected. This effect is much weaker than direct absorption, although for clean, cold samples it dominates the linear optical response for photon energy in the range $E_{ig} < h\omega < E_{dg}$, where the indirect and direct energy gaps are $E_{ig} = 0.744$ eV and $E_{dg} = 0.898$ eV at 1.5 K [54, 74]. Coherences between the excited state and the semiconductor vacuum are expected to vanish on a time scale $\Delta t \approx \hbar/E_{dg}$ on the order of a femtosecond, and are neglected.

Expressions in the text are given in the Gaussian system of quantities and cgs units; plots in figures use mks units and the Système International. Chapter 4 and Chapter 6 have been published (© American Physical Society) in Rioux and Sipe, Phys. Rev. B 81, 155215 (2010) and Rioux, Burkard, and Sipe, Phys. Rev. B 83, 195406 (2011).
Chapter 2

Optimization of band parameters in thirty-band \( k \cdot p \) theory

The \( k \cdot p \) method is a semi-empirical approach to energy-band structure calculations. It provides a description of the electronic states expressed in a basis of known eigenstates at a high symmetry point [77]. The dimension of this basis influences the agreement of the model with experimental data or \textit{ab initio} band structures; in principle, an exact expansion is achieved with an infinite basis. Eight-band \( k \cdot p \) models describe appropriately the top of the valence bands and the bottom of the conduction band for direct band gap semiconductors, but their validity is limited to a range of \( k \) points near the center of the Brillouin zone [77]. By increasing the expansion basis to 14 bands [44, 78–81], the resulting \( k \cdot p \) band structure matches experimental observations for energies typically up to 0.5 eV above and below the semiconducting band gap.

With a 30-band basis, the joint density of states responsible for the \( E_1 \) optical absorption edge and the conduction-band valleys at the L and X points are reproduced [82–84]. The 30-band model is successful at describing the dispersion of the top valence bands and lower conduction bands in a range of 10 eV over the entire Brillouin zone, both for direct and indirect band gaps [82]. It also gives reasonably accurate \( \Gamma \)-point effective masses [82] and electron \( g \) factor [85], although in the latter case it does so at the expense of full-Brillouin zone coverage. Current 30-band models do not rely on remote-band effects, where contributions from states that are outside the expansion basis are folded into the Hamiltonian by Löwdin perturbation theory [86]. Remote-band effects are necessary for the accurate description of the valence bands and lowest conduction band in 8-band and 14-band models [77, 78].
The band structure obtained from a $\textbf{k} \cdot \textbf{p}$ model is a function of the appropriate energies and matrix elements at the expansion point—the band or material parameters. Only some of these are known experimentally; most are to be determined indirectly. Different strategies for extracting these parameters from experimental data have led to different sets of parameter values, as pointed out by Serre et al. [87]. This suggests that published parameter sets are tied to the context in which they were initially determined, and cannot be applied elsewhere. Serre et al. offered a strategy to address this, but their approach treats the spin-orbit coupling perturbatively, neglects zone-edge values in the fitting procedure, and does not yield a complete and usable parameter set [87].

In this chapter, I present a strategy for the systematic optimization of band parameters of the 30-band $\textbf{k} \cdot \textbf{p}$ model aimed at an accurate $\Gamma$-point and full-Brillouin zone description. Electron and hole effective masses, gyromagnetic factors, and band energies at zone center and zone edges are calculated and fitted to experimental data in a least $\chi^2$ procedure. Calculations are based on the eigenstates of the $\textbf{k} \cdot \textbf{p}$ Hamiltonian, including spin-orbit interaction, and are performed consistently to obtain an optimized parameter set. The chapter is divided as follows. The material parameters for the 30-band model of diamond and zinc-blende crystal structures are defined in Section 2.1. Discrepancies with existing parameter sets are presented in Section 2.2. The optimization procedure is described in Section 2.3. The resulting $\textbf{k} \cdot \textbf{p}$ model, summarized in Section 2.4, gives accurate electronic properties both at the zone center and zone edges.

### 2.1 Thirty-band $\textbf{k} \cdot \textbf{p}$ theory

The $\textbf{k} \cdot \textbf{p}$ method seeks solutions to the single-electron Schrödinger equation for an eigenstate $\psi$ of energy $E$ under the action of the Hamiltonian $\mathcal{H}$:

$$\mathcal{H}\psi = [\mathcal{H}_0 + \mathcal{H}_{\text{S-O}}] \psi = E\psi.$$  \hspace{1cm} (2.1)

The Hamiltonian $\mathcal{H}_0$ includes a periodic potential $V(\textbf{r})$ attributable to the crystalline structure,

$$\mathcal{H}_0 = \frac{\textbf{p}^2}{2m} + V(\textbf{r}),$$  \hspace{1cm} (2.2)

and $\mathcal{H}_{\text{S-O}}$ is the spin-orbit interaction,

$$\mathcal{H}_{\text{S-O}} = \frac{\hbar}{4m^2c^2} \sigma \cdot (\nabla V \times \textbf{p}),$$  \hspace{1cm} (2.3)
where the momentum operator is given by $p = -i\hbar \nabla$, $\hbar$ is Planck’s constant divided by $2\pi$, $m$ is the electron mass, $c$ is the speed of light in vacuum, and $\sigma = 2S/\hbar$ is the dimensionless spin operator. Other relativistic corrections, including those proportional to $|\sigma \times \nabla V|^2$, are neglected [77].

The solutions to Equation (2.1) are Bloch functions, $\psi_{nk}(r) = e^{ik \cdot r} u_{nk}(r)$, products of plane waves and lattice periodic spinor functions $u_{nk}(r)$, with energy eigenvalues $E_n(k)$ [88]. The band index is denoted by $n$ and $k$ is the wavevector. The $u_{nk}(r)$ are eigenfunctions of the $k \cdot p$ Hamiltonian

$$H_k = H_0 + H_{S-O} + \frac{\hbar^2 k^2}{2m} + \frac{\hbar}{m} k \cdot p,$$

(2.4)

neglecting the anomalous velocity [77]. The transformation properties of the eigenstates at $k = 0$ ($\Gamma$ point) are determined by the symmetry of the lattice. These $\Gamma$-point eigenstates serve as an infinite basis for expansion of the eigenstates of $H_k$. However, applications of the model need to limit this expansion to a finite set. The basis states of interest in a finite set are those closest in energy to the band gap at the $\Gamma$ point.

### 2.1.1 Basis states

The zinc-blende and diamond structures belong to the full-tetrahedral ($T_d$) and full-octahedral ($O_h$) symmetry groups, respectively. A set of thirty $\Gamma$-point states is used to expand the eigenstates of the $k \cdot p$ Hamiltonian (2.4) describing these materials. Starting from the 15-band model of Cardona and Pollak [89], the basis is expanded, in the manner of Pollak et al. [90], by direct product with the spin-$1/2$ subspace. The eigenstates of $\sigma^z$, $\{ |\uparrow\rangle , |\downarrow\rangle \}$, are used as a basis; they satisfy

$$\langle \uparrow | \sigma | \uparrow \rangle = - \langle \downarrow | \sigma | \downarrow \rangle = \hat{z},$$

$$\langle \uparrow | \sigma | \downarrow \rangle = (\langle \downarrow | \sigma | \uparrow \rangle)^* = \hat{x} - i\hat{y}.$$

The symmetry of the orbital states used by Cardona and Pollak are determined from an empty lattice calculation. The lowest-energy eigenstates of the empty diamond or zinc-blende lattice are plane waves whose $\Gamma$-point energies are 0, 3, or 4, in units of $\hbar^2 (2\pi/a)^2 / 2m$. They correspond to $k$ vectors of $[0,0,0]$, $[1,1,1] 2\pi/a$, or $[2,0,0] 2\pi/a$, respectively. Part of the justification for cutting off the basis at thirty states is that the next lowest-energy plane waves, at $8 \hbar^2 (2\pi/a)^2 / 2m$, are separated by a sizeable gap.

The thirty basis states are shown schematically in Figure 2.1 on page 11, along with their $\Gamma$-point energies. The $T_d$ double group notation is used throughout, even
Chapter 2. Optimization of band parameters in thirty-band $k \cdot p$ theory

Figure 2.1: Diagram of the bands included in the 30-band model. The Γ-point energies (center), irreducible representations under the $T_d$ double and simple group (right), and basis functions within each level (far right) are shown. In the simple group notation, Koster [91] and Yu and Cardona [92] interchange $\Gamma_4$ and $\Gamma_5$. The choice $\Gamma_4$ is in the notation of Yu and Cardona.
for Ge which has $O_h$ symmetry. In addition to the levels of a 14-band model, $\Gamma_{4v}$, $\Gamma_{1c}$, and $\Gamma_{4c}$, the levels considered here include an $s$-like valence band, $\Gamma_{6v}$, and four supplemental conduction levels: $\Gamma_{6a}$, $\Gamma_{3d}$, $\Gamma_{7d/8d}$, and $\Gamma_{6q}$. The $\Gamma_{3d}$ level is doubly degenerate without counting spin degeneracy. The basis states for this level are $d$-like atomic functions that have the symmetry of $D_2 = 3z^2 - r^2$ and $D_x = \sqrt{3}(x^2 - y^2)$ [91]. The complete basis for the 30-band model, including spin, is given by $\langle \psi \rangle$ and complex conjugates of these relations. The allowed forms of atomic functions that have the symmetry of $\Gamma_4$, and $\Gamma_3$ or $\Gamma_4$ or $\Gamma_5$ or $\Gamma_4$. In a notation similar to Richard et al. [82], independent momentum matrix elements are:¹

\[
\begin{align*}
\langle S_c | p^x | X_c \rangle & \equiv imP_0/h, \\
\langle S_d | p^x | X_d \rangle & \equiv imP_3/h,
\end{align*}
\]

\[
\begin{align*}
\langle S_a | p^x | X_a \rangle & \equiv imP_2/h, \\
\langle S_b | p^x | X_b \rangle & \equiv imP_3/h,
\end{align*}
\]

\[
\begin{align*}
\langle D_z | p^x | X_z \rangle & \equiv imP_3/h, \\
\langle D_y | p^x | X_y \rangle & \equiv imP_3/h,
\end{align*}
\]

\[
\begin{align*}
\langle S_u | p^x | X_u \rangle & \equiv imP_4/h, \\
\langle S_v | p^x | X_v \rangle & \equiv imP_4/h.
\end{align*}
\]

¹By symmetry of the diamond and zinc-blende structures, the nonzero momentum matrix elements are given by: $\langle S | p^x | X \rangle = \langle S | p^y | Y \rangle = \langle S | p^z | Z \rangle$, $\langle X | p^y | X \rangle = \langle Y | p^z | Y \rangle = \langle Z | p^z | Z \rangle = \langle Y | p^z | x \rangle$, $\langle D_z | p^x | X \rangle = \langle D_z | p^y | Y \rangle = \langle D_z | p^z | Z \rangle = \langle D_z | p^z | x \rangle = \langle D_z | p^z | y \rangle = \langle D_z | p^z | y \rangle$, and complex conjugates of these relations.

2.1.2 Matrix elements

The representation of the $k \cdot p$ Hamiltonian (2.4) within the thirty basis states forms the $30 \times 30 k \cdot p$ matrix. Nonzero matrix elements are identified by applying the symmetry properties of the Hamiltonian and basis states. Under the symmetry operations of $T_d$, the momentum operator $p$ transforms like the representation $\Gamma_4$ [92]. Matrix elements of the form $\langle \Gamma_n | \Gamma_4 | \Gamma_n \rangle$ survive if and only if the irreducible representation $\Gamma_m$ appears in the direct sum associated with the direct product $\Gamma_4 \otimes \Gamma_n$. Thus the nonzero momentum matrix elements are dictated by symmetry considerations and must have one of the allowed forms $\langle \Gamma_4 | \Gamma_4 | \Gamma_1 \rangle$, $\langle \Gamma_4 | \Gamma_4 | \Gamma_3 \rangle$, or $\langle \Gamma_4 | \Gamma_4 | \Gamma_4 \rangle$. In a notation similar to Richard et al. [82], independent momentum matrix elements are:¹

\[
\begin{align*}
\langle S_c | p^x | X_c \rangle & \equiv imP_0/h, \\
\langle S_d | p^x | X_d \rangle & \equiv imP_3/h,
\end{align*}
\]

\[
\begin{align*}
\langle S_a | p^x | X_a \rangle & \equiv imP_2/h, \\
\langle S_b | p^x | X_b \rangle & \equiv imP_3/h,
\end{align*}
\]

\[
\begin{align*}
\langle D_z | p^x | X_z \rangle & \equiv imP_3/h, \\
\langle D_y | p^x | X_y \rangle & \equiv imP_3/h,
\end{align*}
\]

\[
\begin{align*}
\langle S_u | p^x | X_u \rangle & \equiv imP_4/h, \\
\langle S_v | p^x | X_v \rangle & \equiv imP_4/h,
\end{align*}
\]

¹By symmetry of the diamond and zinc-blende structures, the nonzero momentum matrix elements are given by: $\langle S | p^x | X \rangle = \langle S | p^y | Y \rangle = \langle S | p^z | Z \rangle$, $\langle X | p^y | x \rangle = \langle Y | p^z | y \rangle = \langle Z | p^z | z \rangle = \langle Z | p^y | z \rangle$, $\langle D_z | p^x | X \rangle = \langle D_z | p^y | Y \rangle = \langle D_z | p^z | Z \rangle = \langle D_z | p^z | x \rangle = \langle D_z | p^z | y \rangle = \langle D_z | p^z | y \rangle$, and complex conjugates of these relations.
Table 2.1: Nonzero momentum matrix elements of the 30-band $\mathbf{k} \cdot \mathbf{p}$ model under $O_h$ symmetry.

\[
\begin{align*}
\langle S_{\delta} | p^x | X_{\delta} \rangle & \equiv imP'_{u_d}/\hbar, & \langle S_{\theta} | p^x | X_{\theta} \rangle & \equiv imP'_{2}/\hbar, \\
\langle S_{\iota} | p^x | X_{\iota} \rangle & \equiv imP'_{sd}/\hbar, & \langle S_{\eta} | p^x | X_{\eta} \rangle & \equiv imP'_{3}/\hbar, \\
\langle S_{\varsigma} | p^x | X_{\varsigma} \rangle & \equiv imP'_{ud}/\hbar, & \langle S_{\pi} | p^y | Z_{\pi} \rangle & \equiv imQ'_{vd}/\hbar.
\end{align*}
\]

A primed parameter denotes that the matrix element vanish identically under $O_h$ due to the additional center-of-inversion symmetry. Ten of the 18 momentum matrix elements survive this symmetry operation.

The orbital angular momentum appearing in the spin-orbit coupling $\mathcal{H}_{S-O}$ has the symmetry $\Gamma_5$ under $T_d$ [92]. Nonzero matrix elements have the form $\langle \Gamma_4 | \Gamma_5 | \Gamma_3 \rangle$ or $\langle \Gamma_4 | \Gamma_5 | \Gamma_4 \rangle$, with independent terms:\footnote{Nonzero spin-orbit terms connecting $\Gamma_3$ and $\Gamma_4$ levels are related by $\langle D_{\delta} | (\nabla V \times \hat{p})^y | x \rangle = \langle D_{\delta} | (\nabla V \times \hat{p})^y | y \rangle = -\frac{1}{2} \langle D_{\delta} | (\nabla V \times \hat{p})^x | z \rangle = -\frac{1}{2\sqrt{3}} \langle D_{\delta} | (\nabla V \times \hat{p})^x | x \rangle = \frac{1}{2\sqrt{3}} \langle D_{\delta} | (\nabla V \times \hat{p})^y | y \rangle$.}

\[
\begin{align*}
\langle X_{\iota} | (\nabla V \times \hat{p})^y | Z_{\iota} \rangle & \equiv i \frac{4m^2c^2}{3\hbar} \Delta_{so}, & \langle x_{\sigma} | (\nabla V \times \hat{p})^y | z_{\sigma} \rangle & \equiv i \frac{4m^2c^2}{3\hbar} \Delta_{c}, \\
\langle X_{\iota} | (\nabla V \times \hat{p})^z | Z_{\iota} \rangle & \equiv i \frac{4m^2c^2}{3\hbar} \Delta_d, & \langle X_{\iota} | (\nabla V \times \hat{p})^x | Z_{\iota} \rangle & \equiv i \frac{4m^2c^2}{3\hbar} \Delta_{vd},
\end{align*}
\]
Table 2.2: Additional nonzero momentum matrix elements under $T_d$ symmetry.

<table>
<thead>
<tr>
<th>$\langle S_q \rangle$</th>
<th>$\langle X_d \rangle$</th>
<th>$\langle Y_d \rangle$</th>
<th>$\langle Z_d \rangle$</th>
<th>$\langle D_z \rangle$</th>
<th>$\langle D_x \rangle$</th>
<th>$\langle S_u \rangle$</th>
<th>$\langle x_c \rangle$</th>
<th>$\langle y_c \rangle$</th>
<th>$\langle z_c \rangle$</th>
<th>$\langle S_c \rangle$</th>
<th>$\langle X_v \rangle$</th>
<th>$\langle Y_v \rangle$</th>
<th>$\langle Z_v \rangle$</th>
<th>$\langle S_v \rangle$</th>
</tr>
</thead>
</table>

\[
\langle D_z \rangle (\nabla \times \mathbf{p})^x | x_c \rangle \equiv i \frac{4m^2c^2}{3\hbar} \Delta_{3c}, \quad \langle X_v \rangle (\nabla \times \mathbf{p})^y | z_c \rangle \equiv i \frac{4m^2c^2}{3\hbar} \Delta'_{(vc)}, \quad (2.6e,f)
\]
\[
\langle x_c \rangle (\nabla \times \mathbf{p})^y | Z_d \rangle \equiv i \frac{4m^2c^2}{3\hbar} \Delta'_{cd}, \quad \langle D_z \rangle (\nabla \times \mathbf{p})^y | X_v \rangle \equiv i \frac{4m^2c^2}{3\hbar} \Delta'_{3v}, \quad (2.6g,h)
\]
\[
\langle D_z \rangle (\nabla \times \mathbf{p})^x | X_d \rangle \equiv i \frac{4m^2c^2}{3\hbar} \Delta'_{3d}. \quad (2.6i)
\]

Five of the 9 spin-orbit matrix elements survive center-of-inversion symmetry. The $P$'s, $Q$'s, and $\Delta$'s appearing in Equations (2.5) and (2.6) are real parameters defined by those equations. They build the second block of band parameters in the 30-band $\mathbf{k} \cdot \mathbf{p}$ model. The momentum matrix elements are presented schematically in Tables 2.1 and 2.2 for $O_h$ and $T_d$ symmetry groups, respectively.

### 2.2 Problems with existing $\mathbf{k} \cdot \mathbf{p}$ parameter sets

The $\mathbf{k} \cdot \mathbf{p}$ theory provides the basis for the expansion of a crystal Hamiltonian about a point $\mathbf{k}_0$ in reciprocal space, provided the energy eigenvalues and momentum matrix elements evaluated at $\mathbf{k}_0$ are known. For III–V and elemental semiconductors, a natural point of
expansion is the $\Gamma$ point, which coincides with the valence-band maximum and, often, with the conduction-band minimum. The band ordering at the $\Gamma$ point is well-established from optical data [93]. Nonzero matrix elements are identified by symmetry and their values are usually determined indirectly by empirical data or by \textit{ab initio} calculations. Since the 30-band model supercedes the 14-band model, a number of parameters appear in both models, but their values often differ. And even among 30-band models, several different parameter sets result in reasonable band structures [82, 84, 85].

The band parameters of the 30-band model are defined in Section 2.1. Important for the calculation of optical data for GaAs are the parameters $P_0$, $P'_0$, and $\Delta'$: $P_0$ is the oscillator strength in optical absorption; $P'_0$ is the largest contribution to the second-order susceptibility $\chi^{(2)}$; and $\Delta'$ leads to spin splitting. All three also contribute to the effective mass $m^*_c$ and the effective $g^*_c$ factor [82, 85]. Table 2.3 shows the values of $P_0$, $P'_0$, and $\Delta'$ in the 14-band model of Pfeffer and Zawadzki [81] and the 30-band models of Richard \textit{et al.} [82] and Fraj \textit{et al.} [85]. These three highlighted quantities show major discrepancies among the models: $P_0$ varies by 10%, $P'_0$ varies by a factor of 6, while $\Delta'$ varies almost by a factor of 3 between Pfeffer and Zawadzki and Fraj \textit{et al.}, and is neglected by Richard \textit{et al.}

The calculation of the effective Landé factor $g^*_c$ in the conduction band of GaAs is a particularly difficult challenge. Compared to the experimentally established value $g^*_c = -0.44$ [74], band parameters from Richard \textit{et al.} yield a calculated $g^*_c = 0.20$: the model not only gives the wrong magnitude, but the wrong sign. Thus, although the band energies of GaAs are well described by the 30-band model of Richard \textit{et al.} over the full Brillouin zone within 6 eV of the valence-band maximum [82], the conduction-band gyromagnetic factor is better described by the 14-band model of Pfeffer and Zawadzki, which gives $g^*_c = -0.44$ [47, 81]. The parameters of Fraj \textit{et al.} succeed in improving the calculated $g^*_c$ in GaAs, but does so at the expense of full-Brillouin zone coverage.

### Table 2.3: Discrepancy in the $k \cdot p$ parameters for GaAs: 14-band model of Pfeffer and Zawadzki (Ref. 81) and 30-band models of Richard \textit{et al.} (Ref. 82) and Fraj \textit{et al.} (Ref. 85).

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$P_0$ (eV Å)</td>
<td>10.30</td>
<td>9.232</td>
<td>10.124</td>
</tr>
<tr>
<td>$P'_0$ (eV Å)</td>
<td>3.00</td>
<td>0.500</td>
<td>0.851</td>
</tr>
<tr>
<td>$\Delta'$ (eV)</td>
<td>$-0.061$</td>
<td>0</td>
<td>$-0.17$</td>
</tr>
</tbody>
</table>
Discrepancies also appear among the published parameters for Ge [82, 84]. Values for $P_0$ are 9.681 eV Å from Richard et al. and 8.539 eV Å from Rideau et al., a variation by 12% [82, 84].

In their work, Serre et al. offer a treatment yielding values of $P_0 = 9.895$ eV Å, $P_0' = 0.436$ eV Å, and $\Delta' = -1.1$ eV for GaAs [87]. Their method assumes that (i) $P_0'$ is uniquely determined from the anticrossing in the conduction bands and that (ii) the spin-orbit coupling can be sufficiently treated as a perturbation. Since Serre et al. do not provide a complete $k \cdot p$ parameter set, I do not include their values in Table 2.3.

In the following, I present a strategy for the optimization of band parameters that avoids the highlighted shortcomings. Effective masses, gyromagnetic factors, and band energies at zone center and zone edge are calculated and fitted to their experimental values as closely as possible within a single, consistent parameter set.

### 2.3 Determination of band parameters

The band parameters of the 30-band $k \cdot p$ model consist of the $\Gamma$-point energies, defined by Figure 2.1 on page 11, momentum matrix elements, defined by Equation (2.5), and orbital angular momentum matrix elements, defined by Equation (2.6). The intent is to find sets $\{x\}$ of band parameters that describe the materials Ge and GaAs as closely to experimental data as possible. An objective function

$$f(x) = \sum_i w_i (\alpha_i(x) - \alpha_{i,\text{exp}})^2$$

(2.7)

is constructed, which consists of the sum of squared differences between computed values $\alpha_i$ and experimentally-determined values $\alpha_{i,\text{exp}}$, for a given set of objective quantities $\{\alpha\}$ and weights $\{w\}$. The parameter set $\{x\}$ is allowed to vary to minimize $f(x)$.

The minimization is done by means of a gradient path. A random starting point $x_0$ is chosen in parameter space. The local gradient is obtained by evaluating the objective function $f(x)$ at and in the vicinity of $x_0$. A step is taken in the direction opposite of the gradient towards the greatest downward error change. The gradient vector is constructed and another step follows. This is repeated, moving towards the local minimum, $x_{0,\text{min}}$. A new random starting point $x_1$ is chosen, and the process is repeated to find the nearby local minimum $x_{1,\text{min}}$. The minimization process is repeated several times using random starting points in order to find the minimum with the smallest error. The search generally
starts with zero hindsight. After several thousand runs, the optimal outcomes are used to
guide further searches into the most promising areas of parameter space.

The quantities \( \alpha_i \) included in the objective function are the band energies at high-
symmetry points, band energy differences at the Brillouin-zone edges, effective masses, and
gyromagnetic factors describing the valence bands and the conduction band valleys. They
are presented in detail in the following subsections. There are no absolute in determining
the weights \( w_i \). Rather, more weight is given to the quantities that are deemed important.

2.3.1 Effective masses

Effective masses at a general \( \mathbf{k}_0 \) are computed by diagonalizing the \( \mathbf{k} \cdot \mathbf{p} \) Hamiltonian and
expanding band energies up to the second-order in \( (\mathbf{k} - \mathbf{k}_0) \), following Boykin [94]. At \( \Gamma \),
effective masses are computed for the conduction band and for the heavy-hole, light-hole,
and split-off valence bands. For the conduction band, longitudinal and perpendicular
effective masses are computed at \( L \) and \( \Delta_{\text{min}} \), where \( \Delta_{\text{min}} \) is the (local) conduction-band
minimum on the \( \Gamma \)–\( X \) line, near the \( X \) point.

Split-off and conduction-band effective masses are computed straightforwardly since
no degeneracy occurs besides spin degeneracy. The effective-mass tensor \( M_n \) for band \( n \)
is obtained according to

\[
(M_n^{ab})^{-1} = \frac{1}{m} \delta^{ab} + \frac{1}{m^2} \sum_{s \neq n} \frac{p^{a}_{ns}(\mathbf{k}) p^{b}_{sn}(\mathbf{k}) + p^{b}_{ns}(\mathbf{k}) p^{a}_{sn}(\mathbf{k})}{E_n(\mathbf{k}) - E_s(\mathbf{k})}. \tag{2.8}
\]

The first term in Equation (2.8) corresponds to the bare-electron mass. If the model
had included any remote-band effects, they would appear here. The second term is
the renormalization of the bare-electron mass due to the coupling between bands. The
effective-mass tensor is also available by numerically evaluating the second derivative of
the band dispersion \( E_n(\mathbf{k}) \) with respect to \( \mathbf{k} \). Although the summation in Equation (2.8)
is truncated at 30 bands in the present work, both methods yield very similar results. At \( \Gamma \),
for nondegenerate bands, symmetry dictates that the inverse-mass tensor is proportional
to identity, yielding a scalar effective mass in those cases. Diagonalizing \( M_c \) at \( X \) (and \( L \))
yields two distinct eigenvalues: one value is associated with the \( X \) (\( L \)) direction, and a
twofold degenerate value is associated with directions perpendicular to \( X \) (\( L \)). These are
the longitudinal and perpendicular effective masses, respectively \( m^*_\parallel \) and \( m^*_\perp \).

For the heavy- and light-hole bands at \( \Gamma \), the same approach is taken using degenerate
perturbation theory. The inverse effective mass is treated as an operator, with matrix
elements between bands $m$ and $n$ given by

$$\left(M_{mn}^{ab}\right)^{-1} = \frac{1}{m} \delta^{ab} + \frac{1}{m^2} \sum_{s \in \{m, \ldots, n\}} \frac{p_{ms}^a(k) p_{sn}^b(k) + p_{ms}^b(k) p_{sn}^a(k)}{E_n(k) - E_s(k)},$$

(2.9)

where $\{m, \ldots, n\}$ represents the subset of degenerate bands. A unitary transformation within this subset yields the diagonal form $M_{mn} = \text{diag} (M_n)$. The projection $\hat{e} \cdot M_n \cdot \hat{e}$ is computed for the three directions $\hat{e} = [100], [110], \text{and} [111]$, corresponding to the components of the effective-mass tensor for which experimental data is typically available [74].

### 2.3.2 Effective gyromagnetic factors

Three values of the gyromagnetic ratio in semiconductors are generally known experimentally: $g_c^*$ at the conduction-band minimum, $g_{so}^*$ for the split-off band at $\Gamma$, and the $\kappa$ factor describing the magnetization of the heavy- and light-hole bands, also at $\Gamma$ [74]. For the conduction band, $g_c^*$ is computed at $\Gamma, L, \text{and} \Delta_{\text{min}}$. For the valence bands, $g_{so}^*$ is computed at $\Gamma$. The magnetization for a nondegenerate, spin-up band $n$ at wavevector $k$ is computed by the Roth formula [95]:

$$\mu_n^z(k) = -g_0 \frac{\mu_B}{2} - \frac{i}{m} \sum_{s \neq n} \frac{[p_{ns}(k) \times p_{sn}(k)]^z}{E_n(k) - E_s(k)}.$$

(2.10)

The effective $g$ factors are defined by the following expressions [96]:

$$\mu_c(k) = -g_c^* \mu_B S/\hbar,$$

(2.11)

and

$$\mu_{so}(k) = -g_{so}^* \mu_B J/\hbar.$$

(2.12)

Fraj et al. have used perturbation theory at third and fourth order to include spin-orbit contributions to $g_c^*$ [85]. In contrast, the present approach diagonalizes the Hamiltonian $H_k$ numerically and uses those eigenstates as the basis in Equation (2.10); this method treats the spin-orbit interaction exactly and eliminates the need for third- and fourth-order perturbation terms.

### 2.3.3 Band energies

Energy eigenvalues are computed at the high-symmetry points $\Gamma, X, L$, and the conduction-band minimum, and fitted to optical data whenever possible. In addition, the minimum direct band gap is required to occur at the $\Gamma$ point, as predicted by $ab\ initial$ calculations [36]. This is checked along the paths from $\Gamma$ to $K$, $\Gamma$ to $L$, and $\Gamma$ to $X$. 


2.3.4 Continuity at boundaries

Since the \( \mathbf{k} \cdot \mathbf{p} \) Hamiltonian is an expansion about the zone center, the symmetry properties of zone-edge \( \mathbf{k} \) points are not intrinsically taken into account. For example, symmetry dictates that the divergence of the band dispersion through a zone boundary is zero for nondegenerate bands. These constraints are not present in the \( \mathbf{k} \cdot \mathbf{p} \) Hamiltonian expanded about the zone center. Instead, this requirement is numerically enforced on the top valence bands and the lowest two conduction bands by adding their slopes, evaluated at the boundaries, to the objective function \( f(x) \). This is done for \( X \), \( L \), and the following points on the square and hexagonal surfaces of the Brillouin zone, in units of \( 2\pi/a \):

\[
\begin{align*}
\left[ 1, 0, 0 \right], & \quad \left[ 1, \frac{1}{4}, 0 \right], \quad \left[ 1, \frac{1}{8}, \frac{1}{8} \right], \\
\left[ 1, \frac{1}{2}, 1 \right], & \quad \left[ \frac{3}{4}, \frac{3}{8}, \frac{3}{8} \right], \quad \left[ \frac{5}{8}, \frac{1}{8}, \frac{1}{4} \right], \quad \left[ \frac{3}{4}, \frac{1}{2}, 1 \right].
\end{align*}
\]

The points \( \text{K} \) and \( \text{U} \) are symmetrically equivalent points. Since the \( \mathbf{k} \cdot \mathbf{p} \) method does not satisfy this symmetry by construction, it is enforced numerically for the top valence bands and the lowest conduction band. For materials of \( O_h \) symmetry, a cross-over of the two lowest conduction bands is required at \( X \), where symmetry dictates their degeneracy \([92]\).

In applications of the \( \mathbf{k} \cdot \mathbf{p} \) model where a full-Brillouin zone treatment is not necessary, these symmetry restrictions could be relaxed to improve the fitting of zone-center properties.

2.4 Results and summary

The calculated effective masses and \( g \) factors are presented in Tables 2.4 and 2.5 for GaAs and Tables 2.6 and 2.7 for Ge, starting on page 21.

In Ge, the experimental data at the \( \Gamma \)-point are well reproduced by the \( \mathbf{k} \cdot \mathbf{p} \) model using the parameters from the current work and from Richard et al. [82]. At the \( L \) point, the 30-band model gives good effective masses but fails to reproduce the anisotropy in the electron \( g \) factor: \( g_\parallel^* = 1.76 \) compared to 0.824 experimentally. All three parameter sets show this discrepancy, and it might be necessary to use a larger basis in order to fit this quantity.

In GaAs, the magnetization-related quantities differ significantly between parameter sets. For example, the conduction-band gyromagnetic factor varies between \( g_c^* = 0.20 \) for Richard et al. and \(-0.48 \) for Fraj et al. This quantity depends largely on the parameters
Chapter 2. Optimization of band parameters in thirty-band $k \cdot p$ theory

$P_0, P'_0, P_d$, and $\Delta'$ [85], and there is disagreement as to the values of these as used in $k \cdot p$ theory [cf. Table 2.3 on page 15]. The presented 30-band $k \cdot p$ model is consistent with the measured value $g^*_c = -0.44$ [74].

Table 2.8 presents the $k \cdot p$ band parameters for GaAs, determined from the fitting procedure described in Section 2.3. The parameters $P_0, P'_0, P_d$ are the most important in the calculation of conduction-band properties for GaAs. They appear in the lowest-order terms in the perturbative calculation of the conduction-band effective mass [82] and of the conduction-band gyromagnetic factor [85]. I find that while better than 1% accuracy is achievable on either $m^*_c$ or $g^*_c$ in comparison with experimental data, it is difficult to obtain both values accurately. With the parameters from the current work, $m^*_c$ has 8% deviation and $g^*_c$ has 25% deviation from experimental values. In comparison, the parameters of Richard et al. yield a good effective mass but a poor $g$ factor, with respectively 1.5% and 145% deviation.

The $k \cdot p$ band parameters for Ge are presented in Table 2.9. The fitting of the heavy- and light-hole masses is notably very good, with less than 1% and 2% deviation, respectively. This is as good or better a fit than the effective masses for the conduction and split-off bands. In GaAs, such small deviations were only achieved for the effective mass of the split-off band. The vanishing of material parameters under inversion symmetry for Ge removes many coupling between bands. As a result the objective function behaves more linearly and is easier to minimize than for GaAs. The hole effective masses are fitted by increasing the parameters $P_2$ and $Q_{vc}$ from the values from Richard et al., with the side effect that $g^*_so$ is not as well described. However, this does not affect the calculations of optical data as much as the effective masses do, through the density of states.

In summary, I have determined 30-band $k \cdot p$ parameters for Ge and GaAs. Calculated effective masses and $g$ factors are in good agreement with experimental data. The calculations treat the spin-orbit coupling exactly, eliminating the need for third- and fourth-order perturbation theory. Further, the model determines both valence-bands and conduction-band properties, as well as zone-center and zone-edge properties, within the same parameter set.
Table 2.4: Comparison of the effective masses for GaAs, in units of the free-electron mass, obtained with the parameter sets from this work, from Richard et al. (Ref. 82), and from Fraj et al. (Ref. 85) to experimental data.

<table>
<thead>
<tr>
<th></th>
<th>GaAs</th>
<th>Richard2004</th>
<th>Fraj2007</th>
<th>(exp)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$m_c^* (\Gamma)$</td>
<td>0.062</td>
<td>0.068</td>
<td>0.058</td>
<td>0.067$^{a,c,d}$</td>
</tr>
<tr>
<td>$m_{th}^* (\Gamma)$</td>
<td>0.360</td>
<td>0.365</td>
<td>0.383</td>
<td>0.45$^{a,b}$</td>
</tr>
<tr>
<td>$m_{so}^* (\Gamma)$</td>
<td>0.076</td>
<td>0.086</td>
<td>0.073</td>
<td>0.082$^{a,b,c}$</td>
</tr>
<tr>
<td>$m_{\parallel}^* (\Delta_{\min})$</td>
<td>1.405</td>
<td>1.049</td>
<td>0.829</td>
<td>1.8$^c$, 1.3$^d$</td>
</tr>
<tr>
<td>$m_{\perp}^* (\Delta_{\min})$</td>
<td>0.238</td>
<td>0.220</td>
<td>0.215</td>
<td>0.257$^a$, 0.23$^d$</td>
</tr>
<tr>
<td>$m_{\parallel}^* (L)$</td>
<td>1.823</td>
<td>1.680</td>
<td>1.248</td>
<td>1.90$^d$</td>
</tr>
<tr>
<td>$m_{\perp}^* (L)$</td>
<td>0.112</td>
<td>0.110</td>
<td>0.080</td>
<td>0.0754$^d$</td>
</tr>
</tbody>
</table>

$^a$ Experimental value from Vrehen [97].
$^b$ Experimental value from Skolnick et al. [98].
$^c$ Experimental value compiled by Madelung [74].
$^d$ Experimental value compiled by Vurgaftman et al. [99].

Table 2.5: Comparison of the effective Landé $g^*$ factors in GaAs obtained with the parameter sets from this work, from Richard et al. (Ref. 82), and from Fraj et al. (Ref. 85) to experimental data.

<table>
<thead>
<tr>
<th></th>
<th>GaAs</th>
<th>Richard2004</th>
<th>Fraj2007</th>
<th>(exp)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$g_c^* (\Gamma)$</td>
<td>$-0.33$</td>
<td>0.20</td>
<td>$-0.48$</td>
<td>$-0.44^a$</td>
</tr>
<tr>
<td>$g_{so}^* (\Gamma)$</td>
<td>$-6.95$</td>
<td>$-6.10$</td>
<td>$-7.50$</td>
<td>$-4.26^{b,c}$</td>
</tr>
</tbody>
</table>

$^a$ Experimental value compiled by Madelung [74].
$^b$ Experimental value from Reine et al. [100].
$^c$ This value is corrected to account for the accepted value of $g_c^* (\Gamma)$ [74].
Table 2.6: Comparison of the effective masses for Ge, in units of the free-electron mass, obtained with the parameter sets from this work, from Richard et al. (Ref. 82), and from Rideau et al. (Ref. 84) to experimental data from Madelung (Ref. 74), except otherwise noted.

<table>
<thead>
<tr>
<th></th>
<th>Ge</th>
<th>Richard2004</th>
<th>Rideau2006</th>
<th>(exp)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$m^*_c (\Gamma)$</td>
<td>0.038</td>
<td>0.038</td>
<td>0.048</td>
<td>0.0380</td>
</tr>
<tr>
<td>$m^*_{hh} (\Gamma)$</td>
<td>0.284</td>
<td>0.213</td>
<td>0.256</td>
<td>0.284</td>
</tr>
<tr>
<td>$m^*_{lh} (\Gamma)$</td>
<td>0.045</td>
<td>0.049</td>
<td>0.061</td>
<td>0.0438</td>
</tr>
<tr>
<td>$m^*_{so} (\Gamma)$</td>
<td>0.096</td>
<td>0.100</td>
<td>0.125</td>
<td>0.095</td>
</tr>
<tr>
<td>$m^*<em>\parallel (\Delta</em>{\text{min}})$</td>
<td>0.897</td>
<td>0.937</td>
<td>0.872</td>
<td>0.900$^a$</td>
</tr>
<tr>
<td>$m^*<em>\perp (\Delta</em>{\text{min}})$</td>
<td>0.228</td>
<td>0.198</td>
<td>0.202</td>
<td>0.200$^a$</td>
</tr>
<tr>
<td>$m^*_\parallel (L)$</td>
<td>1.543</td>
<td>1.609</td>
<td>1.557</td>
<td>1.57</td>
</tr>
<tr>
<td>$m^*_\perp (L)$</td>
<td>0.061</td>
<td>0.083</td>
<td>0.099</td>
<td>0.0807</td>
</tr>
</tbody>
</table>

$^a$Estimated value from Boykin et al. [101].

Table 2.7: Comparison of the effective Landé $g^*$ factors in Ge obtained with the parameter sets from this work, from Richard et al. (Ref. 82), and from Rideau et al. (Ref. 84) to experimental data from Aggarwal (Ref. 102), except otherwise noted.

<table>
<thead>
<tr>
<th></th>
<th>Ge</th>
<th>Richard2004</th>
<th>Rideau2006</th>
<th>(exp)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$g^*_c (\Gamma)$</td>
<td>-2.42</td>
<td>-2.44</td>
<td>-1.59</td>
<td>-3</td>
</tr>
<tr>
<td>$g^*_{so} (\Gamma)$</td>
<td>-13.8</td>
<td>-10.49</td>
<td>-7.79</td>
<td>-10</td>
</tr>
<tr>
<td>$g^*_\parallel (L)$</td>
<td>1.97</td>
<td>2.01</td>
<td>1.84</td>
<td>0.824$^a$</td>
</tr>
<tr>
<td>$g^*_\perp (L)$</td>
<td>2.00</td>
<td>2.00</td>
<td>2.00</td>
<td>1.933$^a$</td>
</tr>
</tbody>
</table>

$^a$Experimental value compiled by Yablonovitch et al. [53].
Table 2.8: Material parameters for GaAs.

<table>
<thead>
<tr>
<th>(eV)</th>
<th>GaAs</th>
<th>(eV)</th>
<th>GaAs</th>
<th>(eV Å)</th>
<th>GaAs</th>
<th>(eV Å)</th>
<th>GaAs</th>
</tr>
</thead>
<tbody>
<tr>
<td>(E_7q)</td>
<td>14.13</td>
<td>(E_6c)</td>
<td>1.512</td>
<td>(P_0)</td>
<td>9.220</td>
<td>(P_d)</td>
<td>0.187</td>
</tr>
<tr>
<td>(E_{7d/8d})</td>
<td>12.17</td>
<td>(E_{6v})</td>
<td>-12.83</td>
<td>(P_2)</td>
<td>4.893</td>
<td>(P_{2d})</td>
<td>9.688</td>
</tr>
<tr>
<td>(E_{3d})</td>
<td>10.21</td>
<td>(\Delta_{so})</td>
<td>0.3386</td>
<td>(P_3)</td>
<td>4.288</td>
<td>(P_{3d})</td>
<td>5.997</td>
</tr>
<tr>
<td>(E_{6u})</td>
<td>8.362</td>
<td>(\Delta_{vd})</td>
<td>0.2448</td>
<td>(P_s)</td>
<td>3.154</td>
<td>(Q_{vc})</td>
<td>8.093</td>
</tr>
<tr>
<td>(E_{8c})</td>
<td>4.667</td>
<td>(\Delta_c)</td>
<td>0.1780</td>
<td>(P_u)</td>
<td>8.555</td>
<td>(Q_{cd})</td>
<td>4.011</td>
</tr>
<tr>
<td>(E_{7c})</td>
<td>4.489</td>
<td>(\Delta_d, \Delta_{3c})</td>
<td>0</td>
<td>(P'_0)</td>
<td>2.516</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 2.9: Material parameters for Ge.

<table>
<thead>
<tr>
<th>(eV)</th>
<th>Ge</th>
<th>(eV)</th>
<th>Ge</th>
<th>(eV Å)</th>
<th>Ge</th>
<th>(eV Å)</th>
<th>Ge</th>
</tr>
</thead>
<tbody>
<tr>
<td>(E_7q)</td>
<td>18.36</td>
<td>(E_{6v})</td>
<td>-13.14</td>
<td>(P_0)</td>
<td>9.722</td>
<td>(P_d)</td>
<td>-1.1</td>
</tr>
<tr>
<td>(E_{7d})</td>
<td>17.0</td>
<td>(\Delta_{so})</td>
<td>0.2885</td>
<td>(P_2)</td>
<td>16.1</td>
<td>(P_{2d})</td>
<td>10.08</td>
</tr>
<tr>
<td>(E_{3d})</td>
<td>10.47</td>
<td>(\Delta_{vd})</td>
<td>0.240</td>
<td>(P_3)</td>
<td>4.0</td>
<td>(P_{3d})</td>
<td>7.4</td>
</tr>
<tr>
<td>(E_{6u})</td>
<td>7.77</td>
<td>(\Delta_c)</td>
<td>0.190</td>
<td>(P_s)</td>
<td>3.4</td>
<td>(Q_{vc})</td>
<td>7.3</td>
</tr>
<tr>
<td>(E_{7c})</td>
<td>3.01</td>
<td>(\Delta_d)</td>
<td>0.2</td>
<td>(P_u)</td>
<td>7.8</td>
<td>(Q_{cd})</td>
<td>5.826</td>
</tr>
<tr>
<td>(E_{6c})</td>
<td>0.90</td>
<td>(\Delta_{3c})</td>
<td>0</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 2.2: Energy band structure of Ge.
Chapter 3

Carrier, spin, current, and spin current injection in GaAs

In this chapter, I present a theoretical review of optical injection processes in semiconductors and my full-band structure calculations of these processes in GaAs. Response tensors for the injection rates are derived within a multiple-scale approach for degenerate and semidegenerate bands. The injection and coherent control of charge, spin, current, and spin current in GaAs are investigated within the full-Brillouin zone, 30-band $k \cdot p$ model. Carrier injection and optical orientation are presented for one- and two-photon absorption, including anisotropy and linear-circular dichroism in the two-photon absorption coefficients. Quantum-mechanical interference effects are considered in carrier, spin, current, and spin current excitation using coherent optical field components at frequencies $\omega$ and $2\omega$. The combination of first- and second-order coefficients that are frequency-matched yields the so-called “1+2” interference term. I calculate the spectral dependence of these all-optical effects for excitation energy in the range 0–4 eV. It is found that significant spin and spin current injection occurs for transitions away from the Brillouin-zone center at the $E_1$ resonance.

The chapter is structured as follows. The theoretical basis for the perturbative treatment of the light-matter interaction, the definition of optical response tensors, and the evaluation of matrix elements within the $k \cdot p$ model are presented in Section 3.1. Injection processes in the presence of a monochromatic field are studied in Section 3.2. Details of the one- and two-photon carrier and spin injection are presented, including anisotropy and dichroism. Coherent control processes in the presence of a fundamental and its second harmonic are studied in Section 3.3. Carrier, spin, current, and spin current
injection are presented. The results are summarized in Section 3.4.

### 3.1 Theoretical background

This section provides the theoretical basis on which optical injection processes in semiconductors are approached in this work. The electron-photon interaction and its treatment within perturbation theory are presented, with the goal to identify injection processes due to perturbations up to second order in the interaction. The effects presented here do not rely on the electromagnetic (EM) field being quantized; it is sufficient to treat it classically. On the other hand, the quantization of electron excitations is necessary. Hence this corresponds to a semiclassical theory. The quantum state \( |\psi(t)\rangle \) of the semiconductor system evolves into a superposition of \( n^{th} \)-order perturbative corrections \( |\psi^{(n)}\rangle \),

\[
|\psi(t)\rangle = |\psi^{(0)}\rangle + |\psi^{(1)}\rangle + |\psi^{(2)}\rangle + \ldots,
\]

where \( |\psi^{(0)}\rangle \) is the initial state. For an observable \( \vartheta \), its expectation value evolves as

\[
\langle \psi(t) | \vartheta | \psi(t) \rangle,
\]

and is categorized into contributions arising from the first-order correction \( |\psi^{(1)}\rangle \),

\[
\langle \psi^{(1)} | \vartheta | \psi^{(1)} \rangle,
\]

the second-order correction \( |\psi^{(2)}\rangle \),

\[
\langle \psi^{(2)} | \vartheta | \psi^{(2)} \rangle,
\]

and mixed-order contributions,

\[
\langle \psi^{(1)} | \vartheta | \psi^{(2)} \rangle + \langle \psi^{(2)} | \vartheta | \psi^{(1)} \rangle.
\]

Terms of the form \( \langle \psi^{(0)} | \vartheta | \psi^{(n)} \rangle \), corresponding to correlations between the ground state and the excited state, have an energy uncertainty on the order 1 eV for a typical semiconductor band gap. Thus, they are expected to vanish on femtosecond time scales and are neglected. Response tensors are defined for the material-dependent part of the expectation value of observables. The framework for the evaluation of these response tensors within \( k \cdot p \) theory is presented. This theory section is based on References 2, 103, and 104.
3.1.1 Crystal electrons in an electromagnetic field

Consider the single-electron Hamiltonian

\[ H_0 = \frac{p^2}{2m} + V(r) + H_{S-O}, \]  

(3.1)

where \( p \) is the momentum operator, \( m \) is the rest mass of the electron, \( V(r) \) is a periodic potential attributable to the crystal structure of a solid, and \( H_{S-O} \) is the spin-orbit coupling,

\[ H_{S-O} = \frac{\hbar}{4mc^2} \sigma \cdot (\nabla V \times p); \]  

(3.2)

\( \hbar \) is Planck’s constant divided by \( 2\pi \), \( c \) is the speed of light in vacuum, and \( \sigma = 2S/\hbar \) is the dimensionless spin operator. In the presence of a spatially uniform EM field, following minimal coupling the momentum operator is replaced by

\[ p \rightarrow p - \frac{e}{c} A(t), \]

where \( A \) is the vector potential of the field, \( e = -|e| \) is the charge of the electron, and the scalar potential \( \phi \) satisfies \( \nabla \phi = 0 \), setting the choice of gauge [105]. This prescription yields the Hamiltonian \( H = H_0 + H_1 + H_2 \), where \( H_0 \) is given by Equation (3.1) and the additional terms by

\[ H_1 = -\frac{e}{mc} A(t) \cdot p, \]  

(3.3)

\[ H_2 = \frac{e^2}{2mc^2} |A(t)|^2. \]  

(3.4)

The first is the electron-photon interaction and affects the electron motion. The second affects only the overall phase of the electron wavefunction and has no consequence on expectation values calculated here.

Moving to second quantization form, the original Hamiltonian without EM field becomes

\[ H_0 = \sum_{nk} \hbar \omega_n(k) a_{nk}^\dagger a_{nk}, \]  

(3.5)

where the \( a_{nk}^\dagger \) and \( a_{nk} \) are creation and annihilation operators for an electron of band index \( n \), crystal momentum \( k \), and energy \( \hbar \omega_n(k) \). In the following the subscript \( c \) (v) is used exclusively to label conduction (valence) bands. The semiconductor vacuum is considered as the initial state of the system: valence bands are fully occupied and conduction bands empty. In this context, band-to-band excitations are understood as the creation of an
electron-hole pair. Operators acting on the valence bands are introduced according to $b^\dagger_{vk}, a^\dagger_{vk}$ are creation operators for electrons and holes, respectively. The general $a^\dagger_{nk}$ and $a_{nk}$ obey the fermion anti-commutation relation, and it follows that

$$\{a_{c'k'}, a^\dagger_{ck}\} = \delta_{c'c}\delta_{kk'}$$

and

$$\{b_{v'k'}, b^\dagger_{vk}\} = \delta_{vv'}\delta_{kk'}.$$  

Using the hole operators and renormalizing the zero-point energy, Equation (3.5) becomes

$$H_0 = \sum_{ck} \hbar \omega_c(k) a^\dagger_{ck}a_{ck} - \sum_{vk} \hbar \omega_v(k) b^\dagger_{vk}b_{vk}.$$

In the interaction picture, the electron-photon term, Equation (3.3), takes the second-quantized form

$$H_1 = -\frac{e}{c} \mathbf{A}(t) \cdot \mathbf{v}(t),$$  

where $\mathbf{v}$ is given by [55]:

$$\mathbf{v}(t) = \sum_{cc'k} a^\dagger_{ck}a_{c'k} \mathbf{v}_{cc'}(k) e^{i\omega_{cc'}(k)t}$$

$$- \sum_{vv'k} b^\dagger_{vk}b_{v'k} \mathbf{v}_{vv'}(k) e^{i\omega_{vv'}(k)t}$$

$$+ \sum_{cv'k} a^\dagger_{ck}b^\dagger_{v'k} \mathbf{v}_{cv'}(k) e^{i\omega_{cv'}(k)t}$$

$$+ \sum_{vc'k} b_{vk}a_{c'k} \mathbf{v}_{vc'}(k) e^{i\omega_{vc'}(k)t}.$$  

In the above, $\omega_{mn}(k) \equiv \omega_m(k) - \omega_n(k)$ and the $v_{mn}(k)$ are matrix elements of $\mathbf{p}/m$. The crystal momentum $k$ is taken discrete for the present section. At the end of the derivations, the continuous limit is taken by substituting $\delta_{kk'} \rightarrow \frac{8\pi^3}{V}\delta(k - k')$ and $\sum_k \rightarrow V \int \frac{d^3k}{8\pi^3}$, where $V$ is the volume of the crystal, and the number operator becomes the number density operator, i.e.

$$a^\dagger_{nk}a_{nk} \rightarrow \frac{8\pi^3}{V} a^\dagger_{nk}a_{nk}.$$

### 3.1.2 Analysis using perturbation theory

The approach used here treats $H_1$ as a perturbation to the crystal Hamiltonian $H_0$. The system is initially in the ground electronic state $\psi(0) = |0\rangle$ corresponding to the semiconductor vacuum. After being subjected to laser excitation the system evolves into $\psi(t)$. The lowest non-vanishing order in the electron-hole pair is considered:

$$\psi(t) = c_0(t) |0\rangle + \sum_{cvk} c_{cvk}(t) e^{-i\omega_{cv}(k)t} |cvk\rangle,$$  

(3.9)
where \(|cvk⟩\) is the state obtained by acting with electron and hole creation operators on the vacuum:
\[
|cvk⟩ \equiv a_cke_k^\dagger |0⟩.
\] (3.10)

Equation (3.9) is a perturbative solution where electron-hole pairs are created with amplitude coefficients \(c_{cvk}(t)\). The coefficients are solved at lowest non-vanishing order by performing the time evolution of the initial ground state \(|0⟩\) under the action of the Hamiltonian \(H_0 + H_1\):
\[
|ψ(t)⟩ = U(t) |0⟩ = c_0(t) |0⟩ + \sum_{cvk} c_{cvk}(t) e^{-iH_0t/\hbar} |cvk⟩,
\] (3.11)

where \(U(t)\) is the time-evolution operator. Therefore,
\[
c_{cvk}(t) = \langle cvk | e^{iH_0t/\hbar} U(t) |0⟩. \tag{3.12}
\]

This is solved in the interaction picture using the following approach from the derivation of Fermi’s golden rule. A rising exponential term \(e^{\epsilon t}\), where \(\epsilon\) is a small positive constant, is introduced in every integral over time \(t\). This term represents a slow turn on of the perturbation. The continuous perturbation is recovered by taking the \(\epsilon \to 0\) limit at the end of the derivation. The interaction-picture Hamiltonian is
\[
H_{\text{int}} = e^{iH_0t/\hbar} H_1 e^{-iH_0t/\hbar}, \tag{3.13}
\]
and from the time-evolution operator \(U(t) = e^{-iHt/\hbar}\) it follows that \[105\]:
\[
e^{iH_0t/\hbar} U(t) = 1 + (i\hbar)^{-1} \int_{-∞}^{t} H_{\text{int}}(t') e^{i\epsilon t'} dt' \\
+ (i\hbar)^{-2} \int_{-∞}^{t} \int_{-∞}^{t'} H_{\text{int}}(t') e^{i\epsilon t'} H_{\text{int}}(t'') e^{i\epsilon t''} dt'' dt' \\
+ \ldots \tag{3.14}
\]

The first term represents the expansion to zeroth order in perturbation and does not correspond to a transition. The second term is first order in the perturbation and yields a first-order coefficient \(c_{cvk}^{(1)}(t)\); a second-order coefficient \(c_{cvk}^{(2)}(t)\) and higher orders coefficients are identified in a similar way.
3.1.3 Expectation value of observables

Consider the expectation value of a single-particle operator \( \vartheta \) computed within the state given in Equation (3.9). Of interest are Hermitian operators for which (a) the expectation value vanishes in the ground state: \( \langle 0 | \vartheta | 0 \rangle = 0 \), (b) the operator does not excite the ground state: \( \langle cvk | \vartheta | 0 \rangle = 0 \), (c) the operator only connects electron or hole states with the same crystal momentum: \( \langle c'v'k' | \vartheta | cvk \rangle = \langle c'v'k | \vartheta | cvk \rangle \delta_{kk'} \), and (d) electron and hole contributions are separable:

\[
\langle c'v'k | \vartheta | cvk \rangle = \langle c'k | \vartheta | ck \rangle \delta_{vv'} - \langle v'k | \vartheta | vk \rangle \delta_{cc'},
\]

where the \(|ck\rangle \) and \(|vk\rangle \) are single-particle states. In the following, the notation \( \langle \vartheta \rangle \) is used as shorthand to \( \langle \psi(t) | \vartheta | \psi(t) \rangle \). The expectation value has the form \( \langle \vartheta \rangle = \langle \vartheta \rangle_e + \langle \vartheta \rangle_h \), where the electron contribution \( \langle \vartheta \rangle_e \) and hole contribution \( \langle \vartheta \rangle_h \) are identified. Using the perturbative solution for \( |\psi(t)\rangle \), Equation (3.9), it follows that

\[
\langle \vartheta \rangle = \sum_{cc'dv'k} \left( \langle c'k | \vartheta | ck \rangle \delta_{vv'} - \langle v'k | \vartheta | vk \rangle \delta_{cc'} \right) \times \left[ c_{cvk}^*(t) c_{cvk}(t) e^{-i\omega_{cv}(k)t} e^{i\omega_{cv'}(k)t} \right].
\]

The time dependence of \( \langle \vartheta \rangle \) lies in the quantity within square brackets. For a continuous-wave perturbation, the time derivative of this quantity has the form

\[
\frac{\partial}{\partial t} \left[ c_{cvk'}^*(t) c_{cvk}(t) e^{-i\omega_{cv}(k)t} e^{i\omega_{cv'}(k)t} \right] = \begin{cases} 2\pi \Omega_{cv'}(k) \Omega_{cv}(k) \delta[\lambda_{cv}(k)] \lambda_{cv}(k) = \lambda_{cv'}(k), \\
0 \end{cases}
\]

where \( \Omega_{cv} \) is the transition amplitude and \( \lambda_{cv} \) is an energy-matching condition. For each \( n \)th-order coefficient \( c_{cvk}^{(n)} \), there correspond a transition amplitude \( \Omega_{cv}^{(n)} \) and an energy-matching condition \( \lambda_{cv}^{(n)} \); here only a single such term is shown for simplicity. Consequently, the time derivative of \( \langle \vartheta \rangle \) is

\[
\frac{\partial}{\partial t} \langle \vartheta \rangle = 2\pi \sum_{cc'dv'k} \left( \langle c'k | \vartheta | ck \rangle \delta_{vv'} - \langle v'k | \vartheta | vk \rangle \delta_{cc'} \right) \times \Omega_{cv'}^*(k) \Omega_{cv}(k) \delta[\lambda_{cv}(k)],
\]

where the prime over the summation indicates that \( c \) and \( c' \) (\( v \) and \( v' \)) are energy-matched. Taking \( \vartheta \) to be the number operator, the above is equivalent to Fermi's golden rule.
The transition amplitude $\Omega_{cv}$ and energy-matching condition $\lambda_{cv}$ are obtained by treating the Hamiltonian $H_1$ in perturbation theory. The first perturbative order yields the one-photon transition amplitude $\Omega_{cv}^{(1)}$ and energy-matching condition $\lambda_{cv}^{(1)}$. The second perturbative order yields the two-photon transition amplitude $\Omega_{cv}^{(2)}$ and energy-matching condition $\lambda_{cv}^{(2)}$. For a monochromatic field of frequency $\omega$, the transition amplitudes are given by [39, 106]:

$$\Omega_{cv}^{(1)}(\omega, k) = \Upsilon_{cv}^{(1)}(\omega, k) \cdot E(\omega),$$  \hspace{1cm} (3.19)

$$\Omega_{cv}^{(2)}(\omega, k) = \Upsilon_{cv}^{(2)}(\omega, k) : E(\omega)E(\omega),$$  \hspace{1cm} (3.20)

where the $:$ denotes the double-dot (colon) product on dyadics, the vector $\Upsilon_{cv}^{(1)}$ and tensor $\Upsilon_{cv}^{(2)}$ are given by

$$\Upsilon_{cv}^{(1)}(\omega, k) = \frac{i e}{\hbar \omega} v_{cv}(k),$$  \hspace{1cm} (3.21)

$$\Upsilon_{cv}^{(2)}(\omega, k) = \frac{e^2}{\hbar^2 \omega^2} \sum_n \frac{v_{cn}(k) v_{cv}(k)}{\omega_n(k) - \bar{\omega}_{cv}(k)},$$  \hspace{1cm} (3.22)

and $\bar{\omega}_{mn}(k) \equiv (\omega_{m}(k) + \omega_{n}(k)) / 2$. The energy-matching conditions for the one- and two-photon processes are

$$\lambda_{cv}^{(1)}(\omega, k) = \omega_{cv}(k) - \omega$$  \hspace{1cm} (3.23)

and

$$\lambda_{cv}^{(2)}(\omega, k) = \omega_{cv}(k) - 2\omega.$$  \hspace{1cm} (3.24)

### 3.1.4 Two-color quantum interference

Quantum mechanically, transition amplitudes are added for transitions sharing the same initial and final states, leading to pathway interference in the transition probability. The interfering transition terms each provide a fixed amount of energy required to excite the initial state to the final state. Thus, when two or more transition terms share the same energy-matching condition, their amplitudes are added and an interference term occurs in the transition probability. The terms can be of different perturbative orders as long as they satisfy the same energy-matching condition.

In the following, consider a two-color optical field

$$E(t) = E(\omega)e^{-i\omega t} + E(2\omega)e^{-2i\omega t} + c.c.,$$  \hspace{1cm} (3.25)

consisting of two monochromatic beams of frequency $\omega$ and $2\omega$. With such harmonically-related components, one-photon absorption at $2\omega$ matches two-photon absorption at $\omega$. The cross-terms of one- and two-photon amplitudes yield the “1+2” interference effect.
In a coherent “1+2” setup, the transition amplitude includes contributions from one- and two-photon processes,

$$\Omega_{cv}(k) = \Omega_{cv}^{(1)}(2\omega, k) + \Omega_{cv}^{(2)}(\omega, k), \quad (3.26)$$

with $\Omega_{cv}^{(1)}$ given by Equation (3.19) and $\Omega_{cv}^{(2)}$ by Equation (3.20). These transitions are energy-matched since $\lambda_{cv}^{(1)}(2\omega, k) = \lambda_{cv}^{(2)}(\omega, k)$. To obtain the transition probability, the absolute value squared of the total transition amplitude $\Omega_{cv}$ is taken, resulting in a term strictly due to the one-photon process, one strictly due to the two-photon process, and cross-terms. From Equations (3.19) and (3.20), the transition probabilities for one- and two-photon processes are respectively first and second order in the intensity of the field (respectively second and fourth order in the EM field). The transition probability for the cross-term is third order in the EM field. Thus, generally the expectation value $\langle \vartheta \rangle$ has an injection rate

$$\frac{\partial}{\partial t} \langle \vartheta \rangle = \frac{\partial}{\partial t} \langle \vartheta \rangle_1 + \frac{\partial}{\partial t} \langle \vartheta \rangle_2 + \frac{\partial}{\partial t} \langle \vartheta \rangle_I, \quad (3.27)$$

where the subscripts 1 and 2 denote the contributions at first and second order in the intensity, and $I$ denotes the interference term. Response tensors $\Theta_1$, $\Theta_2$, and $\Theta_I$ are implicitly defined for each order by the following equations:

$$\frac{\partial}{\partial t} \langle \vartheta \rangle_1 = \Theta_1 : E(-2\omega)E(2\omega), \quad (3.28)$$

$$\frac{\partial}{\partial t} \langle \vartheta \rangle_2 = \Theta_2 : E(-\omega)E(-\omega)E(\omega)E(\omega), \quad (3.29)$$

and

$$\frac{\partial}{\partial t} \langle \vartheta \rangle_I = \Theta_I : E(-\omega)E(-\omega)E(2\omega) + c.c. \ . \quad (3.30)$$

Microscopic expressions for the response tensors are obtained by substituting Equation (3.26) into Equation (3.18) and identifying the terms. The derivation for the interference term $\Theta_I$ is presented for degenerate, nearly degenerate, and nondegenerate bands.

**Nondegenerate bands**

For transitions where no degeneracies occur in the initial or final states, the standard treatment in perturbation theory applies. The contribution of the cross-terms of one- and two-photon transition amplitudes to the rate of change of the expectation value is given
Chapter 3. Carrier, spin, current, and spin current injection in GaAs

\[
\frac{\partial}{\partial t} \langle \vartheta \rangle_I = 2\pi \sum_{c'v'k} \left( \langle c'k | \vartheta | ck \rangle \delta_{vv'} - \langle v'k | \vartheta | vk \rangle \delta_{c'c} \right) \times \left[ \Omega_{cv'}^{(2)}(\omega, k) \Omega_{cv}^{(1)}(2\omega, k) + \Omega_{cv}^{(2)}(\omega, k) \Omega_{cv'}^{(1)}(2\omega, k) \right] \delta[\omega_{cv}(k) - 2\omega]. \tag{3.31}
\]

Assuming that off-diagonal matrix elements for \( \vartheta \) vanish, then only \( c = c' \) and \( v = v' \) terms contribute. This applies, for example, for the number operator (population control) or the current operator (charge current control). Then the two cross-terms within square brackets are exact complex conjugates of each other:

\[
\Omega_{cv'}^{(2)}(\omega, k) \Omega_{cv}^{(1)}(2\omega, k) = \left[ \Omega_{cv}^{(2)}(\omega, k) \Omega_{cv'}^{(1)}(2\omega, k) \right]^*.
\]

and it follows that

\[
\frac{\partial}{\partial t} \langle \vartheta \rangle_I = 2\pi \sum_{ck} \left( \langle ck | \vartheta | ck \rangle - \langle vk | \vartheta | vk \rangle \right) \times \left[ \Omega_{cv'}^{(2)}(\omega, k) \Omega_{cv}^{(1)}(2\omega, k) + \text{c.c.} \right] \delta[\omega_{cv}(k) - 2\omega]. \tag{3.32}
\]

The Hermiticity of \( \vartheta \) allows to move the complex conjugation in Equation (3.32) from inside the square brackets to outside the sum, yielding

\[
\frac{\partial}{\partial t} \langle \vartheta \rangle_{I,e} = 2\pi \sum_{ck} \left( \langle ck | \vartheta | ck \rangle - \langle vk | \vartheta | vk \rangle \right) \times \Omega_{cv'}^{(2)}(\omega, k) \Omega_{cv}^{(1)}(2\omega, k) \delta[\omega_{cv}(k) - 2\omega] + \text{c.c.}, \tag{3.33}
\]

which has the form of Equation (3.30). It follows that the response tensor \( \Theta_I \) is given by

\[
\Theta_I = 2\pi \sum_{ck} \left( \langle ck | \vartheta | ck \rangle - \langle vk | \vartheta | vk \rangle \right) \times \Upsilon_{cv'}^{(2)}(\omega, k) \Upsilon_{cv}^{(1)}(2\omega, k) \delta[\omega_{cv}(k) - 2\omega]. \tag{3.34}
\]

Degenerate and nearly degenerate bands

In order to treat degeneracies, an extension to the above procedure is necessary. The basic idea is to allow coherences between states that are semidegenerate. Such coherences are excited, for example, when the EM field has a finite bandwidth. To include coherences in the theory, the perturbation term is separated into fast and slow time scales. The treatment of fast and slow time scales happens separately. This multiple-scale approach
is presented by Nastos et al. for a monochromatic field \([36]\), and extended here for a two-color field. The field is described by two fast oscillating components of frequency \(\omega\) and \(2\omega\), each having a slow-varying amplitude.

The multiple-scale approach allows to consider off-diagonal matrix elements of the form \(\langle c'k|\vartheta|ck\rangle\) in the expectation value \(\langle \vartheta \rangle = \text{Tr}[\rho\vartheta]\), where \(\rho\) is the single-particle density operator. It is assumed that all coherences between valence and conduction states vanish on fast time scales, and thus \(\rho_{cv}\) is assumed to be zero. It follows that the rate of change of the expectation value is given by

\[
\frac{\partial}{\partial t} \langle \vartheta \rangle = \sum_{cc'} \langle c'k|\vartheta|ck\rangle \frac{\partial}{\partial t} \rho_{cc'}(k) - \sum_{vv'} \langle vk|\vartheta|v'k\rangle \frac{\partial}{\partial t} \rho_{vv'}(k). \tag{3.35}
\]

For two states \(m\) and \(n\), the density operator \(\rho_{mn}(k)\) is found nonzero only if \(h\omega_{mn}(k) = 0\) (degenerate) or \(|h\omega_{mn}(k)| < \epsilon_{\text{cut}}\) (semidegenerate) for a cutoff energy \(\epsilon_{\text{cut}}\) comparable to the bandwidth of the EM field. The time derivative of \(\rho_{cc'}(k)\) between degenerate or semidegenerate conduction states \(c\) and \(c'\) is given for a monochromatic field in Equation (11) of Nastos et al. \([36]\). The same treatment for the two-color field \((3.25)\) yields the interference term

\[
\frac{\partial}{\partial t} \rho_{cc'}(k) = -i(\omega_{cc'}(k) - i\Gamma_{cc'}) \rho_{cc'}(k)
+ i \sum_v \left[ \Omega_{cv}^{(2)*}(\omega,k) \Omega_{cv}^{(1)}(2\omega,k) + \Omega_{cv}^{(1)*}(2\omega,k) \Omega_{cv}^{(2)}(\omega,k) \right]
\times \left( \delta_{\epsilon}[\omega_{cv}(k) - 2\omega] - \delta_{-\epsilon}[\omega_{cv}(k) - 2\omega] \right), \tag{3.36}
\]

where \(\Gamma_{cc'}\) is a small positive value accounting for loss and dephasing \([36]\), \(\delta_{\epsilon}(x) \equiv (x-\epsilon)^{-1}\), and \(\lim_{\epsilon \to 0^\pm} \delta_{\epsilon}(x) = \mathcal{P}(x) \pm i\pi\delta(x)\) \([104]\). A similar expression is found for \(\rho_{v'v}(k)\) with the substitutions \(cc' \leftrightarrow v'v\), \(c'v \leftrightarrow cv\)', and \(\sum_c \leftrightarrow \sum_v\) in the above. It follows that the electron contribution to the injection rate is

\[
\frac{\partial}{\partial t} \langle \vartheta \rangle_{I_e} = \pi \sum_{cc'v} \langle c'k|\vartheta|ck\rangle
\times \left[ \Omega_{cv}^{(2)*}(\omega,k) \Omega_{cv}^{(1)}(2\omega,k) + \Omega_{cv}^{(1)*}(2\omega,k) \Omega_{cv}^{(2)}(\omega,k) \right]
\times \left( \delta[\omega_{cv}(k) - 2\omega] + \delta[\omega_{cv}(k) - 2\omega] \right), \tag{3.37}
\]

and similarly for the hole contribution. Using the Hermiticity of the operator \(\vartheta\), the above is rewritten in the form of Equation \((3.30)\) to yield the expression for the response tensor
$\Theta_I$ within the multiple-scale approach:

$$\Theta_I = \pi \sum_{cc'vv'} \left( \langle c'|\varrho|ck \rangle \delta_{vv'} - \langle v'|\varrho|vk \rangle \delta_{cc'} \right) \times \Upsilon^{(2)*}_{cv'}(\omega, k) \Upsilon^{(1)}_{cv}(2\omega, k) \left( \delta[\omega_{cv'}(k) - 2\omega] + \delta[\omega_{cv}(k) - 2\omega] \right).$$  \hspace{1cm} (3.38)

This equation is to be used instead of Equation (3.34) since it includes coherences.

### 3.1.5 Evaluation within a $k \cdot p$ framework

The material-dependent contribution to the transition amplitude is contained in the vector $\Upsilon^{(1)}_{cv}$ for the one-photon process and in the tensor $\Upsilon^{(2)}_{cv}$ for the two-photon process. Their evaluation using Equations (3.21) and (3.22) relies on band energies and velocity matrix elements obtained from a band structure model. In general, the unperturbed electronic states $|nk\rangle$ satisfying the Hamiltonian $\mathcal{H}_0$ are determined by solving the single-electron Schrödinger equation [cf. Equation (2.1) on page 9]. The solutions are Bloch functions, products of plane waves and lattice periodic spinor functions $u_{nk}(r)$,

$$\langle r|nk\rangle = e^{ikr}u_{nk}(r),$$  \hspace{1cm} (3.39)

and the periodic functions $u_{nk}(r)$ are eigenfunctions of the $k \cdot p$ Hamiltonian $\mathcal{H}_k$ given by Equation (2.4). The velocity operator is also obtained from the $k \cdot p$ Hamiltonian by [107]:

$$v(k) = \frac{1}{\hbar} \frac{\partial}{\partial k} \mathcal{H}_k.$$  \hspace{1cm} (3.40)

The calculations in this Chapter consider the zinc-blende symmetry and use the 30-band $k \cdot p$ model of Chapter 2. Various $k \cdot p$ models with a 14-state basis have been successfully used in calculations of optical responses of semiconductors [35, 44–46]. However, the accuracy of such band structures is limited to a range of roughly 0.5 eV above and below the semiconducting band gap, thus limiting their application [36]. A number of band structure features evidenced by experimental data, such as the joint density of states responsible for the $E_1$ optical absorption edge, are simply missing in 14-band $k \cdot p$ models [92]. Extending the basis to thirty states allows the correct description of the highest valence bands and lowest conduction bands in a range of over 10 eV [82], and the prediction of optical responses at photon energies well above the 0.5 eV window.
3.2 Response to a monochromatic field

This section presents microscopic calculations of the electronic response to a monochromatic field of frequency $\omega$,

$$E(t) = E(\omega)e^{-i\omega t} + \text{c.c.}. \quad (3.41)$$

The rates of injection of carrier and spin densities produced are

$$\dot{n} = \dot{n}_1(\omega) + \dot{n}_2(\omega), \quad (3.42)$$
$$\dot{S} = \dot{S}_1(\omega) + \dot{S}_2(\omega), \quad (3.43)$$

where the subscripts 1 or 2 indicate the order. Injection rates for carrier and spin are obtained by substituting $\theta$ with the number and spin operator, respectively, in Equations (3.28) and (3.29). The responses at first and second order in the intensity are considered separately in the two following sections.

3.2.1 One-photon absorption

The densities linear in the field intensity are obtained by considering only the one-photon transition amplitude. The rate of one-photon carrier injection, $\dot{n}_1$, and spin injection, $\dot{S}_1$, are:

$$\dot{n}_1(\omega) = \xi_1^{ab}(\omega)E^a(-\omega)E^b(\omega), \quad (3.44)$$
$$\dot{S}_1(\omega) = \zeta_1^{abc}(\omega)E^b(-\omega)E^c(\omega). \quad (3.45)$$

The response tensor $\xi_1$ and pseudotensor $\zeta_1 = \zeta_{1;e} + \zeta_{1;h}$ are defined by these equations. Following the microscopic derivation in Section 3.1.3 yields for the carrier-injection tensor the expression

$$\xi_1^{ab}(\omega) = \frac{2\pi e^2}{\hbar^2 \omega^2} \sum_{c,v} \int \frac{d^3k}{8\pi^3} v_{cv}^a(k) v_{cv}^b(k) \delta \left[ \omega_{cv}(k) - \omega \right], \quad (3.46)$$

and for the spin-injection pseudotensor

$$\zeta_{1;e}^{abc}(\omega) = \frac{e^2}{\hbar^2 \omega^2} \sum_{c',v'} \int \frac{d^3k}{8\pi^3} S_{cv}^a(k) v_{cv}^{b*}(k) v_{cv'}^{c*}(k)$$
$$\times \left[ \delta \left[ \omega_{cv}(k) - \omega \right] + \delta \left[ \omega_{cv'}(k) - \omega \right] \right]. \quad (3.47)$$
The quantities $v_{mn}(k)$ and $S_{mn}(k)$ denote the matrix elements of the velocity and spin operators, respectively, between the Bloch states of bands $m$ and $n$ at wavevector $k$:

$$\langle mk | v | nk' \rangle = v_{mn}(k) \delta(k - k'), \quad (3.48)$$

$$\langle mk | S | nk' \rangle = S_{mn}(k) \delta(k - k'). \quad (3.49)$$

From symmetry of the zinc-blende lattice for GaAs, $\xi_1$ and $\zeta_1$ each have one independent nonzero component:

$$\xi_{1xx}^x = \xi_{1yy}^y = \xi_{1zz}^z, \quad (3.50)$$

$$\zeta_{1}^{xyz} = \zeta_{1}^{yxx} = \zeta_{1}^{zxy} = -\zeta_{1}^{xxy} = -\zeta_{1}^{yxz} = -\zeta_{1}^{zyx} ; \quad (3.51)$$

$\xi_1$ is related to the imaginary part of the susceptibility $\chi(\omega)$ by $\Im \chi(\omega) = \frac{\hbar}{2} \xi_1(\omega) \text{ [2]}$.

In Figure 3.1 on page 37, the calculated spectra of the linear response tensors for carrier and spin injection are presented. The band dispersion and matrix elements of the spin and velocity operators are computed from the 30-band $k \cdot p$ model. Within the single-particle approximation, $\xi_{1xx}^x$ is purely real and $\zeta_{1}^{xyz}$ purely imaginary. At the onset of absorption, with $\hbar \omega$ equal or greater than the direct band-gap energy $E_{dg}$, the responses follow a square-root turn on characteristic of the joint density of states (JDOS). A second turn on appears 340 meV above the gap energy, and corresponds to absorption from the split-off band. The features identified by $E_1$ and $E_1 + \Delta_1$ at high energy are caused by a critical point around the $k$-vector $[0.2, 0.2, 0.2] 2\pi/a$ in the $\Gamma$–L valley, and are $M_1$-type peaks [108].

In spin injection, the contributions from electrons and holes mostly mirror each other by a negative sign. For the remainder of this chapter, the hole contribution to spin properties will be neglected, due to the significantly shorter spin-relaxation times for holes compared to electrons in GaAs [51, 52]; I return to this in Chapter 4. As in carrier injection, spin injection response follows closely the JDOS at low photon energy. The onset of spin injection from the split-off band contributes a dip in $\zeta_{1}^{xyz}$, indicating that spins from this transition are polarized in the opposite direction compared to the heavy- and light-hole transitions. A strongly peaked feature occurs at the $E_1$ resonance due to the spin-orbit splitting in the valence band and the large JDOS in the $\Gamma$–L valley. The increase in spin injection is negated at the $E_1 + \Delta_1$ resonance where opposite spins are injected. Spin injection is weak at higher photon energy.

Using the zinc-blende symmetry, it is possible to rewrite Equations (3.44) and (3.45)
Figure 3.1: The linear response of GaAs as a function of photon energy $h\omega$, computed from the 30-band $k \cdot p$ model. The imaginary part of the susceptibility $\chi(\omega)$ is shown in black with the $E_1$ and $E_1 + \Delta_1$ absorption features identified; $\Delta_1 = 200$ meV. The dashed red (dotted blue) curve shows the electron (hole) spin-injection component $\zeta_{1,e}(\omega)$. The scale is such that the amount of spin polarization is obtained directly by taking the ratio of both quantities.

Figure 3.2: The degree of spin polarization (DSP) of electrons injected in GaAs by one-photon absorption. Solid black, dashed red, and dotted blue curves: DSP for transitions originating from the heavy-hole, light-hole, and split-off bands, respectively, to any conduction band; green thick curve: total DSP for all transitions.
without summation convention to

\[
\dot{n}_1 = \xi_{1xx} E(-\omega) \cdot E(\omega), \tag{3.52}
\]

\[
\dot{S}_1 = \zeta_{1xy} E(-\omega) \times E(\omega). \tag{3.53}
\]

The injection rate \(\dot{S}_1\) is maximized by maximizing the cross product \(E(-\omega) \times E(\omega)\): A light source which is polarized circularly accomplishes this. For \(\sigma^-\) light\(^1\) and a positive \(\Im [\zeta_{1xy}]\), the resulting spin polarization is parallel with the \(z\)-axis [36]. The excess of spin-up versus spin-down polarized carriers is quantified by the degree of spin polarization (DSP), defined by

\[
\text{DSP}^z = \frac{n_\uparrow - n_\downarrow}{n_\uparrow + n_\downarrow}, \tag{3.54}
\]

and given in terms of the injection rates by

\[
\text{DSP}^z = \frac{\dot{S}_1^z}{\hbar \dot{n}_1} = \frac{\Im [\zeta_{1xy}]}{\hbar \xi_{1xx}}. \tag{3.55}
\]

A simple model for spin injection at the band edge considers the hole bands as \(j = 3/2\) states quantized along \(\hat{z}\). The selection rules for \(\sigma^-\) light allow transitions from \(j = 3/2, m_z = 3/2\) to the spin-up conduction state and from \(j = 3/2, m_z = 1/2\) to the spin-down conduction state. Transition probabilities for these two processes are given in the ratio \(3:1\), yielding a DSP of 50\% [3]. In the Kane model, hole bands are \(j = 3/2\) states quantized along \(\hat{k}\): the heavy-hole state has \(m_k = 3/2\), while the light-hole state has \(m_k = 1/2\) [109]. Their contribution to the DSP is calculated by averaging over the direction of \(\hat{k}\). From the sum rule

\[
\int \frac{d\hat{k}}{4\pi} \left| \langle j, m(\hat{k}) | \langle j, m(\hat{k}) \rangle = \frac{1}{2j + 1} \sum_{m_z} \left| \langle j, m_z(\hat{k}) \rangle \langle j, m_z(\hat{k}) \rangle \right| \right| \tag{3.56}
\]

and from band-edge values of the transition amplitudes for states quantized along \(\hat{z}\), a DSP of 50\% is obtained [36]. Thus, individual contributions from transitions originating from either the heavy- or light-hole bands each yield 50\% spin-polarized electrons at the band edge.

The DSP of injected electrons, calculated from the 30-band model, is shown as a function of photon energy in Figure 3.2 on page 37. Electrons are 50\% spin polarized at the band edge, as predicted by the simple model. The injection from the split-off band contributes \(-100\%\) spin-polarized electrons at the onset. This corresponds to a sharp

\(^1\)Equivalent to left-circularly polarized light and positive helicity for propagation in the \(-\hat{z}\) direction.
drop in the total DSP at photon energy of 1.75 eV. The total spin polarization is affected by the mixing of states away from the Γ point: at those energies the light-hole band has acquired a significant split-off-like character, and the injected spins are less polarized than at the band edge. As a result the contribution from the light-hole band decreases and eventually changes sign at about 2 eV. Nevertheless, the spins associated with the heavy-hole transition remain the dominant contribution due to the larger JDOS, and the total DSP remains positive. At the \( E_1 \) critical point, the large JDOS and the 200 meV gap between heavy- and light-hole states yield an enhancement of the DSP to about 30%.

At higher photon energy, above the \( E_1 + \Delta_1 \) resonance, spin injection is negligible due to cancellation of the spin polarizations from the transitions originating from the heavy- and light-hole bands.

### 3.2.2 Two-photon absorption

This section considers the electronic response at second order in the intensity of the incident field. Following Equation (3.29), two-photon carrier injection takes the form

\[
\dot{n}_2(\omega) = \xi^{abcd}_2(\omega) E^a(-\omega) E^b(-\omega) E^c(\omega) E^d(\omega).
\]

The microscopic expression for the carrier-injection tensor \( \xi_2 \) is

\[
\xi^{abcd}_2(\omega) = \frac{2\pi e^4}{h^4 \omega^4} \sum_{c,v} \int \frac{d^3k}{8\pi^3} w^{ab}_{cv}(k) w^{cd}_{cv}(k) \delta \left[ \omega_{cv}(k) - 2\omega \right],
\]

where \( w^{ab}_{cv}(k) \) is the symmetrized two-photon amplitude, up to a unit-conversion factor [2]:

\[
w^{ab}_{cv}(k) \equiv \frac{1}{2} \sum_m \frac{\nu^a_{cm}(k) \nu^b_{mv}(k) + \nu^b_{cm}(k) \nu^a_{mv}(k)}{\omega_m(k) - \bar{\omega}_{cv}(k)},
\]

which follows from the invariance of Equation (3.57) under the interchanges \( a \leftrightarrow b \) and \( c \leftrightarrow d \). By symmetry of the zinc-blende lattice, \( \xi_2 \) has 21 nonzero and three independent components:

\[
\begin{align*}
\xi^{xxx}_2 &= \xi^{yyy}_2 = \xi^{zzz}_2, \\
\xi^{xxy}_2 &= \xi^{yyz}_2 = \xi^{zzx}_2 \\
&= \xi^{xyy}_2 = \xi^{yyx}_2 = \xi^{zzy}_2.
\end{align*}
\]
and
\[
\xi_{2}^{yxy} = \xi_{2}^{yzy} = \xi_{2}^{zxx} \\
\xi_{2}^{xzx} = \xi_{2}^{yx} = \xi_{2}^{zxy} \\
\xi_{2}^{xy} = \xi_{2}^{yz} = \xi_{2}^{zx} \\
\xi_{2}^{xyz} = \xi_{2}^{yxz} = \xi_{2}^{zyx}.
\]

(3.60c)

The injection tensor $\xi_{2}$ is related to the third-order nonlinear susceptibility $\chi^{(3)}$ by $\Im \left[ \chi^{(3)}(\omega; -\omega, \omega, \omega) \right] = \frac{\hbar}{2} \xi_{2}(\omega)$ \[2\]. The spectral dependence of the injection and susceptibility tensors is presented in Figure 3.3 on page 42. At photon energy $\hbar \omega = E_{dg}/2$, the energy supplied by two photons matches the semiconducting gap energy in GaAs, resulting in the onset of two-photon absorption. The onset of absorption from the split-off band occurs at excess photon energy $2\hbar \omega - E_{dg} = 340$ meV, corresponding to the energy splitting in the valence bands due to spin-orbit coupling. The transition from split-off to conduction band contributes the absorption edge near $\hbar \omega \approx 0.9$ eV in the spectra of $\xi_{2}^{xxxx}$ and $\xi_{2}^{xxyy}$; the same feature is present although not strongly apparent in $\xi_{2}^{xyxy}$. The spectra generally decreases with increasing photon energy due to the $\omega^{4}$ term in the denominator of Equation (3.58). At photon energies of 1.6 and 1.75 eV, two additional absorption features are visible. Similar to the $E_{1}$ and $E_{1} + \Delta_{1}$ peaks in the linear response [cf. Figure 3.1 on page 37], these stem from the high JDOS for absorption from the heavy- and light-hole bands in the $\Gamma$–L valley.

For spin injection, the rate of two-photon injection is given by
\[
\hat{S}_{2}^{a}(\omega) = \zeta_{2}^{abde}(\omega) E^{b}(-\omega) E^{c}(-\omega) E^{d}(\omega) E^{e}(\omega).
\]

(3.61)

The microscopic expression for the response pseudotensor $\zeta_{2}$ is
\[
\zeta_{2}^{abde}(\omega) = \left( -\right) \frac{\pi e^{4}}{h^{4} \omega^{4}} \sum_{c,c',v} \int \frac{d^{3}k}{8\pi^{3}} S_{c,c',v}^{a}(k) w_{cv}^{bc*}(k) w_{c'v}^{de}(k)
\times \left( \delta[\omega_{cv}(k) - 2\omega] + \delta[\omega_{cv}(k) - 2\omega] \right).
\]

(3.62)

By symmetry the pseudotensor $\zeta_{2}$ has 48 nonzero and two independent components:
\[
\zeta_{2}^{xxy} = \zeta_{2}^{yyz} = \zeta_{2}^{zxx} \\
\zeta_{2}^{xzx} = \zeta_{2}^{yx} = \zeta_{2}^{zxy} \\
\zeta_{2}^{xy} = \zeta_{2}^{yz} = \zeta_{2}^{zx} \\
\zeta_{2}^{xyz} = \zeta_{2}^{yxz} = \zeta_{2}^{zyx}.
\]
\[ \begin{align*}
\zeta_{xxz} &= -\zeta_{xyy} = -\zeta_{yxx} = -\zeta_{zyz} \\
\zeta_{xyz} &= -\zeta_{yyz} = -\zeta_{zxy} \\
\zeta_{zzx} &= -\zeta_{zxx} = -\zeta_{zyy} \\
\zeta_{xzy} &= -\zeta_{xyx} = -\zeta_{yyx} \\
\zeta_{zyz} &= -\zeta_{zyy} = -\zeta_{zxx},
\end{align*} \] (3.63a)

and
\[ \zeta_{xyzz} = \zeta_{yxxx} = \zeta_{zxyy} \\
\zeta_{yyzz} = \zeta_{xzzzz} = \zeta_{xxzy} \\
\zeta_{yyzz} = \zeta_{xzzz} = \zeta_{zzxy} \\
\zeta_{xyzz} = \zeta_{yxxx} = \zeta_{zxyy} \\
\zeta_{yyzz} = \zeta_{xzzzz} = \zeta_{xxzy} \\
\zeta_{yyzz} = \zeta_{xzzz} = \zeta_{zzxy} \\
\zeta_{xyzz} = \zeta_{yxxx} = \zeta_{zxyy} \\
\zeta_{yyzz} = \zeta_{xzzzz} = \zeta_{xxzy} \\
\zeta_{yyzz} = \zeta_{xzzz} = \zeta_{zzxy} \\
\zeta_{xyzz} = \zeta_{yxxx} = \zeta_{zxyy}. \] (3.63b)

The components \( \zeta_{xyzz} \) and \( \zeta_{xxyzz} \) are purely imaginary in the independent-particle approximation. Their spectral dependence and their decomposition into contributions from heavy-hole, light-hole, and split-off transitions are presented in Figure 3.4 on the following page. Both spectra are dominated by the contribution from the heavy-hole transition and have positive values in the range of energy considered. The spin injection peaks near the onset of absorption from the split-off band and then decreases significantly, and has a second peak at the \( E_1 \) resonance. For the heavy-hole band contribution at low energy, there is roughly a factor of two difference between \( \Im [\zeta_{xyzz}] \) compared to \( \Im [\zeta_{xxyzz}] \). This ratio, as I will present below, corresponds to an isotropic heavy-hole contribution. On the contrary, transitions from the light-hole and split-off bands contribute almost identically to \( \Im [\zeta_{xyzz}] \) and \( \Im [\zeta_{xxyzz}] \): The light-hole contribution is positive and proportional to the JDOS at the onset of absorption, switches sign near \( \hbar \omega \approx 1.1 \text{eV} \), and features a negative peak at the \( E_1 + \Delta_1 \) resonance. The split-off contribution is negative since it is dominated by a two-band process, involving an intraband transition and a interband transition. This contribution follows the spin selection rules of the one-photon process and is weak due to the small JDOS associated with the split-off band. It peaks at about 100 meV above the onset, then dies off. The contributions from heavy- and light-hole bands at the \( E_1 \) resonance at \( \hbar \omega \approx 1.7 \text{eV} \) are opposite according to selection rules in \( \Gamma-L \) valley.

Convenient expressions for carrier and spin injection are obtained when using the
Figure 3.3: The two-photon absorption tensor $\xi_2(\omega)$ and the imaginary part of the degenerate third-order nonlinear susceptibility $\chi^{(3)}(\omega, -\omega, \omega, \omega)$. Black, dashed red, and dotted blue curves: independent components of $\xi_2^{abcd}$ in GaAs, as a function of photon energy $\hbar \omega$.

Figure 3.4: Independent components of the two-photon spin-injection pseudotensor $\zeta_2(\omega)$ in GaAs: (a) $\text{Im} \left[ \zeta^{xxyzzz}_{2e}(\omega) \right]$, (b) $\text{Im} \left[ \zeta^{xxyzzz}_{2e}(\omega) \right]$. Solid black, dashed red, and dotted blue curves: contributions from transitions originating from the heavy-hole, light-hole, and split-off bands, respectively; green thick curves: total from all bands.
zinc-blende symmetry to rewrite Equations (3.57) and (3.61). Two-photon carrier injection takes the form

\[
\dot{n}_2 = \zeta^{xxxx}_2 \left[ \mathbf{E}(-\omega) \cdot \mathbf{E}(\omega) \right] \left[ \mathbf{E}(-\omega) \cdot \mathbf{E}(\omega) \right] \\
+ \delta' \zeta^{xxxx}_2 \left[ \mathbf{E}(-\omega) \times \mathbf{E}(\omega) \right] \cdot \left[ \mathbf{E}(-\omega) \times \mathbf{E}(\omega) \right] \\
- \sigma \zeta^{xxxx}_2 \Xi^{abcd} E^a(-\omega) E^b(-\omega) E^c(\omega) E^d(\omega),
\]

(3.64)

where \( \delta' = \delta - \sigma/6 \), the anisotropy \( \sigma \) and linear-circular dichroism \( \delta \) \([43, 44]\) are given by

\[
\sigma = \frac{\zeta^{xxxx}_2 - 2\zeta^{xyxy}_2 - \zeta^{xxyy}_2}{\zeta^{xxxx}_2},
\]

(3.65)

\[
\delta = \frac{\zeta^{xxxx}_2 - 2\zeta^{xyxy}_2 + \zeta^{xxyy}_2}{2\zeta^{xxxx}_2} = \frac{\zeta^{xxyy}_2}{\zeta^{xxxx}_2} + \frac{\sigma}{2},
\]

(3.66)

\( \Xi \) is the symmetric and traceless fourth-rank tensor

\[
\Xi^{abcd} = \frac{1}{3} \delta^{ab} \delta^{cd} + \frac{1}{3} \delta^{ac} \delta^{bd} + \frac{1}{3} \delta^{ad} \delta^{bc} - \Sigma^{abcd},
\]

(3.67)

and in the last expression the \( \delta \)'s are Kronecker deltas and \( \Sigma \) is the fourth-rank generalized Kronecker tensor, given in the crystal axes basis by

\[
\Sigma^{abcd} = \begin{cases} 
1 & a = b = c = d, \\
0 & \text{otherwise.}
\end{cases}
\]

(3.68)

The linear-circular dichroism \( \delta \) describes a change in the two-photon absorption coefficient between linearly- and circularly-polarized light. The anisotropy \( \sigma \) describes the dependence on crystal orientation; \( \sigma = 0 \) for materials with an isotropic band structure model \([43, 44]\). The spectra of \( \sigma \) and \( \delta \), obtained from the 30-band \( \mathbf{k} \cdot \mathbf{p} \) model, are presented in Figure 3.5(a) on the next page. With increasing photon energy, the calculated \( |\sigma| \) increases in the energy range \( \hbar \omega = 0.75-1.45 \text{ eV} \) and decreases in the energy range \( \hbar \omega = 1.45-2 \text{ eV} \). The smallest value of the anisotropy parameter is \( \sigma \approx -0.32 \) near the band edge;\(^2\) the maximal value is \( \sigma = -0.65 \) at \( \hbar \omega = 1.45 \text{ eV} \). The decrease at larger photon energy corresponds with the \( E_1 \) resonant feature in the two-photon absorption coefficient. The calculated linear-circular dichroism varies from \( \delta \approx 0.14 \) near the band edge to \( \delta \approx 0.3 \) at high photon energy, with a dip to \( \delta \approx 0.02 \) at \( \hbar \omega = 0.95 \text{ eV}, \) \( 50 \text{ meV} \) above the onset of absorption from the split-off band. A value of \( \delta' = 0 \) would indicate

\(^2\) The band-edge limits for \( \sigma \) and \( \delta \) are of the undetermined 0/0 form. The values quoted are from 3\text{ meV} above the band edge, where convergence is numerically checked.
Figure 3.5: (a) Anisotropy $\sigma(\omega)$ (plain black) and linear-circular dichroism $\delta(\omega)$ (dashed red) of the two-photon absorption in GaAs. (b) Anisotropy $\alpha(\omega)$ of the two-photon electron spin injection in GaAs.

Figure 3.6: The degree of spin polarization of electrons injected by two-photon absorption of $\sigma^{-}$ light incident along $\langle 001 \rangle$. Solid black, dashed red, and dotted blue curves: DSP for transitions originating from the heavy-hole, light-hole, and split-off bands; green thick curve: total DSP for all bands.
that the two-photon absorption coefficient is identical for linear and circular polarization of light [cf. Equation (3.64)]. In the present work, the smallest calculated value is \( \delta' = 0.1 \) at \( \hbar \omega = 0.95 \text{eV} \), thus linear-circular dichroism is present over the range of photon energy considered.

For two-photon spin injection, Equation (3.61) takes the form

\[
\dot{S}_2 = 2\zeta^{xyzzz}_2 \left[ \mathbf{E}(-\omega) \cdot \mathbf{E}(\omega) \right] \left[ \mathbf{E}(-\omega) \times \mathbf{E}(\omega) \right] \\
- 2\alpha \xi^{xyzzz}_2 \sum_{abcd} E^a(-\omega) E^b(\omega) \left[ \mathbf{E}(-\omega) \times \mathbf{E}(\omega) \right] E^c \hat{x}^d,
\]

(3.69)

where I introduce the anisotropic parameter \( \alpha \) in the spin response,

\[
\alpha = \frac{\xi^{xyzzz}_2 - 2\zeta^{xyzzz}_2}{\xi^{xyzzz}_2},
\]

(3.70)

which is analogous to \( \sigma \) in the carrier response; \( \alpha = 0 \) for an isotropic model [35]. The calculated anisotropy for electronic spin injection in the 30-band model for GaAs is shown in Figure 3.5(b) on the preceding page. The anisotropy \( |\alpha| \) is \( \approx 0 \) near the band edge and increases with photon energy in a range of 700 meV above the band edge. For photon energies near 1.5 eV and above 1.9 eV, the anisotropy is large, \( |\alpha| > 2 \), but the total spin injection is weak; spin injection is strong mostly within 290 meV of the band edge and between the \( E_1 \) and \( E_1 + \Delta_1 \) resonances at \( \hbar \omega \approx 1.65 \text{eV} \) [cf. Figure 3.4 on page 42]. The value of \( \alpha \approx -1.15 \) at \( \hbar \omega \approx 1.65 \text{eV} \) indicates that spin injection making use of the \( E_1 \) resonance is significantly anisotropic.

Two-photon spin polarization injection is characterized by computing the DSP of injected carriers, analogous to one-photon spin injection. Due to the anisotropic terms in \( \dot{n}_2 \) and \( \dot{S}_2 \), the two-photon DSP depends on the orientation of the beam. However, the calculated injection for GaAs shows that anisotropy in the carrier and spin injection are mostly cancelled out in the DSP. It follows from Equation (3.69) that two-photon spin injection is largest for light polarization which maximizes the cross product \( \mathbf{E}(-\omega) \times \mathbf{E}(\omega) \), as is the case in one-photon spin injection.

For \( \mathbf{s}^- \) light, which injects electrons with a spin polarization in the \( \hat{z} \) direction, the degree of electron spin polarization is shown in Figure 3.6 on page 44. The resulting spectrum is very similar to spin injection by one-photon absorption, although three differences stand out. First, band-edge values are modified: the DSP is respectively 47\%, 60\%, and \(-92\%\) for heavy-hole, light-hole, and split-off band transitions. Second, sharp features are softened, in particular around the \( E_1 \) resonance. These two differences are a
consequence of the additional sum over intermediate states in Equation (3.59). Third, the contribution from the split-off band transition actually switches sign and reaches 50% polarization at $h\omega \approx 1.5$ eV.

### 3.3 Response to a bichromatic field:

**Coherent control**

This section considers the injection terms due to an optical field that contains a fundamental frequency and its second harmonic,

$$E(t) = E(\omega)e^{-i\omega t} + E(2\omega)e^{-2i\omega t} + $c.c.$,$

and focuses in particular on the contribution from interference of the one- and two-photon processes. The interference part of the injection rate has the form given in Equation (3.30). The field components $E(\omega)$ and $E(2\omega)$ appearing in this expression are not matched one-to-one with their complex conjugates $E(-\omega)$ and $E(-2\omega)$. As a result, the injection is a function of the phases of the field components. Consider

$$E(\omega) = E_\omega e^{i\varphi_\omega} \hat{e}_\omega,$$

$$E(2\omega) = E_{2\omega} e^{i\varphi_{2\omega}} \hat{e}_{2\omega},$$

where $E_{\omega,2\omega}$ and $\varphi_{\omega,2\omega}$ are real amplitudes and phases of the fields, and $\hat{e}_{\omega,2\omega}$ their polarizations. Then Equation (3.30) becomes

$$\langle \dot{\nu} \rangle_I = E_\omega^2 E_{2\omega} (\Re \Theta_I : \hat{e}_\omega^* \hat{e}_{2\omega} \cos \Delta \varphi + \Im \Theta_I : \hat{e}_\omega^* \hat{e}_{2\omega} \sin \Delta \varphi),$$

where $\Delta \varphi \equiv 2\varphi_\omega - \varphi_{2\omega}$ is a relative phase parameter. This last expression shows that the magnitude and sign of the interference term is controlled by altering the relative phase parameter $\Delta \varphi$ between the beams, provided that this phase parameter is adjustable and remains coherent. This allows the partial modulation of the injection of carrier and spin populations.

The following sections describe carrier population control, spin population control, and photocurrent generation originating from two-color interference.

#### 3.3.1 Carrier population control

The carrier injection due to the field (3.71) is given by

$$\dot{n} = \dot{n}_1(2\omega) + \dot{n}_2(\omega) + \dot{n}_f(\omega),$$

where $\dot{n}_1(2\omega)$, $\dot{n}_2(\omega)$, and $\dot{n}_f(\omega)$ represent the injection due to one- and two-photon processes, and $\dot{n}_f(\omega)$ represents the injection due to the fundamental frequency.
where \( \dot{n}_1(2\omega) \) is the first-order response at frequency \( 2\omega \), \( \dot{n}_2(\omega) \) is the second-order response at frequency \( \omega \), and \( \dot{n}_I(\omega) \) is the interference term. In noncentrosymmetric materials this interference term yields a nonvanishing contribution to the carrier injection rate in bulk [110, 111]. It is given in terms of the field components by

\[
\dot{n}_I(\omega) = -\xi_I^{abc} E^a(-\omega) E^b(-\omega) E^c(2\omega) + \text{c.c.},
\]

(3.75)

where \( \xi_I \) is a third-rank tensor describing the material response. The microscopic expression for \( \xi_I \) is given by Fraser et al. [110]:

\[
\xi_I^{abc}(\omega) = -\frac{i\pi e^3}{\hbar^3 \omega^3} \sum_{cv} \int \frac{d^3k}{8\pi^3} w_{cv}^{ab}(k) v^c_{cv}(k) \delta[\omega_{cv}(k) - 2\omega].
\]

(3.76)

Under zinc-blende symmetry, only one independent nonzero component exists [46]:

\[
\xi_I^{xyz} = \xi_I^{xyz} = \xi_I^{yzx} = \xi_I^yxz = \xi_I^zxy = \xi_I^{zyx}.
\]

(3.77)

In the independent-particle approximation this component is purely real. This quantity and the imaginary part of the second-order susceptibility are connected by the relation

\[
\text{Im} \left[ \chi^{(2)}(-2\omega; \omega, \omega) \right] = \frac{\hbar}{2} \xi_I(\omega) \quad [110];
\]

\( \xi_I^{xyz} \) calculated from the 30-band \( \mathbf{k} \cdot \mathbf{p} \) model is shown in Figure 3.7 on page 48.

The ratio \( R = \dot{n}_I/(\dot{n}_1 + \dot{n}_2) \) quantifies the relative change in the carrier injection due to the interference. The ratio is maximal when the fields have opposite circular polarization, propagate along the \( \langle 111 \rangle \) crystal axis, and have the correct phase relation [46, 112]:

\[
R = \frac{2\xi_I^{xyz}(\omega)}{\sqrt{3\xi_I^{xx}(2\omega)\xi_I^{xx}(\omega)\left(1 - \frac{1}{3}\sigma(\omega) - \delta'(\omega)\right)}}.
\]

(3.78)

This expression is computed from the calculated response tensors that have been presented for one-photon absorption, two-photon absorption, and population control. The ratio is 17% for photon energy 100 meV above the onset of absorption and increases with excess photon energy until a peak value of 38% at the \( E_1 \) resonance.

Experimentally, Fraser et al. have detected the change in the differential transmission due to the interference term. Their experiment used a wavelength 1550 nm, corresponding to 800 meV [110]. The \( \mathbf{k} \cdot \mathbf{p} \) model calculation gives a ratio \( R \) of 19% at \( \hbar \omega = 800 \) meV and 38% at the \( E_1 \) resonance, where it peaks. The ratio is thus twice as large at \( \hbar \omega = 1.6 \) eV than at \( \hbar \omega = 0.8 \) eV, indicating that population control would be more effective near the \( E_1 \) resonance.
Figure 3.7: The population control tensor $\xi_I$ and the imaginary part of the second-order susceptibility $\chi^{(2)}$ in GaAs.

Figure 3.8: The spectral dependence of the spin control tensor $\zeta_I$ in GaAs. The wiggles above 1.7 eV is numerical noise and not physical. On the other hand, the sharp features near 1.6 eV are converged numerically and steam from absorption in the $\Gamma \rightarrow L$ region of the Brillouin zone.
3.3.2 Spin population control

Analogous to Equation (3.74) for carrier injection, the rate of spin injection is given by

\[ \dot{S} = \dot{S}_1(2\omega) + \dot{S}_2(\omega) + \dot{S}_I(\omega). \]  

(3.79)

The one- and two-photon spin injection terms have been described in Sections 3.2.1 and 3.2.2, and the spin-injection interference term

\[ \dot{S}_a^I(\omega) = \zeta_{abcd}^{I(E)_{E}} I^{E} b (\omega) E_c (-\omega) E_d (2\omega) + \text{c.c.} \]  

(3.80)

is described in the following.

Within the multiple-scale approach, the spin control tensor \( \zeta_{abcd}^{I(E)_{E}} \) is given by

\[
\zeta_{abcd}(\omega) = (-) \frac{i\pi e^3}{2\hbar^3 \omega^3} \sum_{c,c',v} \int \frac{d^3k}{8\pi^3} S_{ca}^{I(E)_{E}}(k) u_{c'}^{E}(k) v_{cv}^{E}(k) \times \left( \delta_{[(\omega_{cv}(k) - 2\omega]} + \delta_{[(\omega_{cv}(k) - 2\omega)]} \right). \]  

(3.81)

Using zinc-blende symmetry yields two independent nonzero components, purely imaginary in the single-particle approximation [46]:

\[
\zeta_{xxyy}^{I(E)_{E}} = \zeta_{yyzz}^{I(E)_{E}} = \zeta_{zzxx}^{I(E)_{E}} = -\zeta_{xzzx}^{I(E)_{E}} = -\zeta_{xzyy}^{I(E)_{E}} = -\zeta_{zyzy}^{I(E)_{E}}. \]  

(3.82a)

\[
\zeta_{xyyx}^{I(E)_{E}} = \zeta_{yzzy}^{I(E)_{E}} = \zeta_{zxxz}^{I(E)_{E}} = -\zeta_{xzxz}^{I(E)_{E}} = -\zeta_{xyxy}^{I(E)_{E}} = -\zeta_{zyzy}^{I(E)_{E}}. \]  

(3.82b)

They are shown in Figure 3.8 on page 48.

3.3.3 Charge and spin current injection

The charge current due to the cross-term of transition amplitudes from \( \omega \) and \( 2\omega \) beams has an injection rate given by

\[ \dot{J}_a^I = \eta_{abcd}^I(\omega) E^b(-\omega) E^c(-\omega) E^d(2\omega) + \text{c.c.} \]  

(3.83)
following Equation (3.30); the fourth-rank tensor $\eta_I$ describes 1+2 current injection and includes contributions from both electrons and holes. The current-injection tensor has the form

$$
\eta_{I;e}^{abcd}(\omega) = (-) \frac{i\pi e^4}{h^3\omega^3} \sum_{cv} \int \frac{d^3k}{8\pi^3} v_{cv}^a(k) w_{cv}^{b*}(k) v_{cv}^d(k) \delta[\omega_{cv}(k) - 2\omega],
$$

(3.84)

which is obtained in the FGR approach from Equation (3.34) by substituting $\vartheta$ with the current operator $ev^a$ [20]. Similarly, the expectation value for the spin-current operator $K_{ab} = \langle v^a S^b + S^a v^b \rangle / 2$ is given by

$$
\dot{K}_{ab} = \mu_{I;e}^{abcd}(\omega) E^c(-\omega) E^d(-\omega) E^e(2\omega) + c.c.,
$$

(3.85)

where the fifth-rank pseudotensor $\mu_I$ follows from Equation (3.38) in the multiple-scale approach:

$$
\mu_{I;e}^{abcd}(\omega) = (-) \frac{i\pi e^3}{2h^3\omega^3} \sum_{cvv'}^t \int \frac{d^3k}{8\pi^3} K_{cv}^{ab}(k) w_{cv}^{d*}(k) v_{cv}^e(k)
$$

$$
\times \left( \delta[\omega_{cv}(k) - 2\omega] + \delta[\omega_{cv'}(k) - 2\omega] \right).
$$

(3.86)

The quantities $K_{mn}(k)$ denote the matrix elements of the spin-current operator between the Bloch states of bands $m$ and $n$ at wavevector $k$:

$$
\langle mk \mid \frac{1}{2} (vS + Sv) \mid nk' \rangle = K_{mn}(k) \delta(k - k').
$$

(3.87)

They are evaluated in terms of matrix elements of the velocity and spin operators by inserting a resolution of unity between those operators on the left-hand side.

The nonzero components of $\eta_I$ and $\mu_I$ in GaAs are plotted in Figures 3.9 and 3.10 on page 52. By definition [cf. Equation (3.83)], the current-injection tensor is invariant under the exchange of the second and third indices: $\eta_{I;e}^{abcd} = \eta_{I;e}^{acbd}$, and similarly $\mu_{I;e}^{abcd} = \mu_{I;e}^{adbc}$. Under the symmetry operations of the zinc-blende structure, the independent nonzero tensor components are for current injection

$$
\eta_{I;e}^{xxxx} = \eta_{I;e}^{yyyy} = \eta_{I;e}^{zzzz},
$$

(3.88a)

$$
\eta_{I;e}^{xyyx} = \eta_{I;e}^{yzzy} = \eta_{I;e}^{zxxz} = \eta_{I;e}^{yxxy} = \eta_{I;e}^{zyyz},
$$

(3.88b)
and
\[ \eta^{xxyy}_I = \eta^{yyzz}_I = \eta^{zzxx}_I = \eta^{xxzz}_I = \eta^{xyyz}_I = \eta^{yzzy}_I = \eta^{zxzx}_I = \eta^{xzxz}_I \]
(3.88c)
and for spin current injection
\[ \mu^{xxxy}_I = \mu^{yyzx}_I = \mu^{zzzy}_I = \mu^{zzyx}_I = \mu^{xyzx}_I = \mu^{zyxy}_I = \mu^{zxxyz}_I = \mu^{xzyxz}_I \]
(3.89a)
\[ \mu^{xyxx}_I = \mu^{yxxy}_I = \mu^{yxzx}_I = \mu^{xxxy}_I = \mu^{yzyy}_I = \mu^{zyzy}_I \]
(3.89b)
\[ \mu^{xyyz}_I = \mu^{yxzy}_I = \mu^{zxyz}_I = \mu^{zyxz}_I = \mu^{zxzy}_I = \mu^{zyx}_I \]
(3.89c)
\[ \mu^{xyzz}_I = \mu^{yzzx}_I = \mu^{zxzy}_I = \mu^{zyxz}_I = \mu^{zyxx}_I = \mu^{zyzy}_I \]
(3.89d)
\[ \mu^{xyzx}_I = \mu^{yzyx}_I = \mu^{zxzy}_I = \mu^{zyx}_I = \mu^{zyy}_I = \mu^{zyx}_I \]
(3.89e)
and
\[ \mu^{xyyz}_I = \mu^{yzzx}_I = \mu^{zxzy}_I = \mu^{zyxz}_I = \mu^{zyxx}_I = \mu^{zyyy}_I \]
(3.89f)
Figure 3.9: The “1+2” current-injection tensor $\eta_{\alpha \beta \gamma \delta}^I(\omega)$ in GaAs as a function of the fundamental photon energy $\hbar \omega$. Thin lines show the independent components by including only the electronic current; thick lines are the total injected current, including holes.

Figure 3.10: Independent components of $\mu_{\alpha \beta \gamma \delta \epsilon}^I(\omega)$, the spin-current-injection pseudotensor, in GaAs. Thick lines: total injected spin current; thin lines: electron contribution only.
3.3.4 Anisotropy and disparity

Analogous to $\sigma$ and $\delta$ in two-photon absorption, I introduce two dimensionless parameters to characterize the current injection: $s$, the anisotropy, and $d$, the disparity, defined by

\[
\begin{align*}
    s &\equiv \frac{\eta_{I}^{xxx} - 2\eta_{I}^{xxyy} - \eta_{I}^{xyyx}}{\eta_{I}^{xxx}}, \\
    d &\equiv \frac{\eta_{I}^{xxx} - 2\eta_{I}^{xxyy} + 2\eta_{I}^{xyyx}}{3\eta_{I}^{xxx}} = \frac{\eta_{I}^{xyyx}}{\eta_{I}^{xxx}} + \frac{s}{3}.
\end{align*}
\]  

Equation (3.83) is then rewritten in terms of $d$ and $s$, which yields

\[
\dot{J} = \eta_{I}^{xxx} E(-\omega) [E(-\omega) \cdot E(2\omega)] - d\eta_{I}^{xxx} E(-\omega) \times [E(-\omega) \times E(2\omega)] - s\eta_{I}^{xxx} \Xi^{abcd} E^{a}(-\omega) E^{b}(-\omega) E^{c}(2\omega) \hat{x}^{d} + \text{c.c.,} \tag{3.92}
\]

with $\Xi$ given by Equation (3.67). The first and second terms correspond to current injection due to polarization vectors that are either parallel or perpendicular, respectively. The disparity parameter $d$ characterizes how current injection differs between those two polarization configurations. The third term is the non-isotropic part of the current injection, characterized by the anisotropic parameter $s$. In an isotropic model, tensor components satisfy $\eta_{I}^{xxx} = 2\eta_{I}^{xxyy} + \eta_{I}^{xyyx}$ and thus $s = 0$ [55]. The parabolic-band model originally considered by Atanasov et al. gives $\eta_{I}^{xyyx} = 0$ and thus $d = 0$ [20].

Spectra of the dimensionless quantities $d$ and $s$ are plotted in Figure 3.11 on page 54. The anisotropy $s$ is $-0.2$ near the band edge, plateaus for $\approx 200$ meV above the band edge, decreases linearly with photon energy between $\hbar\omega \approx (E_g + \Delta_0)/2$ and $\hbar\omega \approx E_1/2$, reaching $-0.6$, and increases at higher photon energy. The anisotropies associated with the electron and hole currents are reinforcing and negative in the entire energy range considered in the present work. The disparity $d$ is $0.07$ near the band edge, quickly drops and reaches a minimum of $-0.16$ at $\hbar\omega \approx (E_g + \Delta_0)/2$, then increases with photon energy, changing sign and reaching a shoulder at $\hbar\omega \approx E_1/2$, where it plateaus at around $0.15$ for higher photon energy. The value of $d$ is greatly influenced by the detail of the hole current: the disparities associated with the electron and hole currents have opposite signs, with the exception of photon energies above the $E_1$ resonance.
Figure 3.11: Anisotropy $s(\omega)$ (plain black) and parallel-perpendicular polarization disparity parameter $d(\omega)$ (dashed red) of the 1+2 current injection in GaAs. Thin lines describe the current due to the electron only; thick lines include both electron and hole contributions.

Figure 3.12: Carrier motion and spin polarization in the two-color coherent control scheme, for light beams incident on $\langle 001 \rangle$ with (a) co-linear, (b) cross-linear, and (c) co-circular polarizations. The blue (red) arrows indicate the polarization state of the fundamental beam at $h\omega$ (second harmonic beam at $2h\omega$). Black-contour arrows indicate charge motion, and small arrows in orange-filled circles represent the direction of spin polarization. White-filled arrows indicate charge currents, plain black arrows indicate spin-polarized currents, and counter-propagating plain black arrows indicate pure spin currents. The relative strength of a current is represented schematically by its arrow thickness. In (a,b), while varying $\Delta \varphi$ the maximal values of the white-filled, charge currents and of the black-filled, spin currents occur out of phase by $\pi/2$. In (c), the velocity and spin components in the $xy$ plane rotate with $\Delta \varphi$. 
3.3.5 Configurations and characterizations

Figure 3.12 on page 54 presents different configuration scenarios in a typical 1+2 coherent control experiment in semiconductors. For a (001)-grown sample, the laboratory coordinates coincide to the crystallographic coordinates. In early experiments [21, 27], the current response with beams co-linearly polarized along ⟨001⟩ was studied [Figure 3.12(a)]. For this configuration the rates of current and spin-current injection yield a charge current parallel with the light polarization, and a spin current in perpendicular directions. Stronger signals occur with the polarization axes directed along ⟨110⟩ [9] or along the bonds in the ⟨111⟩ direction [46], although I do not sketch the resulting currents here.

Current injection is typically characterized by the swarm velocity, the average velocity of the injected carriers [2, 113]. The swarm velocity is defined as

$$v_s = \frac{\dot{J}}{en},$$

where $\dot{J}$ follows from Equation (3.83), and the carrier injection is

$$\dot{n} = \dot{n}_1(2\omega) + \dot{n}_2(\omega),$$

where $\dot{n}_1$ originates from one-photon absorption of the $2\omega$ beam and $\dot{n}_2$ from two-photon absorption of the $\omega$ beam, neglecting the interference term in the population. The swarm velocity is maximized when the relation between the phases $\varphi_\omega$ and $\varphi_{2\omega}$ satisfies $\sin(\Delta \varphi) = 1$, and one- and two-photon absorption are balanced: $\dot{n}_1(2\omega) = \dot{n}_2(\omega)$. To achieve this, the field amplitudes must satisfy $E^4_{\omega}/E^2_{2\omega} = \xi_1(2\omega)/\xi_2(\omega)$ or, equivalently, $I^2_\omega/I_{2\omega} = (c/2\pi)\xi_1(2\omega)/\xi_2(\omega)$ [55]. This yields the following maximal swarm velocities: with both beams co-linearly-polarized in the ⟨100⟩ direction,

$$v_{s,\text{max}}^{(100)} = \frac{\text{Im} [\eta_f^{xxxx}(\omega)]}{e \sqrt[\xi_1^{xxxx}(2\omega)\xi_2^{xxxx}(\omega)}},$$

in the ⟨110⟩ direction,

$$v_{s,\text{max}}^{(110)} = \frac{\text{Im} [\eta_f^{xxxx}(\omega)] \left(1 - \frac{1}{2} s(\omega)\right)}{e \sqrt[\xi_1^{xxxx}(2\omega)\xi_2^{xxxx}(\omega)} \left(1 - \frac{1}{2} \sigma(\omega)\right)},$$

and in the ⟨111⟩ direction,

$$v_{s,\text{max}}^{(111)} = \frac{\text{Im} [\eta_f^{xxxx}(\omega)] \left(1 - \frac{2}{3} s(\omega)\right)}{e \sqrt[\xi_1^{xxxx}(2\omega)\xi_2^{xxxx}(\omega)} \left(1 - \frac{2}{3} \sigma(\omega)\right)}.$$
In the above, $\sigma$ is the two-photon anisotropy parameter from Section 3.2.2.

Figure 3.13 on page 57 presents field intensities required to achieve maximal charge current injection with co-linearly-polarized beams, and the resulting swarm velocity. The necessary ratio of $I_1^2/I_2\omega$ to achieve balanced absorption, $\dot{n}_1(2\omega) = \dot{n}_2(\omega)$, is shown in Figure 3.13(a). The frequency dependence of this quantity is flat for the most part, except at the $E_1$ and $E_1 + \Delta_1$ absorption features. The shoulders due to $E_1$ and $E_1 + \Delta_1$ are sharp in one-photon absorption but smeared out in two-photon absorption. Thus $I_\omega$ needs to be increased to compensate the strong increase in one-photon absorption at the shoulders.

Using balanced absorption, the resulting maximal swarm velocity of the injected current is shown in Figure 3.13(b) for light linearly-polarized along $\langle 100 \rangle$ and $\langle 111 \rangle$. At the band edge at $\hbar\omega = E_g/2$, only stationary carriers are injected, sitting at the extremum of their respective band. With increasing photon energy, electron and hole swarm velocities increase significantly within only a couple hundreds of meV above the absorption edge, and reach over 100 km/s for the holes and 400 km/s for the electrons. At $\hbar\omega = (E_g + \Delta_0)/2$, sufficient photon energy is provided to induce transitions involving the split-off band, and slow-moving zone-center carriers are injected. The zone-center carriers bring the average velocities of electrons and holes down, but because the density of states at the $\Gamma$ point is small this results only in small cusps in the swarm velocity spectra. The hole swarm velocity is further reduced in this energy region due to the warping of the light-hole band some tens of meV away from the absorption edge.

The frequency dependence of the hole swarm velocity is generally flatter than that of the electron. The curving down of the conduction band away from the $\Gamma$ point means that electrons injected at higher photon energy have smaller velocities. This leads to a steady drop of the electron swarm velocity in the energy range $\hbar\omega = 1.1$–1.5 eV. The dips in the swarm velocities around $\hbar\omega \approx 1.55$ eV and 1.65 eV are due to the high JDOS associated with the $E_1$ and $E_1 + \Delta_1$ absorption features. A large number of carriers is injected in the $\Gamma$–$L$ direction of the Brillouin zone with low injection velocities; this includes stationary carriers injected at the $L$ point. At photon energies above $\hbar\omega \approx 1.7$ eV, most of the injection occurs in the $\Gamma$–$X$ direction. In that range, holes have particularly high velocities, making up more than 40% of the total generated current.

The spectra of the electron swarm velocity for $\langle 100 \rangle$ and $\langle 111 \rangle$ polarization of light are similar. The difference in the average electron velocity induced by polarization along $\langle 100 \rangle$ (thick black curve) or $\langle 111 \rangle$ (plain brown curve) becomes significant only at high
Figure 3.13: Optical charge-current injection in GaAs for co-linearly polarized $\omega$ and $2\omega$ beams: (a) The calculated ratio $I_2^2/I_{2\omega}$, as a function of the fundamental photon energy $\hbar\omega$, required to achieve $\dot{n}_1(2\omega) = \dot{n}_2(\omega)$ and a maximal swarm velocity. This ratio diverges at the band edge. (b) Maximal swarm velocity for electrons (plain black) and holes (dashed red) with the polarization axis along $\langle 100 \rangle$; the thin brown curves are with the polarization axis along $\langle 111 \rangle$. The experimental configuration is as in Figure 3.12(a).
photon energies, $\hbar \omega \gtrsim 1.6\text{eV}$. The stronger current injection obtained when \langle 111 \rangle is chosen as the polarization axis cannot be explained by larger electron velocities. Instead, this results from the anisotropy occurring in two-photon absorption, the last term in Equation (3.64), which induces an increased number of injected carriers when the beams are polarized along the bonds. For the hole contribution, while the same effect due to two-photon anisotropy occurs, the hole current also benefits from increased hole swarm velocities for the \langle 111 \rangle polarization: a $9\%$ increase at $\hbar \omega = 0.95\text{eV}$ and $30\%$ at $1.5\text{eV}$, where this anisotropy is the largest.

### 3.3.6 Normal currents

The injection of a current normal to the surface has been predicted by Bhat and Sipe for beams co-linearly polarized along \langle 11\bar{2} \rangle incident on a \langle 111 \rangle surface [46]. This normal component is given by

$$\dot{J}_I = \frac{\sqrt{2}}{3} s \Im \left[ \eta_{xxxx} \right] E_\omega^2 E_{2\omega} \hat{k} + 2 \left( 1 - \frac{1}{2} s \right) \Im \left[ \eta_{xxxx} \right] E_\omega^2 E_{2\omega} \hat{e}_{2\omega},$$

(3.98)

where $\hat{k}$ points in the direction opposite light propagation [46]. Thus the normal component is proportional to the anisotropic part $s\eta_{xxxx}$ of the current-injection tensor and accompanies an in-plane component. The in-plane component is generally larger than the normal component due to the small and negative value of the anisotropy $s$ as calculated for GaAs [cf. Figure 3.11 on page 54]. A stronger normal component of the current is found for opposite-circularly polarized beams incident on the same, \langle 111 \rangle crystal cut. In this configuration, the current is given by

$$\dot{J}_I = \frac{2}{3} s \Im \left[ \eta_{xxxx} \right] E_\omega^2 E_{2\omega} \hat{k}.$$

(3.99)

The normal term is the only component of the current, and is a factor $\sqrt{2}$ larger than the normal component from co-linear polarization axes along \langle 11\bar{2} \rangle. Due to the small value of $s \approx -0.2$ near the band edge, this current is an order of magnitude smaller than the corresponding current for co-circularly polarized beams. However, at the $E_1$ resonance $|s|$ is increased by a factor of 3 compared to the band-edge value, increasing the magnitude of the normal current by the same amount.
3.4 Conclusion

In conclusion, I have presented full-band structure calculations of optical injection processes in GaAs. Carrier and spin injection have been described for both one- and two-photon absorption, including anisotropic and dichroic effects in the two-photon absorption coefficients. Carrier, spin, current, and spin current injection by two-color, $\omega$ and $2\omega$ coherent control have also been presented.

Calculations of response tensors for these all-optical effects were performed over the full Brillouin zone using a 30-band $\mathbf{k} \cdot \mathbf{p}$ model. I considered the spectral dependence in the range of photon energy $\hbar \omega = 0$–$4$ eV for linear response tensors and $\hbar \omega = 0$–$2$ eV for nonlinear response. In comparison, previous studies considered only zone-center excitation near the band edge. Moreover, calculations using a full band structure model gives access to the conduction-band valleys at the $\Gamma$, $X$, and $L$ symmetry points. The contribution from the $\Gamma$–$L$ region of the Brillouin zone yields the $E_1$ and $E_1 + \Delta_1$ critical points in the optical spectra. I find that significant spin polarizations and spin currents are achievable at photon energies corresponding to these resonances. Anisotropic effects appear in full-band structure calculations and contribute to stronger two-photon spin injection and two-color current injection for light incident along $\langle 111 \rangle$. The effects are more pronounced at energies matching the $E_1$ resonance. Two-photon carrier injection also exhibit anisotropy, and the average electron velocity and spin per injected carrier is not strongly sensitive to the crystal orientation.
Chapter 4

Carrier, spin, current, and spin current injection in Ge

The conduction-band energy minimum in Ge is at the L point, while injection processes across the direct gap occurs at the Γ point. The Γ → L scattering time for electrons, estimated at 230 fs [114], is of the same order of magnitude as typical pulse duration times appearing in optical spin injection and control experiments [5, 27, 35, 40, 41, 47, 49, 115–118]. In GaAs, the spin relaxation time for holes is typically much shorter than for electrons [51, 52], and so the hole contributions to spin population and spin current injection are often neglected [35, 36, 45]. For the same experiments in Ge, intervalley scattering is expected to rapidly take the electrons away from their injection point in k space, leaving the holes as the only zone-center carriers. Thus, the injection of hole spins, currents, and spin currents is expected to play a significantly larger role in Ge than in GaAs.

In this chapter, the optical injection of spin, current, and spin current in bulk Ge is investigated theoretically within the full-Brillouin zone, 30-band $k \cdot p$ model. I present the degree of spin polarization of electrons and holes photoexcited by monochromatic circularly-polarized light through one- and two-photon absorption processes. I also quantify the electron and hole currents that are injected and coherently controlled by interference of one- and two-photon transition amplitudes under simultaneous $\omega$ and $2\omega$ irradiation. The spectral dependence of the corresponding optical response tensors is calculated, including anisotropy and dichroism effects. The range of excitation energy considered is 0–3.5 eV, giving access to injection at the $E_1$ resonance.

The chapter is divided as follows. Calculations of carrier and spin injection for both
one- and two-photon absorption are presented in Section 4.1. Charge and spin currents injected by quantum interference and coherent control are presented in Section 4.2. A careful description of the hole contribution to these effects is included throughout. Results are summarized in Section 4.3.

4.1 Carrier and spin injection

4.1.1 One-photon process

In this section, microscopic calculations of spin injection in Ge are presented. The crystal is subjected to irradiation by a monochromatic field of frequency $\omega$, $E(t) = E(\omega)e^{-i\omega t} + \text{c.c.}$, (4.1)

where $E(\omega)$ contains the amplitude and polarization of the field and $\hbar \omega$ is the photon energy. When considering the direct-gap linear response, $\hbar \omega$ is greater than the direct band-gap energy $E_{dg}$. The rate of one-photon spin injection $\dot{S}_1$ is

$$\dot{S}_1^a(\omega) = \zeta_{abc}^1(\omega)E^b(-\omega)E^c(\omega).$$

(4.2)

Roman superscripts indicate Cartesian components along the cubic axes; summation over repeated indices is implied. A standard Fermi’s golden rule (FGR) derivation of $\zeta_{abc}^1(\omega)$ neglects coherences between nearly-degenerate excited states. Because the bandwidth of a typical laser can excite superpositions of states, such coherences must be included to capture the physics. The multiple-scale approach yields an expression for $\zeta_{abc}^1(\omega) = \zeta_{1,e}^{abc}(\omega) + \zeta_{1,h}^{abc}(\omega)$ including coherences [36]. The electron contribution $\zeta_{1,e}^{abc}(\omega)$ and the hole contribution $\zeta_{1,h}^{abc}(\omega)$ are given by

$$\zeta_{1,e}^{abc}(\omega) = -\frac{\pi e^2}{\hbar^2 \omega^2} \sum_{c,c',v} \int \frac{d^3k}{8\pi^3} \chi^a_{cv}(k) v_{cv}(k) v^b_{cv}(k) v^c_{cv}(k) \delta(\omega_{cv}(k) - \omega + \delta[\omega_{cv}(k) - \omega]),$$

(4.3)

where $e = -|e|$ is the charge of the electron. For a given band $m$, the Bloch state $|mk\rangle$ has energy eigenvalue $\hbar \omega_m(k)$. The quantities $v_{mn}(k)$ and $S_{mn}(k)$ denote the matrix elements of the velocity and spin operators between bands $m$ and $n$ at wavevector $k$:

$$\langle mk | v | nk' \rangle = v_{mn}(k) \delta(k - k'),$$

(4.4)

$$\langle mk | S | nk' \rangle = S_{mn}(k) \delta(k - k').$$

(4.5)
When evaluating the velocity operator, the anomalous part arising from spin-orbit coupling is neglected \[ 77 \]. The following definitions are used: \( \omega_{mn}(k) \equiv \omega_{m}(k) - \omega_{n}(k) \), and \( \bar{\omega}_{mn}(k) \equiv (\omega_{m}(k) + \omega_{n}(k)) / 2 \). When a band index \( c \) or \( v \) is used, it is understood that the corresponding summation is restricted only to conduction or valence bands, respectively. The prime on the summation in Equation (4.3) indicates an additional restriction to degenerate or quasidegenerate pairs of states for which \( |\omega_{c'c}| \) (or \( |\omega_{v'v}| \)) < \( \epsilon_{\text{cut}}/\hbar \). The cutoff value of \( \epsilon_{\text{cut}} = 30 \text{meV} \) is chosen because it matches both \( k_B T \) at room temperature and a typical laser linewidth \[ 36 \]. Its repercussions on the results are discussed below.

The macroscopic spin injection \( \dot{S} \) could be due to a large number of weakly-polarized carriers, or a few highly-polarized ones. These two cases are distinguished by calculating the degree of spin polarization (DSP) of the carriers. The DSP, defined by \( \text{DSP}^a = \frac{\dot{S}^a}{\dot{n}} \), where \( \dot{n} \) is the carrier-injection rate, measures the average spin per carrier. From FGR or from a multiple-scale derivation, the one-photon carrier-injection rate is given by

\[
\dot{n}_1(\omega) = \xi_{ab}^1(\omega) E^a(-\omega) E^b(\omega),
\]

with

\[
\xi_{ab}^1(\omega) = \frac{2\pi e^2}{\hbar^2 \omega^2} \sum_{c,v} \int \frac{d^3k}{8\pi^3} \psi^{\dagger c}_{cv}(k) \psi^{b}_{cv}(k) \delta \left[ \omega_{cv}(k) - \omega \right].
\]

For diamond and zinc-blende crystal structures, a single independent component of the carrier-injection tensor exists: \( \xi_{xx}^1 = \xi_{yy}^1 = \xi_{zz}^1 \). It is related to the susceptibility of the material by \( \text{Im} [\chi(\omega)] = \frac{\hbar}{2} \xi_1(\omega) \). The spin-injection pseudotensor also has an unique independent component: \( \zeta_{xyz}^1 = \zeta_{yxz}^1 = \zeta_{zxy}^1 = \zeta_{xyz}^1 = \zeta_{xzy}^1 = \zeta_{yxz}^1 \). Within the independent particle approximation, the quantities \( \xi_{1}^{xx} \) and \( \zeta_{1}^{xyz} \) are respectively purely real and purely imaginary; \( \chi^{xx}(\omega) \) and \( \zeta_{1}^{xyz}(\omega) \) are plotted for Ge in Figure 4.1 on the following page.

As a sample calculation, take the optical field in Equation (4.1) to be left-circularly polarized and propagating along the \(-\hat{z}\) direction, where \( x \), \( y \) and \( z \) describe three general mutually orthogonal right-handed axes, so that \( \mathbf{E}(\omega) = E_0 \mathbf{\hat{\sigma}^-} \), where \( E_0 \) is the field amplitude and \( \mathbf{\hat{\sigma}^\pm} = (\hat{x} \pm i\hat{y}) / \sqrt{2} \). This results in injected spins that are parallel to the \( z \)-axis, independent of how the laboratory coordinate system is oriented with
Figure 4.1: The linear response of Ge as a function of photon energy $\hbar \omega$, computed from the 30-band $\mathbf{k} \cdot \mathbf{p}$ model. The imaginary part of the susceptibility $\chi(\omega)$ is shown in black, with the $E_1$ and $E_1 + \Delta_1$ absorption features identified. The dashed red (dotted blue) curve shows the electron (hole) spin-injection component $\zeta_1^{xyz}(\omega)$. The scale is such that the DSP can be read off by taking the ratio of both quantities.

Figure 4.2: The degree of spin polarization of carriers optically injected in Ge by left-circularly polarized light. The plain black (dashed red) curve shows the electron (hole) spin. Electron spin polarization in GaAs is shown in a thin brown line for reference.

Inset: DSP of the holes for different values of the cutoff energy $\epsilon_{\text{cut}}$. 
respect to crystallographic axes. The degree of spin polarization is given by
\[
\text{DSP}^z(\omega) = \frac{\Im \left( \xi_{xyz}(\omega) \right)}{\xi_{xx}(\omega)}
\]
and is shown in Figure 4.2 on page 63.

At the onset of absorption, injected electrons are 50% spin-polarized. Such a value as been calculated for GaAs, and is understood from the atomic-like states involved in the \(\Gamma\)-point transitions [36]. The top-valence and bottom-conduction bands of Ge share the same character as those of GaAs. The smaller band gap explains a shift of the spectrum towards lower photon energies. The states involved and the transition amplitudes are presented in Figure 4.3(a).

As the photon energy is increased, the DSP of electrons drops but remains above 40% over a range of energy corresponding to the spin-orbit splitting in the valence bands (290 meV in Ge). At photon energy greater than 1.2 eV, the spin polarization is reduced to as low as 10%. This results from a combination of the onset of absorption from the split-off band and a drop in the polarization from the light-hole–mediated transition. A similar behavior has been seen in spin-injection calculations in GaAs [36]. Spin injection is enhanced again near 2.3 eV, which corresponds to the \(E_1\) absorption edge [cf. Figure 4.1 on the previous page]. This stems from a high joint density of states (JDOS) between conduction and heavy-hole bands in the \(\Gamma-L\) valley of the Brillouin zone [cf. the band structure of Ge, Figure 2.2 on page 23].

Optically-injected holes have a spin polarization which is mostly opposite that of the electrons. At the band edge, however, the degree of hole spin polarization is \(-83.3\%\). This value can be understood from the \(\Gamma\)-point states alone. As shown in the diagram of Figure 4.3(a), circularly-polarized light excites electrons from the \(\langle J^z \rangle = 3\hbar/2\) and \(\langle J^z \rangle = \hbar/2\) valence states in a ratio of 3:1. The expectation value of \(S^z\) within those electronic states is respectively \(\hbar/2\) and \(\hbar/6\), leaving holes which are spin-polarized by

\[
\frac{3 \left( -\frac{\hbar}{2} \right) + 1 \left( -\frac{\hbar}{6} \right)}{(\hbar/2)(3+1)} = -\frac{5}{6},
\]

or \(-83.3\%). Thus at the onset of absorption, where coherences between heavy- and light-hole bands are excited, the injected holes are significantly more spin-polarized than the electrons.

The DSP of the holes is decomposed into contributions from different transitions in Figure 4.4 on page 65. Holes injected in the heavy- and light-hole bands are both \(-83.3\%\) spin-polarized at the band-gap energy. The strong polarization survives increasing photon energy until the heavy- and light-hole band splitting reaches the cutoff energy
Figure 4.3: (a) Γ-point states contributing to spin injection. The electron energy levels are labeled by the expectation values $\langle J^z \rangle$ and $\langle S^z \rangle$, in units of $\hbar$, within those states. The solid red arrows show the transitions induced by left-circularly polarized light. Each adjacent number is the relative strength of that transition at the onset of absorption. (b) Band structure of Ge near the zone center. Optical transitions are identified by arrows as follow: plain black, dashed red, and dotted blue curves correspond to the excitation of electrons from the heavy, light, and split-off valence bands, respectively.

Figure 4.4: The decomposition of the degree of hole spin polarization into transitions involving different valence bands. The transitions are identified in Figure 4.3(b).
\( \epsilon_{\text{cut}} = 30 \text{ meV} \), at which point the coherences between states are no longer kept. This corresponds to excitations into the heavy- and light-hole bands that are roughly 50 and 80 meV, respectively, above the absorption edge. Two significant drops in polarization occur at those energies. Note that the value of 30 meV is a nominal number; what is observed close to the fundamental absorption edge ultimately depends on the bandwidth and other properties of the laser, as well as relaxation processes \([\text{cf. the inset of Figure 4.2 on page 63}]\). At the onset of injection into the split-off band, \(-33.3\%\) spin-polarized holes are excited, whereas the light-hole contribution drops and even changes sign. A similar decomposition of the electron spin by transition gives an almost identical result as GaAs, with corresponding shifts in the band-gap and split-off energies \([\text{cf. Chapter 3, Figure 3.2 on page 37}]\).

### 4.1.2 Two-photon process

Two-photon carrier- and spin-injection processes occur at rates proportional to the square of the intensity of the incident field, rather than at rates linearly proportional to the intensity characteristic of one-photon injection processes. The second-order responses are:

\[
\dot{n}_2(\omega) = \xi_2^{abcd}(\omega) E^a(-\omega) E^b(-\omega) E^c(\omega) E^d(\omega), \tag{4.10}
\]

\[
\dot{S}_2^a(\omega) = \zeta_2^{abode}(\omega) E^b(-\omega) E^c(-\omega) E^d(\omega) E^e(\omega). \tag{4.11}
\]

The fifth-rank pseudotensor \( \zeta_2 \) and fourth-rank tensor \( \xi_2 \) describe two-photon spin and carrier injection, respectively. The latter is related to the degenerate part of \( \chi^{(3)} \), the third-order nonlinear susceptibility, by \( \Im \left[ \chi^{(3)}(\omega; -\omega, \omega, \omega) \right] = \frac{\hbar}{3} \xi_2(\omega) \). From a microscopic derivation, either using FGR (as in van Driel and Sipe [2]) or the more general multiple-scale approach, it is given by

\[
\xi_2^{abcd}(\omega) = \frac{2\pi e^4}{\hbar^4 \omega^4} \sum_{c,v} \int \frac{d^3k}{8\pi^3} w_{cv}^{ab}(k) w_{cv}^{cd}(k) \delta \left[ \omega_{cv}(k) - 2\omega \right], \tag{4.12}
\]

where the second-rank tensor \( w_{cv}(k) \) is defined by

\[
w_{cv}^{ab}(k) \equiv \frac{1}{2} \sum_m t_{cm}^a(k) t_{mv}^b(k) + t_{cm}^b(k) t_{mv}^a(k) \frac{\omega_m(k) - \omega_{cv}(k)}{\omega_{cv}(k)}. \tag{4.13}
\]

The quantity \( w_{cv}^{ab}(k) E^a(\omega) E^b(\omega) \) is essentially the degenerate two-photon transition amplitude at \( k \). Without loss of generality, Equation (4.13) has been explicitly symmetrized with respect to the interchange of Cartesian superscripts; they refer to the same electric field component.
Figure 4.5: Imaginary part of the degenerate third-order nonlinear susceptibility $\chi^{(3)}(\omega; -\omega, \omega, \omega)$, in relation to the two-photon injection tensor $\xi_2(\omega)$. Black, dashed red, and dotted blue curves: independent components of $\xi^{abcd}_2$ in Ge; thin brown curve: $\xi^{xxxx}_2$ in GaAs. The horizontal axis uses excess photon energy, defined as $2\hbar\omega - E_{dg}$; the direct-gap energy is 0.9 eV for Ge and 1.519 eV for GaAs.

Figure 4.6: The anisotropy $\sigma(\omega)$ and linear-circular dichroism $\delta(\omega)$ of the two-photon absorption in Ge (thick black curves) and GaAs (thin brown curves).
The two-photon injection tensor \( \xi_2 \) is purely real within the independent particle approximation, and has three independent components: \( \xi_2^{xxxx}, \xi_2^{xxyy}, \) and \( \xi_2^{xyxy} \). In total, 21 nonzero components are formed by cyclic permutations of Cartesian directions, or by exchanging \( a \leftrightarrow b, c \leftrightarrow d, \) or \( ab \leftrightarrow cd \). In an isotropic model, only two of these components are independent, as \( \xi_2^{xxxx} \) satisfies \( \xi_2^{xxxx} = 2\xi_2^{xyxy} + \xi_2^{xxyy} \) \[43\]. The 30-band model gives access to additional bands whose warping effects on the valence bands of Ge creates anisotropy in the two-photon absorption. Hutchings and Wherrett \[44\] presented two parameters, the anisotropy \( \sigma \) and the linear-circular dichroism \( \delta \), to characterize those effects:

\[
\sigma = \frac{\xi_2^{xxxx} - 2\xi_2^{xyxy} - \xi_2^{xxyy}}{\xi_2^{xxxx}}, \\
\delta = \frac{\xi_2^{xxxx} - 2\xi_2^{xyxy} + \xi_2^{xxyy}}{2\xi_2^{xxxx}}.
\]

In the isotropic limit, \( \sigma = 0 \) and \( \delta = \xi_2^{xxyy}/\xi_2^{xxxx} \) \[43\]. Spectra of the two-photon absorption are plotted in Figure 4.5 on page 67, and the anisotropy and linear-circular dichroism parameters in Figure 4.6.

The onset of direct two-photon absorption occurs when \( 2\hbar \omega \) matches the direct energy gap. The edge at 0.29 eV marks the onset of absorption from the split-off band, a transition that is most sensitive to the field polarization; its effect on the \( xyxy \) component is particularly small. These low-energy contributions are transitions taking place at the zone center that are dominated by allowed-forbidden processes. That is, one of the matrix elements appearing in Equation (4.13) is nonvanishing at the \( \Gamma \) point ("allowed"), while the other vanishes there ("forbidden") and only becomes nonzero with nonzero \( k \) vectors, away from zone center. Within a parabolic-band approximation, the spectral dependence of these transitions is of the form \((2\hbar \omega - E_{dg})^{3/2} / (2\hbar \omega)^5 \) \[119\]. Although the 30-band model goes beyond this approximation, individual contributions retain this spectral dependence. The strong low-energy absorption in Ge relative to GaAs is explained by the smaller effective mass of conduction electrons and the smaller band gap in Ge. The smaller effective mass yields a larger density of states, and the smaller band gap yields a smaller denominator in the two-photon transition amplitude. At excess photon energies of 1.5 and 1.7 eV, two additional absorption edges are visible. These stem from an high JDOS for absorption from the heavy- and light-hole bands in the \( \Gamma-L \) valley. The same states are also responsible for the \( E_1 \) and \( E_1 + \Delta_1 \) peaks in the linear response \[\text{cf. Figure 4.1 on page 63}\].
For reasons described in Section 4.1.1, the multiple-scale approach is necessary to derive the two-photon spin-injection pseudotensor, yielding

\[
\zeta_{abcde}^{(h)}(\omega) = (-) \frac{\pi e^4}{\hbar^4 \omega^4} \sum_{c,c',v} \frac{\hbar}{8\pi^3} \rho_{cv} (k) u_{cv}^{ab} (k) w_{cv}^{cd} (k)
\times \left( \delta[\omega_{cv}(k) - 2\omega] + \delta[\omega_{cv}(k) - 2\omega] \right),
\]

(4.16)

and reproducing the result that Bhat et al. obtained from heuristic arguments [35]. Within the independent particle approximation, \(\zeta_2\) is purely imaginary and has two independent components:

\[
\zeta_{xyzzz}^{xxyxz} = -\zeta_{xxzxy}^{xxyxz}
\]

and

\[
\zeta_{xyzzz}^{xyzzz} = -\zeta_{xyyyz}^{xyzzz} = -\zeta_{xzzyz}^{xyzzz} = -\zeta_{xyzyy}^{xyzzz}.
\]

All 48 nonzero elements are related to \(\zeta_{xyzzz}^{xxyxz}\) and \(\zeta_{xyzzz}^{xyzzz}\) by cyclic permutations of the Cartesian directions, exchanging \(b \leftrightarrow c\), exchanging \(d \leftrightarrow e\), or any combination of these. Electron and hole contributions to the two-photon spin injection are shown in Figure 4.7 on page 70.

Note that Equations (4.12) and (4.16) are derived under the assumption that there is no intermediate energy level exactly midway between initial and final states of the absorption process. Therefore, in applying these formulas one has to be particularly careful at energies where \(2\hbar\omega\) is sufficiently high above the gap that an intermediate state exists at an energy \(\hbar\omega\) above the initial state. An investigation of the 30-band \(k \cdot p\) band structure shows that the lowest photon energy at which this occurs is \(\hbar\omega \approx 1.57\) eV, corresponding to an excess photon energy of \(2.24\) eV, and results from a small region of \(k\) space where the lowest conduction band of germanium is resonant with excitations from the heavy-hole into the second conduction band. It was numerically verified that no resonance occurs within the energy range considered in the present work. In a more general theory, resonances could be included with a dressed-band approach, where the finite lifetime of the intermediate state would also have to be taken into account [120].

For left-circularly polarized light incident on either a \(\langle 001\rangle\) or \(\langle 111\rangle\) direction, the injected spin polarization is anti-parallel with the propagation axis, with degrees of spin polarization given by

\[
\text{DSP}_{2}^{(001)} = \frac{(h/2)^{-1} 2\text{Im} \left[ \zeta_{2}^{xyzzz}(\omega) \right]}{\xi_{2}^{xyzzz}(\omega) - \frac{1}{3} \xi_{2}^{xyyy}(\omega) + \frac{1}{2} \xi_{2}^{xxzz}(\omega)},
\]

(4.17)

\[
\text{DSP}_{2}^{(111)} = \frac{(h/2)^{-1} 2\text{Im} \left[ \zeta_{2}^{xyzzz}(\omega) + \zeta_{2}^{xyzzz}(\omega) \right]}{4 \left[ \xi_{2}^{xyzzz}(\omega) - \frac{1}{3} \xi_{2}^{xyyy}(\omega) + \frac{1}{4} \xi_{2}^{xxzz}(\omega) \right]}. \quad (4.18)
\]

In terms of the anisotropy \(\sigma\) and dichroism \(\delta\), the denominators of these expressions are \(\xi_{2}^{xxzz} (1 - \delta)\) and \(\xi_{2}^{xxzz} (1 - \delta - \frac{1}{6} \sigma)\), respectively. The two-photon DSP is shown for both
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Figure 4.7: The two-photon spin-injection pseudotensor $\zeta_{abde}^2(\omega)$ in Ge. The thick black and dashed red curves are electronic contributions; plain black and dotted blue curves show the hole spin components. The fine structure seen near the onset of absorption in the lower two curves is due to the heavy- and light-hole band splitting. The thin brown curve shows $\text{Im} \left[ \zeta_{2e}^{xyzz} \right]$ for the electrons of GaAs.

Figure 4.8: The DSP of carriers optically injected by two-photon absorption in Ge. The thick (thin) black curve shows the electron (hole) spin for left-circularly polarized light at $\langle 001 \rangle$ incidence. Spin polarization at $\langle 111 \rangle$ incidence is shown in a dashed red line for electrons and a dotted blue line for holes.
orientations in Figure 4.8 on page 70, as a function of the photon energy $\hbar \omega$. The electron spin polarization near the onset of absorption is enhanced by a few percent compared to the value of 50% obtained from linear absorption [cf. Figure 4.2 on page 63]. Cubic anisotropy leads to only a small difference between the two orientations in the average spin per injected carrier.

For the holes, the DSP is again roughly $-5/6$ at the band edge. The drop due to heavy- and light-hole band splitting is more significant than in the linear process; once the heavy- and light-hole bands have an energy separation of 30 meV or more, the polarization falls sharply below $-40\%$. On the other hand, the onset of absorption for transitions from the split-off band is not as pronounced. Although it does contribute to a decreasing DSP, this effect only reinforces a larger drop in polarization from the light-hole transitions. This is analogous to optical orientation under linear absorption [cf. Figure 4.4 on page 65]. At larger photon energy, electron and hole polarizations are almost exactly opposite.

It is instructive to break down the DSP into contributions arising from different intermediate states or levels by restricting the sum over $m$ in Equation (4.13). This is shown for both electron and hole spin polarization in Figure 4.9 on the next page, where two-photon processes mediated by either the highest valence bands ($\Gamma_{7v/8v}^+$) or the lowest conduction band ($\Gamma_{7c}^-$) are distinguished. For the range of photon energy considered, these are two-band transitions; the intermediate state belongs to the same subset as either the initial or final state. Two-band transitions are so-called allowed-forbidden ($a-f$) processes. For processes that are said to be forbidden, the transition probability is truly zero only at the $\Gamma$ point; an energy-denominator argument otherwise favors such transitions. Consider, for example, the next-to-lowest conduction level ($\Gamma_{6c/8c}^-\Gamma_{7c}^-$) as intermediates. For non-centrosymmetric materials, this level ($\Gamma_{7c/8c}$ in $T_d$ double group notation) mediates the most energetically favorable allowed-allowed ($a-a$) transition. In GaAs, it lies 4.488 eV above the top of the valence band, or roughly three times the band-gap energy (1.519 eV). For $\hbar \omega$ on the order of the band gap, this means that the denominator of Equation (4.13) is two to three times larger for this process than for a two-band process. Thus, even the most favorable $a-a$ process dominates only very close to the band edge. Contributions from $a-f$ processes mediated through either the initial or final state are otherwise more important [121]. For germanium, the aforementioned $a-a$ process is in fact allowed-forbidden, since the momentum parameter $P'$ vanishes identically under inversion symmetry. For this reason, Ge does not exhibit the type of variation in the two-photon DSP seen near the band-edge of inversion asymmetric crystals, typically...
Figure 4.9: The decomposition of the two-photon DSP of (a) electrons and (b) holes into transitions involving different intermediate states for left-circularly polarized light incident on ⟨001⟩.

over a range of 10 meV, reported by Bhat et al. for GaAs and other III–V semiconductors [35].

Electrons injected with a transition mediated through the conduction band (dashed red curve in Figure 4.9) have a DSP of roughly 40% at the band edge, compared to 60% for valence-band–mediated transitions (black curve). Complex transition rules within the valence level, which consists of split \( J = \frac{3\hbar}{2} \)- and \( J = \frac{\hbar}{2} \)-like sublevels, explain the stronger spin polarization for the latter type of transitions. This supports the argument that the valence band structure is crucial to the spin injection process. Above the onset of absorption, the DSP of carriers excited through valence-band mediation decreases with increasing photon energy, due to band mixing among heavy- and light-hole bands. The DSP of conduction-band–mediated electrons, on the contrary, is not very sensitive to the substructure of these bands; it goes down by only a few percents over the same energy range. Both types of transitions suffer a significant drop in polarization at energies where the split-off band starts contributing.


### 4.2 Coherent control

This section considers the motion of optically-injected carriers. Consider a semiconductor subjected to a two-color optical field,

\[ E(t) = E(\omega)e^{-i\omega t} + E(2\omega)e^{-2i\omega t} + \text{c.c.}, \tag{4.19} \]

consisting of monochromatic beams of frequency \( \omega \) and \( 2\omega \). With such harmonically-related components, one-photon absorption at \( 2\omega \) matches two-photon absorption at \( \omega \). It has been shown that the interference of the probability amplitudes for the two processes leads to injected charge \([20]\) and spin \([39]\) currents, examples of so-called “1+2” interference. The total injection rate for carrier density is given by

\[ \dot{n} = \dot{n}_1(2\omega) + \dot{n}_2(\omega), \tag{4.20} \]

where \( \dot{n}_1 \) is from one-photon absorption of the \( 2\omega \) beam and \( \dot{n}_2 \) is from two-photon absorption of the \( \omega \) beam, with their respective expressions given in Equations (4.7) and (4.10). The carrier injection due to the interference of one- and two-photon absorption, often called population control, is zero for Ge due to center-of-inversion symmetry \([110]\).

Inversion symmetry also prohibits current injection in centrosymmetric materials from one-color processes alone. Rather, the source of current injection in those materials comes from the cross-term of one- and two-photon amplitudes. So, although “1+2” interference does not lead to population control, it is essential to coherently-controlled current and spin-current injection in Ge.

#### 4.2.1 Current injection

The charge current due to the cross-term of transition amplitudes from \( \omega \) and \( 2\omega \) beams has an injection rate given by

\[ \dot{J}_I^a = \eta_I^{abcd}(\omega)E^b(-\omega)E^c(-\omega)E^d(2\omega) + \text{c.c.}. \tag{4.21} \]

The fourth-rank tensor \( \eta_I \) includes contributions from both electrons and holes. An FGR derivation gives the microscopic expression \([20]\):

\[ \eta_{I;e}^{abcd}(\omega) = (-) \frac{i\pi e^4}{\hbar^3 \omega^3} \sum_{c,v} \int \frac{d^3k}{8\pi^3} v_{cv}^a(k) w_{cv}^{bc}(k) v_{cv}^d(k) \delta [\omega_{cv}(k) - 2\omega] \tag{4.22} \]

This expression sums the contributions to the current from each injected carrier. The first velocity matrix element above is from the expectation value of the current operator; its
superscript corresponds to the direction of the current. The product of \( \omega^b_{vc}(k) \) and \( \nu^d_{cv}(k) \) is directly related to the cross-term of two- and one-photon transition amplitudes, respectively. For zinc-blende and diamond structure crystals there are 21 nonzero components to \( \eta_I(\omega) \), related—by the exchange \( b \leftrightarrow c \), \( ab \leftrightarrow cd \), and cyclic permutations of the indices—to only three independent components: \( \eta_{xxxx}^I \), \( \eta_{xyyx}^I \), and \( \eta_{zyzx}^I \). They are plotted in Figure 4.10 on page 75 as a function of the energy \( 2\hbar\omega \) in excess of the direct energy gap.

### 4.2.2 Spin current injection

Bhat and Sipe \[39\] have shown that upon excitation with the harmonically-related two-color field of Equation (4.19) a carrier population can be injected with a nonzero expectation value of the spin-current operator \( K^{ab} = \langle v^a S^b \rangle \). Spin-current injection results from the interference of two-photon absorption at \( \omega \) and one-photon absorption at \( 2\omega \).

Explicitly:

\[
\dot{K}^{ab} = \mu_I^{abcde}(\omega) E^c(-\omega) E^d(-\omega) E^e(2\omega) + \text{c.c.}. \tag{4.23}
\]

The fifth-rank pseudotensor \( \mu_I \) includes electron and hole contributions. In order to properly treat coherences between excited states, the multiple-scale approach is employed, as in the spin-injection calculations of Section 4.1. This yields:

\[
\mu_I^{abcde}(\omega) = (-) \frac{i\pi e^3}{2\hbar^3\omega^3} \sum_{c',v,v'} \frac{\delta^3 k}{8\pi^3} K^{abc}_{cv'}(k) \omega^c_{cv}(k) \nu^e_{cv'}(k) \nu^{c'}_{cv}(k) \times \left( \delta[\omega_{cv}(k) - 2\omega] + \delta[\omega_{cv'}(k) - 2\omega] \right), \tag{4.24}
\]

where \( K^{ab}_{mn}(k) \) is the spin-current matrix element between bands \( m \) and \( n \) at wavevector \( k \).

\[
\langle m| v^a S^b | n k \rangle = K^{ab}_{mn}(k) \delta(k - k'). \tag{4.25}
\]

It is evaluated from velocity and spin matrix elements, after inserting a resolution of unity between those operators on the left-hand side.

For zinc-blende and diamond structure crystals the spin-current injection pseudotensor \( \mu_I \) has six independent components and, in total, 54 nonzero elements. They are formed by cyclic permutations of the Cartesian indices, and by the following relations:

\[
\mu_I^{xxxxy} = \mu_I^{xxxxy} = -\mu_I^{xxxyy} = -\mu_I^{xxxxy},
\]
\[
\mu_I^{xyxxx} = \mu_I^{xyxxx} = -\mu_I^{xxyxx} = -\mu_I^{xyxxx},
\]
Figure 4.10: The “1+2” current-injection tensor $\eta^{abcd}_I(\omega)$ as a function of excess photon energy. Thin brown line: total $\text{Im} [\eta^{xxxx}_I]$ in GaAs; black, dashed red, and dotted blue lines: Ge; thin lines show only the current due to electron motion, while thick lines include both hole and electron contributions.

Figure 4.11: The spin-current injection pseudotensor $\mu^{abcdef}_I(\omega)$ in Ge. Thin lines correspond to electron motion only; thick lines are the total injected current, including holes. The thin brown line in (a) shows the total $\mu^{yxxx}_I$ in GaAs.
\[ \mu_I^{xyyy} = \mu_I^{yyxy} = -\mu_I^{xzyy} = -\mu_I^{xyzy}, \]
\[ \mu_I^{xxyy} = -\mu_I^{yyzy}, \]
\[ \mu_I^{xyxx} = -\mu_I^{xxyy}, \]
\[ \mu_I^{xyyz} = -\mu_I^{yyzz}. \]

The calculated components for Ge are shown in Figure 4.11 on page 75.

### 4.2.3 Results for different configurations

As an example, consider the two-color field of Equation (4.19) to be propagating along the \(-\hat{z}\) direction, with the laboratory axes now aligned with crystallographic axes. The field components are given by\( E(\omega) = E_\omega e^{i\varphi_\omega} \hat{e}_\omega \) and \( E(2\omega) = E_{2\omega} e^{i\varphi_{2\omega}} \hat{e}_{2\omega}, \) where \( E_\omega, 2\omega \) and \( \varphi_\omega, 2\omega \) are real amplitudes and phases of the fields, and \( \hat{e}_\omega, 2\omega \) their polarizations. The cases of circular, co-linear, and cross-linear polarizations are considered below.

**Circularly-polarized beams**

For co-circularly polarized beams of the same handedness, \( \hat{e}_{2\omega} = \hat{e}_\omega = \hat{\sigma}^\pm, \) Equations (4.21) and (4.23) yield:

\[ \dot{J}_I = \frac{1}{\sqrt{2}} \mathrm{Im} \left[ \eta_I^{xxx} \hat{m}^a \hat{m}^b \right] E_\omega E_{2\omega} \hat{z}^a \hat{z}^b, \quad (4.26) \]
\[ K_I^{ab} = \frac{1}{\sqrt{2}} \left( \mu_I^{xyzz} - \mu_I^{xyxx} + 2\mu_I^{xyyy} \right) E_\omega E_{2\omega} \hat{z}^a \hat{z}^b \]
\[ \mp \frac{1}{\sqrt{2}} \left( \mu_I^{xyzz} - \mu_I^{xyyy} + 2\mu_I^{xyxy} \right) E_\omega E_{2\omega} \hat{z}^a \hat{z}^b. \quad (4.27) \]

Equation (4.26) and the first term of Equation (4.27) correspond to a spin-polarized current with \( \hat{z} \) as the polarization axis. The charge flow is along the direction \( \hat{m}, \) given by \( \hat{m} = \hat{x} \sin(\Delta \varphi) \pm \hat{y} \cos(\Delta \varphi), \) where \( \Delta \varphi \equiv 2\varphi_\omega - \varphi_{2\omega}; \) \( \Delta \varphi, \) a phase-difference parameter, controls the direction of the current. Recall from Section 4.1 that circularly-polarized monochromatic light injects a spin population in the sample. It is perhaps not so surprising, then, that the co-circularly polarized two-component field induces a spin-polarized current.

There is another contribution to the spin-current injection: the second term in Equation (4.27) is associated with carriers moving along the axis of incidence, with their spins polarized along \( \hat{m}. \) This corresponds to a pure spin current, since no net charge current is associated with this component.
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With the polarization \( \hat{e}_\omega = \hat{\sigma}^\mp \), forming opposite-circularly polarized beams, there is a change of sign for the contributions of \( 2\eta_t^{xxyy} \), \( 2\mu_t^{xzxz} \), and \( 2\mu_t^{yyzy} \) in the above expressions.

**Co-linearly polarized beams**

Beams polarized along \( \langle 100 \rangle \) are chosen to keep the expressions simple. With co-linearly polarized beams, both along \( \hat{x} \), the rates of current and spin-current injection are:

\[
\dot{J}_I = 2\Im \left[ \eta_{t}^{xxxx} \right] \hat{x} E_\omega^2 E_{2\omega} \sin (\Delta \varphi),
\]

\[
\dot{K}_{I}^{ab} = 2\mu_{t}^{yyzz} \left( \hat{y}^a \hat{z}^b - \hat{z}^a \hat{y}^b \right) E_\omega^2 E_{2\omega} \cos (\Delta \varphi).
\]

Charge and spin currents are injected with their phase-matching conditions out of phase by \( \pi/2 \), so that one is at a maximum when the other vanishes. Within the independent particle approximation \( \eta_t \) is purely imaginary and \( \mu_t \) is purely real, which leads to the difference in the phases that appear in Equations (4.28) and (4.29).

This configuration offers only a weak spin-current response, due to the complete lack of helicity of the incident beams. Pure spin currents arise in the plane perpendicular to the polarization of the fields, with a magnitude proportional to the small but nonzero pseudotensor component \( \mu_{t}^{xyzzz} \) [cf. Figure 4.11 on page 75]. At low excitation energy (2\( h\omega \) less than 0.4 eV above the absorption edge), the response is almost completely accounted for by the contribution from electrons alone. This is also true for the injection enhancement at 1.6 eV of excess photon energy, which stems from the large number of states available at this energy difference in the \( \Gamma - L \) valley. For mid-range photon energies, the electron contribution nearly vanishes, the hole contribution becomes important, and the total injected spin current is reversed; it reaches a maximum amplitude roughly 25% higher than the low-energy maximum.

Another component of the response to the co-linear beams is the charge current injected parallel to the polarization axis, with a magnitude proportional to \( \eta_{t}^{xxxx} \) [cf. Figure 4.10 on page 75]. The current is better characterized by the average velocity per injected carriers. For this purpose, Sipe et al. introduced the swarm velocity

\[
\nu_s^x = \frac{j_x}{\dot{n}} ,
\]

with \( \dot{n} \) from Equation (4.20) [cf. Chapter 3, and References [2] and [113]]. This quantity is maximized in the following way: First, the phases of the \( \omega \) and \( 2\omega \) beams are adjusted
until $\Delta \varphi$ is a multiple of $\pi/2$. Second, the intensities of the $\omega$ and $2\omega$ beams are adjusted so that the velocity in Equation (4.30) is maximized; this occurs when the injection rates $\dot{n}_1(2\omega)$ and $\dot{n}_2(\omega)$ are equal. When this is done, the swarm velocity, using $\dot{J}^x$ from Equation (4.28), takes its maximal value

$$v_{x,\text{max}}^x(\omega) = \frac{\text{Im} \left[ \eta_{xxxx}^x(\omega) \right]}{e \sqrt{\xi_{1}^{xx}(2\omega)\xi_{2}^{xxxx}(\omega)}}. \quad (4.31)$$

The maximal swarm velocity is plotted versus excess photon energy in Figure 4.12 on the next page. Excitations at the direct band-gap energy inject only stationary electrons at the $\Gamma$ point, but the swarm velocity increases quickly from zero to over 400 km/s within a couple hundred meV of the absorption edge. At the onset of transitions from the split-off band ($2\hbar\omega - E_{dg} = 0.29$ eV), slow-moving zone-center electrons are excited, bringing the average velocity down. They are injected only in a small number, however, and cannot account for the steady drop of the electron swarm velocity in the 0.5–1.4 eV range, culminating in a dip at 220 km/s. This is better explained by the “curving down” of the conduction band at these higher energies. Around the dip, which corresponds to a photon energy of $2\hbar\omega \approx 2.3$ eV, some electrons in the $\Gamma$–L direction of the Brillouin zone have zero injection velocities. Electrons excited by slightly more energetic photons stem predominantly from the high JDOS associated with the $E_1$ and $E_1 + \Delta_1$ absorption features. These have lesser velocities compared to electrons in the $\Gamma$–X direction, which make up for most of the injected current at high energies.

Injected holes are slower and have a much flatter velocity spectrum, which is also apparent simply by looking at their band dispersion. Low-energy holes, excited close to the $\Gamma$ point, have a swarm speed of about 160 km/s, less than half the top electron speed, consistent with their larger average effective mass. Due to warping of the light-hole band only a few tens of meV above the absorption edge, the hole swarm velocity drops. When the excess photon energy matches the spin-orbit splitting, zone-center split-off holes are excited, also bringing the average velocity down. At high photon energies, holes are injected in the $\Gamma$–X direction of the Brillouin zone with large velocities; the current generated by the holes can be as much as 45% of the total current. Both contributions from electrons and holes are reinforcing the current over the entire energy range considered in the calculation.
Figure 4.12: The maximal swarm velocity for the charge current injected with co-linearly polarized $\omega$ and $2\omega$ beams. Plain black, dashed red curves: electron and hole velocity in Ge; brown curves: electron and hole velocity in GaAs.

Figure 4.13: (a) Average velocity and (b) degree of spin polarization of positive-$k^x$ carriers making up the pure spin current injected with cross-linearly polarized $\omega$ and $2\omega$ beams. Carriers with negative $k^x$ have the opposite polarization and velocity.
Cross-linearly polarized beams

With cross-linearly polarized beams, $\omega$ along $\hat{x}$ and $2\omega$ along $\hat{y}$, the injection rates are:

\[
\dot{J}_I = 2 \text{Im} \left[ \eta_{I}^{xyyx} \right] \hat{y} E_\omega^2 E_{2\omega} \sin (\Delta \varphi),
\]

\[
\dot{K}^{ab}_I = 2 \left( \mu_{I}^{xyyyz} \hat{z}^a \hat{x}^b - \mu_{I}^{xyxxz} \hat{x}^a \hat{z}^b \right) E_\omega^2 E_{2\omega} \cos (\Delta \varphi).
\]

The “cross-linear” configuration generates a strong pure spin current (PSC) along the $\omega$-beam polarization axis, with a magnitude determined by $\mu_{I}^{xyxxz}$ and a polarization parallel to the incident beams. Additionally, two weaker currents also occur: a charge current along the second harmonic polarization axis, and another PSC along the axis of incidence. The magnitude of the charge current, given by $\eta_{I}^{xyyx}$, is very small for zone-center excitations. This tensor component is predicted to be null by a parabolic-band model; low-energy deviations from zero are due to band warping \[46\]. At higher energies, the assumption of parabolic bands is not even a good first approximation. The present calculation shows that there is a significant current arising from this tensor component when excess photon energy exceeds $1.4 \text{eV}$, with electrons and holes providing comparable contributions.

The smaller component of the spin-current response, proportional to $\mu_{I}^{xyyyz}$, injects a pure spin current parallel with the axis of incidence. The electronic contribution to this component is zero at the onset of absorption and remains small even when excess photon energy is increased by a few hundred meV’s. For $2\hbar \omega - E_{dg} \gtrsim 1.5 \text{eV}$, however, there is a strong contribution from electrons in the $\Gamma$–$X$ direction of the Brillouin zone. The holes slightly reinforce the electron spin current at this enhancement and at $\Gamma$, but otherwise their contribution has the opposite sign.

Let us now discuss the predominant spin-current response: the PSC along the $\omega$-beam polarization axis, with carriers spin-polarized parallel to the incident beams. The associated pseudotensor component, $\mu_{I}^{xyxxz}$, is particularly strong at an excess photon energy of $0.25 \text{eV}$ (where excitations from the split-off band are still excluded) and again at $1.5 \text{eV}$. This PSC is dominated by electrons, although there is a significant contribution from holes at low energies.

In a pure spin current, spin-up and spin-down carriers are moving in opposite directions. There is no overall spin injection along the polarization axis, and the average carrier velocity along the axis associated with the movement of carriers is zero. Therefore, there is no expression for the swarm velocity of carriers forming a PSC that is directly analogous
to Equation (4.31), because there is no net current injection associated with the motion of carriers described by a spin current if it is pure. However, for a subset of the injected carriers the average velocity need not be zero. Recall, for example, the simpler process of one-photon absorption, where there is no injection of current. An electron, injected above the bottom of the conduction band at wavevector \( k \), has a certain velocity determined from the slope of the band at that \( k \) point, while another, injected at \(-k\), has the same energy but opposite velocity. Averaging the microscopic velocities of carriers injected at \( k \) and \(-k\) results in no net current.

Consider a general response function \( G(\omega) \), determined by a Brillouin-zone integration of the form

\[
G(\omega) = \int \frac{d^3k}{8\pi^3} g(k) \delta [\omega_{cv}(k) - 2\omega],
\]

similar to the spin, current, and spin-current injection tensors of interest here. Clearly the integral \( G(\omega) \) can vanish even though the integrand \( g(k) \) does not. By looking at contributions to \( G(\omega) \) from different parts of the Brillouin zone, the nature of the response is investigated. This strategy is used to better characterize the PSC in the “cross-linear” configuration. The Brillouin zone is cut in half at the \( yz \)-plane (i.e. the plane normal to the direction of the spin current) and perform spin- and current-injection calculations over either of these halves. The present calculations confirm that carriers injected into the two halves (a) move in opposite directions and (b) have opposite average spin polarization. This correlation between motion and spin causes the PSC of Equation (4.33) to materialize.

It is the interference of amplitudes from one- and two-photon absorption that gives rise to the spin injection in this experimental configuration:

\[
\dot{S}^z_I = 2\zeta^{xxxy} I E^2 \omega \cos (\Delta \varphi),
\]

where \( \zeta_I = \zeta_{I;k^x \geq 0} + \zeta_{I;k^x \leq 0} \) is a purely real pseudotensor. In non-centrosymmetric semiconductors, \( \zeta^{xxxy} \) is a manifestation of spin population control [46, 112], but in Ge, \( \zeta^{xxxy} \) vanishes. However, with a calculation including only the contribution from \( k \) points with positive \( k^x \), a DSP analogous to Equation (4.6) is introduced:

\[
\text{DSP}_{\text{PSC}}(\omega) = \frac{(h/2)^{-1} 2\zeta_{I;k^x \geq 0}(\omega)}{\sqrt{\xi_1(2\omega)\xi_{xx}(\omega)}},
\]

where field amplitudes that maximize the spin-current injection are chosen. Likewise, a measure of the swarm velocity of positive-\( k^x \) carriers is given by:

\[
\overline{v}_{\text{PSC}}(\omega) = \frac{\eta^{xyy}_{I;k^x \geq 0}(2\omega)}{e\xi_1(2\omega)} + \frac{\eta^{xxxxx}_{I;k^x \geq 0}(\omega)}{e\xi_{xx}(\omega)}.
\]
Here, $\eta_1$ and $\eta_2$ are tensors for single-beam current injection by one- and two-photon absorption, respectively. The former leads to the (bulk) circular photogalvanic effect, which vanishes in crystal of diamond and zinc-blende structures [122]. Its microscopic expression is given by van Driel and Sipe [2]; $\eta_2$ is constructed in a similar way.

The effective quantities of Equations (4.36) and (4.37) describe PSC injection. They are shown in Figure 4.13 on page 79. Since only carriers with a positive $k^x$ are contributing to Equation (4.37), their effective swarm velocity is greater—close to three times larger—than the maximal swarm velocity of Figure 4.12 for the charge current, which includes all carriers. Carriers with a negative $k^x$ have the opposite effective swarm velocity, and averaging over the whole Brillouin zone yields no net motion.

The calculation of $\zeta_{i, x^y}^z$ is performed with the multiple-scale approach to include coherences. The calculation yields hole polarization close to 80% at the onset of absorption. Breaking the calculation down into contributions from each valence band shows that light-hole polarization is 60% while heavy holes are fully polarized. The polarizations associated with these bands exhibit plateaus over ranges of roughly 40 and 25 meV, respectively. As photon energy is increased further, the combined DSP drops to roughly 35%. At higher energies, transitions involving the heavy-hole band yield electrons and holes with a mirrored polarization; the net spin polarization follows a slow monotonic decline, but does not change sign in the energy range presented here. The light-hole polarization drops more steeply and changes sign at $\hbar \omega \approx 670$ meV. This, combined with additional $-25\%$ polarized holes being injected into the split-off band for $\hbar \omega \geq 595$ meV, provides the decreasing average hole spin polarization visible in Figure 4.13(b).

Electrons are injected with $-40\%$ polarization at the $\Gamma$ point, with roughly equal contributions from transitions originating from the heavy- and light-hole bands. As the excess photon energy increases from the band-gap energy, there is an increase in the spin polarization of electrons excited from the light-hole band. This rise almost exactly balances the decrease in polarization for the heavy-hole-mediated transitions, thus forming a plateau in the combined DSP for a wide range of low energies: $E_{dg} \leq 2\hbar \omega \leq E_{dg} + \Delta_{so}$. At the onset of absorption from the split-off band, electrons excited from the light-hole band exhibit decreasing polarization. Electrons excited from the split-off band have a strong opposite polarization ($70\%$) and largely contribute to a sharp drop in the DSP. At higher energies, hole- and electron-spin polarizations follow the same decreasing trend.
4.3 Conclusion

Calculations were performed of optical spin, current, and spin-current injection in bulk Ge. Their spectral dependence has been presented over a wide range of excitation energy, including the $E_1$ resonance, by virtue of the full-zone band structure offered by the 30-band $\mathbf{k} \cdot \mathbf{p}$ model. High spin injection is achieved at an excess photon energy 200 meV above the direct gap.

In the present work, effective measures are defined and computed to characterize the swarm velocity and polarization for pure spin currents. Average velocity and spin are computed for carriers with positive crystal momentum along the direction of motion of the PSC. It is made evident that a PSC originates from correlated motion and polarization. In the case of cross-linearly polarized, harmonically-related beams incident on $\langle 001 \rangle$, the spectral dependence of the carrier polarization is comparable to both one- and two-photon spin orientation. Carrier velocities in the PSC are three times as large as typical swarm velocities of optically-injected charge currents. For many of the current calculations, a centrosymmetric material has been considered for the first time. Such materials facilitate the study of coherently-controlled interference currents experimentally, since no one-beam currents occur.

I conclude by noting the stronger optical response of Ge compared to GaAs. In two-color coherent control, the response tensor for current injection is about a factor of 5 larger in Ge than in GaAs. In two-photon absorption, the response for Ge is a factor of 10 larger. This results since Ge has (i) a smaller effective mass, yielding a larger JDOS, and (ii) a smaller band gap, yielding a smaller denominator in the two-photon amplitude. For effects that correspond to an even-order susceptibility, the stronger response of Ge allows for stronger signals experimentally. In particular, currents arising from anisotropic contributions could be observed near the $E_1$ resonance, where the calculated anisotropy is large. The direct gap $E_{dg}$ and the resonance energy $E_1$ of these two semiconductors are $E_{dg} = 0.805$ eV and $E_1 = 2.111$ eV in Ge and $E_{dg} = 1.424$ eV and $E_1 = 3.043$ eV in GaAs at room temperature [54, 74].
Chapter 5

Carrier and spin dynamics in Ge

In Ge, electron intervalley scattering in the conduction band occurs at an estimated 230 fs time scale \([114, 123]\). The scattering of injected electrons from the \(\Gamma\) valley to the sidevalleys leaves the holes as the only zone-center carriers. Thus it is expected that hole population and hole spin polarization play a larger role in Ge. The direct-gap energy of Ge, \(E_{dg} = 0.805 \text{eV} \) at 293 K \([54]\), lies within the optical regime, paving the way for the study of hole spin dynamics via time-resolved pump-probe experiments. However, the expected time scale for hole spin relaxation is of the same order of magnitude as electron intervalley scattering \([49]\), and it is unclear if hole-related effects appear at all in the optical response.

Polarization-resolved pump-probe techniques have been used to study circular dichroism effects in GaAs \([116, 124, 125]\). Such experiments are understood at a microscopic level by the injection of spin-polarized carriers and their subsequent dynamics. In GaAs, hole spin relaxation occurs on the order of picoseconds \([3]\), while electronic spin relaxation, recombination and diffusion occur on 100 ps time scales \([49]\). Thus, the fast response from the hole system is difficult to probe and is commonly neglected. It is expected that the dynamics involved in the optical response of Ge is complicated by the electron sidevalley scattering and hole angular momentum relaxation occurring on similar time scales. Nevertheless, whether the hole response outlasts the electron response is an ongoing question.

Fully microscopic models of carrier dynamics exist that are based on the kinetic Bloch equation approach \([126–128]\). Simpler dynamical models based on the approximation of an exponential relaxation to equilibrium distributions, the so-called relaxation-time approximation (RTA), have also been used \([51]\). The validity of the RTA has been studied
in calculations of the Boltzmann equation including carrier-carrier scattering [129]. For
the time scales of interest here, the RTA and a numerical solution to the Boltzmann
equation have been found to yield quantitatively similar results [130].

In this chapter, carrier and spin injection in Ge using circularly-polarized light, its
subsequent dynamics, and its effect on the absorption of a probe beam are studied.
Electron and hole populations in the Γ and L valleys are described by density-matrix-
valued distribution functions. Rate equations are derived that describe their dynamics
under cooling, density-matrix mixing, and intervalley scattering within the RTA.

5.1 Motivation

Optical detection methods are available that are sensitive to a spin polarization in the
sample. The measurement of the Faraday angle, by which the polarization axis of
linearly-polarized light rotates as it propagates through the sample, and the detection of
circularly-polarized photoluminescence are two such techniques. They are understood as
the transfer of angular momentum from the electronic spin system to the electromagnetic
field. The dichroism of a pump-probe response with respect to the circular polarization
of the probe is also understood as a manifestation of spin polarization effects. In the
following, I consider the experimental detection of circular-dichroism in Ge by the pump-
probe technique. Experimentally, the transmission of a probe beam through the sample
is measured in the out-of-equilibrium, pumped regime and compared to the equilibrium,
relaxed regime. The sensitivity of the probe beam to the carrier population for various
pump-probe delays allows to study the average effect of carrier dynamics.

The absorption coefficient $\alpha$ is related to the dielectric function $\epsilon = \epsilon_1 + i\epsilon_2$ in the
limit $\epsilon_1 \gg \epsilon_2$ by

$$\alpha = \frac{\omega \epsilon_2}{c\sqrt{\epsilon_1}}, \quad (5.1)$$

where $\omega$ is the central pulse frequency and $c$ is the speed of light in vacuum. Experimentally,
the pump beam injects a carrier density $n$ that affects the absorption of the probe beam.
The differential transmission $\Delta T/T$ of the probe beam is measured. In the linear regime,
a measurement of $\Delta T/T$ corresponds to a measurement of the differential absorption
coefficient $\Delta \alpha$ through $\Delta T/T = -\alpha L$, where $L$ is the thickness of the sample. In the
following, the differential imaginary part of the dielectric function, $\Delta \epsilon_2 = \epsilon_2(n) - \epsilon_2(n = 0)$,
is computed; assuming a constant real part, the quantity $\Delta \epsilon_2$ is directly proportional to
\[ \Delta T/T. \]

### 5.1.1 Effect of a carrier density on carrier injection

The carrier density is described by the density matrix \( \rho(\mathbf{k}) \). Correlations between conduction and valence states are assumed to vanish on a fast time scale compared to intraband correlations. From multiple-scale perturbation theory, the rate of change of the expectation value \( \langle \vartheta \rangle \) for a single-particle operator \( \vartheta \) is [cf. Equation (3.35) on page 33]

\[
\frac{\partial}{\partial t} \langle \vartheta \rangle = \sum_{cc'k} \langle c'k| \vartheta |ck \rangle \frac{\partial}{\partial t} \rho_{cc'}(k) - \sum_{vv'k} \langle v'k| \vartheta |vk \rangle \frac{\partial}{\partial t} \rho_{v'v}(k). \tag{5.2} \]

An expression is obtained for \( \frac{\partial n}{\partial t} \), the rate of carrier injection, by replacing \( \vartheta \) with the number operator. The matrix element \( \langle c'k| \vartheta |ck \rangle \) yields the density matrix \( \rho_{cc'}(k) \). Except for coherences between valence and conduction bands, the full density matrix is considered. The rate of change of the density matrix, under a monochromatic field of frequency \( \omega \), has the form given by Equation (3.36) in Chapter 3. In terms of the one-photon transition amplitude \( \Omega_{cv}^{(1)} \), this treatment yields

\[
\frac{\partial n}{\partial t} = \pi \sum_{cek} \left[ \Omega_{cv}^{(1)*} \left( \sum_{v'} \Omega_{cv'}^{(1)} \rho_{v'v}(k) - \sum_{c'} \Omega_{c'v}^{(1)} \rho_{cc'}(k) \right) + c.c. \right] \delta[\omega_{cv}(k) - \omega], \tag{5.3} \]

where \( \omega_{mn} \equiv \omega_m - \omega_n \) is the transition frequency, and \( \hbar \omega_m \) is the band energy of state \( m \).

It follows that the one-photon injection tensor is given by

\[
\xi_{1ab}(\omega) = \pi \sum_{cek} \left[ \Upsilon_{cv}^{(1)*}(k) \left( \sum_{v'} \Upsilon_{cv'}^{(1)}(k) \rho_{v'v}(k) - \sum_{c'} \Upsilon_{c'v}^{(1)}(k) \rho_{cc'}(k) \right) + c.c. \right] \\
\times \delta[\omega_{cv}(k) - \omega], \tag{5.4} \]

where \( \Upsilon^{(1)} \) is the material part of the one-photon transition amplitude, given by Equation (3.21).

### 5.1.2 Effect of a carrier density on the dielectric function

The imaginary part of the dielectric function is related to the one-photon carrier injection tensor by \( \epsilon_2(\omega) = 2\pi \hbar \xi_1(\omega) \), where \( \xi_1 \) is given for a general density matrix in Equation (5.4). In terms of the full density matrix \( \rho(\mathbf{k}) \), we have

\[
\epsilon_2^{ab}(n, \hbar \omega) = \frac{2\pi^2 e^2 \hbar^2}{\hbar^2 \omega^2} \sum_{mn} \int \frac{d^3k}{8\pi^3} v_{mn}^{ab}(k) \\
\times \left( \sum_{n'} v_{m'n'}^{b}(k) \rho_{n'n}(k) - \sum_{m'} v_{m'n'}^{b}(k) \rho_{mm'}(k) \right) \delta \left[ \hbar \omega_{mn}(k) - \hbar \omega \right], \tag{5.5} \]
where $e = -|e|$ is the electron charge, $\hbar$ is Planck’s constant divided by $2\pi$, $v_{mn}$ is the velocity matrix element between electronic states $m$ and $n$, $\omega_{mn} \equiv \omega_m - \omega_n$ is the transition frequency, and finally $\hbar \omega_m$ is the energy eigenvalue of state $m$. For a diagonal density matrix $\rho(k) = \text{diag}(f_m)$, where $f_m$ is the filling factor for state $m$, the imaginary part of the dielectric function becomes

$$\epsilon_2^{ab}(n, \hbar\omega) = \frac{4\pi^2 e^2 \hbar^2}{\hbar^2 \omega^2} \sum_{m,n} \frac{d^3 k}{8\pi^3} v_{mn}^a(k) v_{mn}^b(k) \times (f_n(k) - f_m(k)) \delta [\hbar \omega_{mn}(k) - \hbar \omega].$$  (5.6)

The effect of the pump beam appear in $\epsilon_2$ through the injected carrier density. The Fermi filling factor $f_m$ is the $k$-dependent occupancy of the state $m$. The effect of the $(f_m - f_n)$ factor on $\Delta \epsilon_2$ is to contribute phase-space filling (PSF; when $m \in$ the set $C$ of conduction bands, and $n \in$ the set $V$ of valance bands), intervalence-band absorption (IVB; $m,n \in V$) and interconduction-band absorption (ICB; $m,n \in C$). The validity of using Fermi filling factors lies in the assumption of a diagonal density matrix. This assumption will be considered below.

The evaluation of the density matrix $\rho(k)$, or the filling factors $f_m(k)$, and other density-dependent terms requires a dynamical model of the carrier distribution, presented in the next section.

### 5.2 Dynamical model

In this section, carrier and spin dynamics are studied by modeling the time dependence of the single-particle density matrix $\rho(k)$ through reciprocal space. Carrier injection, cooling, state mixing, and sidevalley scattering are phenomenologically described within the RTA. Injected carriers are described by density-matrix valued distribution functions for holes and electrons in each valley: holes at $\Gamma$, electrons at $\Gamma$, and electrons at $L$. Electrons in the central valley occupy a single band, and so their distribution is modeled by a $2 \times 2$ matrix-valued function. Holes are injected into $J=3/2$-like valence bands near the $\Gamma$ point, and we keep the $4 \times 4$ density matrix for their description. This approach neglects coherences between the valence and conduction states, which are expected to decay on much faster time scales than those considered here.

The density matrix for electrons at a wavevector $k$ is given by

$$\rho(k) = \rho^{\text{inj}}(k) + \rho^{\text{quasi}}(k) + \rho^{\text{sidevalley}}(k),$$  (5.7)
where \( \rho^{\text{inj}} \) is the injected density, \( \rho^{\text{quasi}} \) is a quasiequilibrium density in the central valley at \( \Gamma \), and \( \rho^{\text{sidevalley}} \) is a quasiequilibrium density in the sidevalleys at \( L \). The injection term for \( \rho^{\text{inj}} \) follows from interband absorption of the pump probe across the direct band gap, creating an hot, anisotropic distribution of carriers in reciprocal space. By momentum relaxation, the carriers thermalize to isotropic distributions \( \rho^{\text{quasi}} \) within the same valley and \( \rho^{\text{sidevalley}} \) in the sidevalleys. The time scales for these two relaxation processes are parametrized by \( \tau_{\text{fast}} \) and \( \tau_{\text{sidevalley}} \). It is assumed at first approximation that scattering events from \( \mathbf{k}' \) to \( \mathbf{k} \) (i) are isotropic, (ii) do not change the density matrix, and (iii) occur faster within the same valley, \( i.e. \) it is assumed that \( \tau_{\text{fast}} < \tau_{\text{sidevalley}} \). As a result, the source term for \( \rho^{\text{quasi}} \) follows the average of \( \rho^{\text{inj}} \) over reciprocal space, and the source term for \( \rho^{\text{sidevalley}} \) follows the average of \( \rho^{\text{inj}} + \rho^{\text{quasi}} \).

### 5.2.1 Injection term

Carrier injection occurs at the direct gap near \( \Gamma \) due to absorption of a pump beam, with a response linear in the field intensity and proportional to \( |E(t)|^2 \). The rate of change of the density matrix due to carrier injection under irradiation by a \( \sigma^\pm \) pump beam is determined from multiple-scale perturbation theory and has the form

\[
\frac{\partial}{\partial t} \rho^{\text{inj}}(\mathbf{k}) = \xi^{\pm}(\mathbf{k}) |E(t)|^2.
\] (5.8)

The injection is described by a \( 2 \times 2 \) matrix \( \xi^{\pm} \) given by

\[
\xi^{\pm}_{cc'}(\mathbf{k}) = (\sigma^\pm) \cdot \xi^{\pm}_{cc'} \cdot (\sigma^\pm)^*.
\] (5.9)

and a \( 2 \times 2 \) matrix-valued second-rank tensor \( \xi \) given by

\[
\xi_{cc'}(\mathbf{k}) = \pi \sum_v \mathcal{Y}^{(1)*}_{cv}(\omega, \mathbf{k}) \mathcal{Y}^{(1)}_{cv}(\omega, \mathbf{k}) \left( \delta [\omega_{cv}(\mathbf{k}) - \omega] + \delta [\omega_{cv}(\mathbf{k}) - \omega] \right),
\] (5.10)

where \( \mathcal{Y}^{(1)}_{cv}(\omega, \mathbf{k}) \) is the material part of the one-photon transition amplitude, \( \omega_{cv} \equiv \omega_c - \omega_v \) is the transition frequency, and \( \hbar \omega_c \) \((\hbar \omega_v)\) is the conduction (valence) band energy. The transition amplitudes and band energies are determined by the band model. The expression for \( \mathcal{Y}^{(1)}_{cv}(\omega, \mathbf{k}) \) is given in Equation (3.21) of Chapter 3 and was calculated for Ge in Chapter 4.

### 5.2.2 Carrier density

The carrier density is obtained from the density matrix by \( n = \sum_k n(k) \) where \( n(k) = \text{Tr} [\rho(k)] \). The dynamics of the carrier density is described first. The rate of change of the
total carrier density is given by the master rate equation
\[
\frac{\partial n}{\partial t} = \sum_k \text{Tr} \left[ \xi^\pm(k) \right] |E(t)|^2 ,
\]
(5.11)
where \(\xi^\pm\) is the one-photon injection matrix (5.9). I consider time scales that are orders of magnitude faster than the recombination time between conduction and valence bands, and neglect recombination.

The carriers are partitioned into anisotropic injection carriers and quasiequilibrium carrier distributions centered at \(\Gamma\) and \(L\) according to Equation (5.7), and thus
\[
n = n^{\text{inj}} + n^{\text{quasi}} + n^{\text{sidevalley}}.
\]
(5.12)
The rate equations governing the carrier density in each partition are
\[
\frac{\partial}{\partial t} n^{\text{inj}} = \sum_k \text{Tr} \left[ \xi^\pm(k) \right] |E(t)|^2 - \left( \frac{1}{\tau_{\text{fast}}} + \frac{1}{\tau_{\text{sidevalley}}} \right) n^{\text{inj}},
\]
(5.13)
\[
\frac{\partial}{\partial t} n^{\text{quasi}} = \frac{1}{\tau_{\text{fast}}} n^{\text{inj}} - \frac{1}{\tau_{\text{sidevalley}}} n^{\text{quasi}},
\]
(5.14)
\[
\frac{\partial}{\partial t} n^{\text{sidevalley}} = \frac{1}{\tau_{\text{sidevalley}}} \left( n^{\text{inj}} + n^{\text{quasi}} \right).
\]
(5.15)

### 5.2.3 Energy density

The electronic system gains energy as it absorbs light. The excess energy of a carrier injected in band \(c\) at wavevector \(k\) is \(\Delta H(k) = \hbar \omega_c(k) - \hbar \omega_c(0)\), where \(\hbar \omega_c(0)\) is the band-edge energy. The master rate equation governing excess energy density \(E\), including energy relaxation on a time scale \(\tau_{\text{energy}}\), is
\[
\frac{\partial E}{\partial t} = \sum_k \text{Tr} \left[ \Delta H(k) \xi^\pm(k) \right] |E(t)|^2 - \frac{1}{\tau_{\text{energy}}} \left( E - \langle E^{\text{lattice}} \rangle n \right).
\]
(5.16)
The average lattice energy \(\langle E^{\text{lattice}} \rangle\) is determined by the lattice temperature, which I take to be room temperature.

The energy is partitioned into each distribution, as previously discussed. Thus,
\[
E = E^{\text{inj}} + E^{\text{quasi}} + E^{\text{sidevalley}},
\]
(5.17)
and the energy partitions are governed by the following rate equations:

\[ \frac{\partial}{\partial t} E^{\text{inj}} = \sum_k \text{Tr} \left[ \Delta \mathcal{H}(k) \xi^\pm(k) \right] |E(t)|^2 - \left( \frac{1}{\tau_{\text{fast}}} + \frac{1}{\tau_{\text{sidevalley}}} \right) E^{\text{inj}} - \frac{1}{\tau_{\text{energy}}} \left( E^{\text{inj}} - \langle E^{\text{lattice}} \rangle n^{\text{inj}} \right), \]  

\[ \frac{\partial}{\partial t} E^{\text{quasi}} = \frac{1}{\tau_{\text{fast}}} \langle E^{\text{inj}} \rangle n^{\text{inj}} - \frac{1}{\tau_{\text{sidevalley}}} E^{\text{quasi}} - \frac{1}{\tau_{\text{energy}}} \left( E^{\text{quasi}} - \langle E^{\text{lattice}} \rangle n^{\text{quasi}} \right), \]  

\[ \frac{\partial}{\partial t} E^{\text{sidevalley}} = \frac{1}{\tau_{\text{sidevalley}}} \langle E^{\text{inj}} + E^{\text{quasi}} \rangle \left( n^{\text{inj}} + n^{\text{quasi}} \right) - \frac{1}{\tau_{\text{energy}}} \left( E^{\text{sidevalley}} - \langle E^{\text{lattice}} \rangle n^{\text{sidevalley}} \right). \]  

The notation \( \langle \rangle \) indicates a per-carrier average over the distribution: \( \langle A \rangle = \frac{1}{n} \sum_k \text{Tr} [A \rho(k)] \), where \( n = \sum_k \text{Tr} [\rho(k)] \).

### 5.2.4 Density matrix

In order to keep coherences, which are important for spin properties, the model uses the single-particle density matrix to describe carriers. The master rate equation governing the \( k \)-dependent density matrix \( \rho(k) \) for a pump polarization \( \sigma^\pm \) is

\[ \frac{\partial}{\partial t} \rho(k) = \xi^\pm(k) |E(t)|^2 - \frac{1}{\tau_{\text{slow}}} \left( \rho(k) - \frac{1}{2} \text{Tr} [\rho(k)] \right), \]  

where the first term is the injection term, Equation (5.8), and the second term accounts phenomenologically for density matrix mixing, \textit{i.e.}, spin relaxation, on a time scale \( \tau_{\text{slow}} \).

The density matrix is partitioned as in Equation (5.7) into an out-of-equilibrium \( \rho^{\text{inj}} \) and quasiequilibrium distributions \( \rho^{\text{quasi}} \) and \( \rho^{\text{sidevalley}} \). The rate equation governing \( \rho^{\text{inj}} \) is

\[ \frac{\partial}{\partial t} \rho^{\text{inj}}(k) = \xi^\pm(k) |E(t)|^2 - \left( \frac{1}{\tau_{\text{fast}}} + \frac{1}{\tau_{\text{sidevalley}}} \right) \rho^{\text{inj}}(k) - \frac{1}{\tau_{\text{slow}}} \left( \rho^{\text{inj}}(k) - \frac{1}{2} \text{Tr} [\rho^{\text{inj}}(k)] \right), \]  

where the first term is the injection term, the following term describes relaxation into quasiequilibrium distributions centered at \( \Gamma \) and \( L \), and the last term is the mixing of the density matrix. The rate equations for the quasiequilibrium density matrices \( \rho^{\text{quasi}} \) and \( \rho^{\text{sidevalley}} \), I return to the assumptions that go into these distributions.
5.2.5 The quasiequilibrium solution

One of the starting point for the phenomenological dynamical model is that injected carriers relax to quasiequilibrium distributions $\rho^{\text{quasi}}$ and $\rho^{\text{sidevalley}}$ in the central and sidevalley, respectively. These are assumed to have the form

$$\rho^{\text{quasi}}(k) = \bar{\rho}^{\text{quasi}} f(E(k), \mu^{\text{quasi}}, T^{\text{quasi}}),$$

(5.23)

and

$$\rho^{\text{sidevalley}}(k) = \bar{\rho}^{\text{sidevalley}} f(E(k), \mu^{\text{sidevalley}}, T^{\text{sidevalley}});$$

(5.24)

$\rho^{\text{quasi}} (\rho^{\text{sidevalley}})$ is described by an average density matrix $\bar{\rho}^{\text{quasi}} (\bar{\rho}^{\text{sidevalley}})$ and a Fermi-Dirac distribution function with the chemical potential $\mu^{\text{quasi}} (\mu^{\text{sidevalley}})$, the temperature $T^{\text{quasi}} (T^{\text{sidevalley}})$, and the energy dispersion $E(k)$ and density of states at $\Gamma$ (L). The dependence of these distributions on wavevector $k$ lies in the energy dependence of the Fermi-Dirac distribution.

Rate equations describing the average density matrices, $\bar{\rho}^{\text{quasi}}$ and $\bar{\rho}^{\text{sidevalley}}$, are sufficient for the treatment considered here. The notation $\bar{\rho}$ indicates that the density matrix is averaged over reciprocal space and its trace normalized to unity:

$$\bar{\rho} = \sum_k \rho(k) / \sum_k \text{Tr} [\rho(k)].$$

(5.25)

From the master rate equation for the density matrix, Equation (5.21), rate equations are determined for the quantity $\sum_k \rho^{\text{quasi}}(k) = \bar{\rho}^{\text{quasi}} n^{\text{quasi}}$. By the chain rule, rate equations are derived for $\rho^{\text{quasi}}$, and similarly for $\rho^{\text{sidevalley}}$:

$$\frac{\partial}{\partial t} \bar{\rho}^{\text{quasi}} = \frac{1}{\tau_{\text{fast}}} \left( \bar{\rho}^{\text{inj}} - \bar{\rho}^{\text{quasi}} \right) n^{\text{inj}} - \frac{1}{\tau_{\text{slow}}} \left( \bar{\rho}^{\text{quasi}} - \frac{1}{2} \mathbb{I} \right),$$

(5.26)

$$\frac{\partial}{\partial t} \bar{\rho}^{\text{sidevalley}} = \frac{1}{\tau_{\text{sidevalley}}} \left( \frac{n^{\text{inj}} \bar{\rho}^{\text{inj}} + n^{\text{quasi}} \rho^{\text{quasi}}}{n^{\text{inj}} + n^{\text{quasi}}} - \bar{\rho}^{\text{sidevalley}} \right) \frac{n^{\text{inj}} + n^{\text{quasi}}}{n^{\text{sidevalley}}} - \frac{1}{\tau_{\text{slow}}} \left( \bar{\rho}^{\text{quasi}} - \frac{1}{2} \mathbb{I} \right).$$

(5.27)

The source term for $\bar{\rho}^{\text{quasi}}$ is the averaged density matrix at injection, $\bar{\rho}^{\text{inj}}$, which is determined by averaging Equation (5.8) over reciprocal space.

The time-dependent carrier density in quasiequilibrium, $n^{\text{quasi}}$, and their total energy, $E^{\text{quasi}}$, are obtained by solving the rate equation for each quantity, namely Equations (5.14) and (5.19). Equation (5.26) is solved to obtain the average density matrix $\bar{\rho}^{\text{quasi}}$. Finally, the temperature $T^{\text{quasi}}$ and chemical potential $\mu^{\text{quasi}}$ appearing in Equation (5.23) are
obtained by requiring that

\[ n^{\text{quasi}} = \sum_k f(E(k), \mu^{\text{quasi}}, T^{\text{quasi}}) \]  

(5.28)

and

\[ E^{\text{quasi}} = \sum_k E(k) f(E(k), \mu^{\text{quasi}}, T^{\text{quasi}}) \]  

(5.29)

are satisfied for all time \( t \). The time-dependent quantities \( \rho^{\text{quasi}} \), \( \mu^{\text{quasi}} \), and \( T^{\text{quasi}} \) allows to describe the time evolution of the quasiequilibrium density matrix \( \rho^{\text{quasi}} \).

### 5.3 Results

The motivation for this work is not only to describe carrier dynamics theoretically, but to identify specific contributions to the experimental detection of these effects in a pump-probe scenario. The pump is left-circularly polarized and propagating along the \( -\hat{z} \) direction, where \( x, y \) and \( z \) describe three general mutually orthogonal right-handed axes in the laboratory. The field is given by \( E(\omega) = E_0 \hat{\sigma}^- \), where \( E_0 \) is the field amplitude and \( \hat{\sigma}^\pm = (\hat{x} \pm i \hat{y}) / \sqrt{2} \). The illumination of the sample with circularly-polarized light injects out-of-equilibrium carrier distributions that have a net, nonzero spin polarization. The optical injection rate for the expectation value of spin, \( \langle \hat{S} \rangle \), is calculated in the previous chapter for valence and conduction states. The injected spin polarization was found parallel to the \( z \)-axis, independent of how the laboratory coordinate system is oriented with respect to crystallographic axes.

A Gaussian time profile is assumed for the pulse:

\[ |E(t)|^2 = \frac{A}{\sqrt{\pi}} e^{-t^2/\tau_{\text{pump}}^2} \]  

(5.30)

with amplitude \( A \) and time duration \( \tau_{\text{pump}} \). The semiconductor vacuum is considered as initial state, and the initial number of excited carriers is \( n(t = -\infty) = 0 \). Solving for the carrier density from the master rate equation, Equation (5.11), for long time delay we let

\[ \lim_{t \to \infty} n(t) = n_0 \equiv \text{number of injected carriers} \]

and obtain \( A \) in terms of \( \xi = \sum_k \text{Tr}[\xi^-(k)] \), \( n_0 \), and \( \tau_{\text{pump}} \): \( \xi A = n_0 / \tau_{\text{pump}} \). The pump pulse duration \( \tau_{\text{pump}} \) and the number of injected carriers \( n_0 \) are determined from the experiment, while \( \xi \) is calculated from the band model. For this work the carrier density is \( n_0 = 3 \times 10^{-17} \text{ cm}^{-3} \) and the time scales of interest are listed in Table 5.1.
Table 5.1: Dynamical time scales for injection and relaxation in Ge.

<table>
<thead>
<tr>
<th>Description</th>
<th>Symbol</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermalization time</td>
<td>$\tau_{\text{fast}}$</td>
<td>50 fs</td>
</tr>
<tr>
<td>Pump pulse duration</td>
<td>$\tau_{\text{pump}}$</td>
<td>60 fs</td>
</tr>
<tr>
<td>Sidevalley scattering time</td>
<td>$\tau_{\text{sidevalley}}$</td>
<td>200 fs</td>
</tr>
<tr>
<td>Energy relaxation time (cooling)</td>
<td>$\tau_{\text{energy}}$</td>
<td>250 fs</td>
</tr>
<tr>
<td>Electron spin relaxation time</td>
<td>$\tau_{\text{slow}}$</td>
<td>50 ps</td>
</tr>
</tbody>
</table>

First, the source term appearing in Equation (5.8) is calculated. Band energies and matrix elements are computed within the 30-band $k \cdot p$ model. In the following, I use the “$z$ basis” consisting of the eigenstates of $\sigma^z$, such that

$$
\sigma^z \rightarrow_{\text{basis}} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}.
$$

For a pump pulse with 200 meV of excess photon energy, the resulting density matrix at injection, averaged over reciprocal space and renormalized to unit trace, is

$$
\bar{\xi}^- \rightarrow_{\text{basis}} \begin{pmatrix} 0.722 & 0 \\ 0 & 0.278 \end{pmatrix}.
$$

The $z$ basis is thus a convenient basis to work in since it yields a diagonal density matrix, and we may talk of spin up and spin down electrons. The calculated carrier density is shown in Figure 5.1 on page 94.

In the calculations the effect of phase-space filling is considered on across-gap and interconduction-band transitions. The calculated differential transmission $\Delta T$ is shown in Figure 5.2 on page 95 for two different probe energies, $\hbar \omega = 0.790$ eV and $\hbar \omega = 0.855$ eV. In the first case, the probe is tuned below the band gap, and only interconduction-band absorption occurs. This contribution is not dichroic and decays quickly as the carriers cool down. In the second case, the probe is above the band gap, and electron phase space filling takes effect.

### 5.4 Dynamics in the valence bands

The occupation in the valence bands is described by a $4 \times 4$ density matrix. Without solving the valence-band contribution here, I will derive the equation for hole dynamics
and highlight its key components. First, in line with the phenomenology used for the electrons, the holes are assumed to quickly relax to a quasiequilibrium distribution $\rho_{\text{holes}}^{\text{quasi}}$. This distribution is thermal and follows Fermi-Dirac statistics, with a chemical potential $\mu_{\text{holes}}^{\text{quasi}}$ and a temperature $T_{\text{holes}}^{\text{quasi}}$. Further, it is described by an average density matrix, $\bar{\rho}_{\text{holes}}^{\text{quasi}}$. The density matrix can be written as

$$\rho_{\text{holes}}^{\text{quasi}}(k) = \bar{\rho}_{\text{holes}}^{\text{quasi}} f(H(k), \mu_{\text{holes}}^{\text{quasi}}, T_{\text{holes}}^{\text{quasi}}) + f(H(k), \mu_{\text{holes}}^{\text{quasi}}, T_{\text{holes}}^{\text{quasi}}) \bar{\rho}_{\text{holes}}^{\text{quasi}},$$

(5.31)

where the crystal Hamiltonian $H$ accounts for the energy factor in the Fermi-Dirac distribution, and the operators have been symmetrized. Using this prescription for the density matrix, one can derive a set of rate equations describing its dynamics. These equations have the same form as those describing the electron dynamics and are obtained from the above equations for the carrier density, energy density, and density matrix in the limit $\tau_{\text{sidevalley}} \rightarrow \infty$, since there are no sidevalleys in the valence bands. The remaining time scales are the energy relaxation time $\tau_{e,h}$, the density-matrix conserving relaxation time $\tau_{f,h}$, and the state mixing relaxation time $\tau_{s,h}$. The injection term for the density matrix is obtained from Equation (5.10) by letting $cc' \rightarrow v'v$, $c'v \rightarrow cv'$, and $\sum_v \rightarrow \sum_c$.

The model is thus seemingly similar to the electron case. The difference lies in the lifting of the degeneracy between heavy-hole and light-hole bands, which enter into $\rho(k)$ due to the energy dependence of the Fermi-Dirac distribution. The result is that
Chapter 5. Carrier and spin dynamics in Ge

Figure 5.2: Results for the differential transmission in the pump-probe simulations. (a) The probe is tuned below the band gap at $\hbar \omega = 0.790 \text{eV}$. Only interconduction-band absorption occurs. (b,c) The probe is tuned above the band gap at $\hbar \omega = 0.855 \text{eV}$. Interconduction-band absorption (dotted blue) and electron phase-space filling (dashed red) compete. (b) Same circular polarization for the pump and the probe. (c) Opposite circular polarization for the pump and the probe.
\( \rho_{\text{holes}}^{\text{quasi}}(\mathbf{k}) \propto \rho_{\text{holes}}^{\text{quasi}} \), and the density matrix at each \( \mathbf{k} \) is mixed to a certain degree. The thermalization of the \( J=3/2 \) state into eigenstates that are energy split induces density-matrix mixing. This occurs on the time scale \( \tau_{\text{fast}} \), independently of the phenomenological density matrix mixing term that appear in Equation (5.21) and occurs on the time scale \( \tau_{\text{slow}} \). The degree of mixing that occurs through the thermalization process is a function of the energy difference between the heavy- and light-hole bands.

It follows from the energy separation between heavy- and light-hole bands that the valence-band density matrix is in general not diagonal in the eigenstates basis. Thus the use of the density matrix and Equation (5.5) is necessary rather than Fermi filling factors and Equation (5.6). Fermi factors can only rigorously be introduced once the density matrix has fully relaxed and is proportional to the identity matrix.

In summary, I have presented simulations of the differential absorption of a probe beam in a pump-probe scenario due to conduction-band phase-space filling. Carrier populations are described by distribution density matrices whose time evolution is dictated by a closed set of rate equations. Within this phenomenological model, electron densities can be described by Fermi filling factors in the usual way, provided the \( z \) basis is used for the conduction-band eigenstates at \( \mathbf{k} \). For the holes, however, their description require the full density matrix within the valence bands. Because of the energy splitting between heavy- and light-hole bands, density-matrix mixing results from thermalization alone.
Chapter 6

Carrier and current injection in graphene and bilayer graphene

Single-layer graphene (henceforth simply graphene) is a one-atom-thick layer of carbon atoms with unconventional electronic and optical properties [64]. Its linear optical absorption coefficient approximates a fundamental constant over a wide range of frequencies [66, 131, 132]. The nonlinear optical response in graphene has recently started to garner interest [133–135], including a report of remarkably large third-order susceptibility [136]. Mele et al. have studied the coherent control of carrier distributions under linearly-polarized light in graphene and carcon nanotubes [71]. They found that the larger carrier velocities and longer estimated relaxation times lead to stronger photocurrent injection in carbon-based materials than in conventional semiconductors such as GaAs.

In this chapter, calculations of the optical injection of carriers and electrical currents in single-layer and bilayer graphene are presented. Two-photon absorption and two-color coherent control are studied, including polarization dichroism and interlayer coupling effects. The work of Mele et al. on the two-color scheme is extended to consider circularly-polarized light and interlayer coupling. Expressions for the injection rates are derived within Fermi’s golden rule (FGR). The band dispersion and matrix elements are obtained from the tight-binding model of graphene and bilayer graphene, and the extension to graphite is discussed.

The chapter is organized as follows. The effective Hamiltonians used for the calculations are presented in Section 6.1. One- and two-photon absorption coefficients in single-layer graphene, the resulting distributions of injected carriers, and the generated photocurrents due to interference are presented in Section 6.2. The treatment is repeated for bilayer
graphene, and the effects of interlayer coupling on one- and two-photon absorption and photocurrent injection are presented in Section 6.3. The results are summarized in Section 6.4.

6.1 Hamiltonians

The crystal structure of graphene consists of two triangular sublattices \{A, B\}, as shown in Figure 6.1(a) on the next page. In the basis of the sublattices, the tight-binding model is expanded near the K point to yield the effective Hamiltonian

\[ H_1(K + k) \rightarrow \hbar v_F \sigma \cdot k = v_F \begin{pmatrix} 0 & \hbar k_- \\ \hbar k_+ & 0 \end{pmatrix}, \]  

(6.1)

where \( v_F \) is the Fermi velocity, \( \sigma \) are the Pauli matrices, \( k \) is the crystal momentum in the plane of the crystal relative to the K point and \( k_\pm = k_x \pm i k_y \). The Fermi velocity is determined by the sublattice hopping term \( \gamma_0 \) [64, 65]. The resulting band energies are linear in crystal momentum \( k \) and are shown in Figure 6.2 on the following page.

The structure of Bernal-stacked bilayer graphene is sketched in Figure 6.1(b); there are four atoms per unit cell, each contributing a \( p_z \) orbital to the \( \pi \) bands [137]. The corresponding \( 4 \times 4 \) tight-binding Hamiltonian, written in the basis \{A, B’, A’, B\} and expanded near the K point, is given by

\[ H_2(K + k) \rightarrow \begin{pmatrix} 0 & 0 & 0 & v_F \hbar k_- \\ 0 & 0 & v_F \hbar k_+ & 0 \\ 0 & v_F \hbar k_- & 0 & \gamma_1 \\ v_F \hbar k_+ & 0 & \gamma_1 & 0 \end{pmatrix}. \]  

(6.2)

This tight-binding model includes \( \gamma_0 \), the intralayer coupling, and \( \gamma_1 \), the hopping term between sublattices A’ and B from the two different layers. A low-energy expansion yields

\[ H'_2(K + k) \rightarrow \frac{\hbar^2}{2m^*} \begin{pmatrix} 0 & k_-^2 \\ k_+^2 & 0 \end{pmatrix}, \]  

(6.3)

where \( m^* = \gamma_1/2v_F^2 \). This is the “massive” Dirac equation, describing the carriers near the K point for \( |v_F \hbar k| \ll \gamma_1 \). The energy dispersion consists of a pair of gapless conduction and valence bands touching at the Dirac point (\( k = 0 \)), with a quadratic dependence on crystal momentum [64, 65, 67].
Figure 6.1: The crystal structure of (a) single-layer graphene and (b) bilayer graphene. The basis vectors $a_1$ and $a_2$ define the unit cell, $\gamma_0$ and $\gamma_1$ are the intralayer and interlayer coupling strengths, and the sublattices are denoted by A (A’) and B (B’).

Figure 6.2: The reciprocal space and linear energy-crystal momentum dispersion of graphene near K. The basis vectors $b_1$ and $b_2$ form the reciprocal unit cell, enclosing one K and one K’ valley. The dispersion shows the initially empty conduction band $c$ and occupied valence band $v$ touching at the K point. The excitation scheme employs interference between two-photon absorption at $\omega$ (red arrows) and one-photon absorption at $2\omega$ (blue arrows), leading to generation of charge and current.
Near the K’ point, similar Hamiltonians are obtained by letting \(k_x \rightarrow -k_x\) in Equations (6.1), (6.2), and (6.3); for the purposes of this work, the two valleys are equivalent. All model Hamiltonians are isotropic. Next-to-nearest neighbor coupling parameters, which break the isotropy and introduce trigonal warping, are neglected \([65]\). Their inclusion does not significantly change the conductivity spectrum in graphene \([131]\) or bilayer graphene \([138, 139]\).

6.2 Single-layer graphene

In this section, the model Hamiltonian (6.1) is used to calculate one- and two-photon absorption coefficients, and the coherent control of chiral carriers in graphene. The velocity operator \(\mathbf{v} = \frac{\hbar}{m} \nabla_k \mathcal{H}\), when written in the eigenstates basis, takes the form

\[
\mathbf{v} \rightarrow v_F \left( \begin{array}{cc} \hat{k} & i \hat{\phi} \\ -i \hat{\phi} & -\hat{k} \end{array} \right),
\]

where \(\hat{k}\) is the unit vector parallel to the direction of \(\mathbf{k}\) and \(\hat{\phi} = \hat{z} \times \hat{k}\).

6.2.1 Carrier injection

Consider the interaction Hamiltonian \(\mathcal{H}_{\text{int}} = -\frac{e}{mc} \mathbf{A} \cdot \mathbf{p}\), where \(\mathbf{A}\) is the vector potential of the optical field, \(m\) is the free-electron mass, \(c\) is the speed of light in vacuum and \(e = -|e|\) is the electron charge. The carrier density induced by this interaction is obtained by performing a perturbation calculation up to second order, assuming a monochromatic field of frequency \(\omega\). The rates of injection of carrier density due to one- and two-photon absorption processes have the form

\[
\dot{n}_1 = \xi_1^{ab}(\omega) E^a(-\omega) E^b(\omega),
\]

\[
\dot{n}_2 = \xi_2^{abcd}(\omega) E^a(-\omega) E^b(-\omega) E^c(\omega) E^d(\omega),
\]

where \(\mathbf{E}\) is the electric field and superscripts \(a, b, c,\) and \(d\) indicate Cartesian components; repeated superscripts are summed over. Microscopic expressions for the tensors \(\xi_1\) and \(\xi_2\) are derived in the independent-particle approximation following FGR \([2, 20]\). For a two-dimensional crystal, this approach yields

\[
\dot{n}_\ell = 2\pi \sum_{c,v} \int \frac{d^2k}{4\pi^2} \left| \Omega_{cv}^{(\ell)}(\omega, \mathbf{k}) \right|^2 \delta[\omega_{cv}(\mathbf{k}) - \ell\omega],
\]
where \( \omega_{cv}(k) \equiv \omega_c(k) - \omega_v(k) \), \( \hbar \omega_n(k) \) are the band energies, and \( \Omega^{(\ell)}_{cv}(\omega, k) \) is the \( \ell \)-photon transition amplitude between valence band \( v \) and conduction band \( c \) at wavevector \( k \) [2]:

\[
\Omega^{(1)}_{cv}(\omega, k) = \frac{ie}{\hbar \omega} \mathbf{v}_{cv}(k) \cdot \mathbf{E}(\omega),
\]

\[
\Omega^{(2)}_{cv}(\omega, k) = \frac{2e^2}{\hbar^2 \omega^2} \sum_m \mathbf{v}_{cm}(k) \cdot \mathbf{E}(\omega) \mathbf{v}_{mv}(k) \cdot \mathbf{E}(\omega),
\]

where \( \mathbf{v}_{mn}(k) \) indicate matrix elements of the velocity operator, and \([\omega_{mc}(k) + \omega_{mv}(k)]/2 = \omega_m(k) - [\omega_v(k) + \omega] \) is the usual energy denominator appearing in second-order perturbation theory.

By the symmetry of graphene and bilayer graphene, the tensors \( \xi_1 \) and \( \xi_2 \) have respectively one and three nonzero independent components in the \( xy \) plane: \( \xi^{xx}_{1}, \xi^{xxxx}_{2}, \xi^{xyy}_{2}, \) and \( \xi^{yxy}_{2} = \xi^{xyy}_{2} \); however, the model Hamiltonians considered here are isotropic, reducing \( \xi_2 \) to two independent terms: \( \xi^{xxxx}_{2} \) and the linear-circular dichroism \( \delta = \xi^{xyy}_{2}/\xi^{xxxx}_{2} \). Other nonzero components of the isotropic model are \( \xi^{yxy}_{2} = \xi^{xyx}_{2} = \frac{1}{2} \xi^{xxxx}_{2}(1 - \delta) \), and those obtained by \( x \leftrightarrow y \) permutations [43].

The electric field \( \mathbf{E}(\omega) \) in an arbitrary beam at normal incidence can be written as \( \mathbf{E}(\omega) = E_\omega e^{i\phi_\omega} (\mathbf{x}_\omega + \mathbf{y}_\omega e^{i\delta_\phi_\omega})/\sqrt{2} \), for an appropriate choice of orthonormal vectors \( \mathbf{x}_\omega \) and \( \mathbf{y}_\omega \) in the \( xy \) plane, a real amplitude \( E_\omega \), and real phase parameters \( \phi_\omega \) and \( \delta_\phi_\omega \). The injection rates of the carrier density due to one- and two-photon processes are given by

\[
\dot{n}_1 = \xi^{xx}_1(\omega) |E_\omega|^2,
\]

\[
\dot{n}_2 = \xi^{xxxx}_2(\omega) |E_\omega|^4 \left( 1 - \delta \sin^2(\delta_\phi_\omega) \right).
\]

Both are insensitive to rotation of the crystal axes with respect to the normal, but one-photon absorption is independent of polarization, while two-photon absorption depends on the phase difference \( \delta\phi_\omega \) between the linearly-polarized components of the incident light.

The nonzero tensor components are obtained from Equations (6.4) to (6.9): For the linear response, \( \xi^{xx}_1 \equiv \bar{\xi}_1 \), with

\[
\bar{\xi}_1(\omega) = 2\sigma_0/\hbar \omega, \tag{6.12}
\]

where \( \sigma_0 \) is the universal optical conductivity of graphene: \( \sigma_0 = g_s g_v \frac{e^2}{16\hbar} \), with \( g_s = 2 \) and \( g_v = 2 \) denoting spin and valley degeneracy, respectively [66, 140]. For the nonlinear two-photon response, \( \xi^{xxxx}_2 = \xi^{xyy}_2 = \xi^{xyx}_2 = -\xi^{xxyy}_2 \equiv \bar{\xi}_2 \), with

\[
\bar{\xi}_2(\omega) = 8g_s g_v \hbar e^4 v_F^4 (2\hbar \omega)^{-5}. \tag{6.13}
\]
Thus, for chiral carriers, \( \delta = -1 \) and it follows from Equation (6.11) that circularly-polarized light \((\delta \varphi_\omega = \pm \frac{\pi}{2})\) provides twice as much two-photon absorption as linearly-polarized light.

### 6.2.2 Current injection

In the presence of a two-color optical field with frequency components \( \omega \) and \( 2\omega \), there exist two transition amplitudes connecting the same initial and final states: \( \Omega^{(1)}_{cv}(2\omega, k) \) results from light at \( 2\omega \) to first order in perturbation, and \( \Omega^{(2)}_{cv}(\omega, k) \) results from light at \( \omega \) to second order in perturbation. The cross-term of these amplitudes yields the coherent control term. This has no effect on the total number of carriers optically injected in centrosymmetric crystals because under center-of-version symmetry

\[
\dot{n}_I = \xi_{abc} I^{(\omega)} \mathbf{E}_a(-\omega) \mathbf{E}_b(-\omega) \mathbf{E}_c(2\omega) + \text{c.c.}
\]

which imposes \( \xi_I = 0 \). However, the coherent control term yields an injection term for the current density,

\[
\dot{J}^a = \eta^{abcd}_{I}(\omega) \mathbf{E}^b(-\omega) \mathbf{E}^c(-\omega) \mathbf{E}^d(2\omega) + \text{c.c.},
\]

where \( \eta_I(\omega) \) is a fourth-rank current-injection tensor [20]. The symmetry of graphene or bilayer graphene yields \( \eta^{xxx}_{I}, \eta^{xyy}_{I}, \) and \( \eta^{xxy}_{I} = \eta^{xyx}_{I} \) as independent components; an isotropic model additionally satisfies \( 2\eta^{xyy}_{I} = \eta^{xxx}_{I} - \eta^{xyx}_{I} \) [46, 55]. Current injection in the isotropic model is given by

\[
\dot{J} = \eta^{xxx}_{I}(\omega) \left( \mathbf{E}(-\omega) \cdot (\mathbf{E}(-\omega) \times \mathbf{E}(2\omega)) \right)
\]

where the disparity parameter \( d = \eta^{xyy}_{I}/\eta^{xxx}_{I} \) is introduced [cf. Chapter 3, Section 3.3.4]. This parameter characterizes how current injection due to linearly-polarized beams depends on whether the polarization axes are perpendicular or parallel. For a parallel configuration, \( \mathbf{E}(-\omega) \cdot \mathbf{E}(2\omega) \) is maximal and \( \mathbf{E}(-\omega) \times \mathbf{E}(2\omega) \) is zero; for a perpendicular configuration, \( \mathbf{E}(-\omega) \cdot \mathbf{E}(2\omega) \) is zero and \( \mathbf{E}(-\omega) \times \mathbf{E}(2\omega) \) is maximal.

For the model Hamiltonian (6.1) the current-injection tensor components are related by \( \eta^{xxx}_{I} = \eta^{xyy}_{I} = \eta^{xxy}_{I} = -\eta^{xyx}_{I} \equiv i\bar{\eta}_I \), and thus \( d = -1 \). In the independent-particle approximation, \( \bar{\eta}_I \) is purely real. An FGR derivation predicts equal conduction- and valence-band contributions, for a total current injection

\[
\bar{\eta}_I(\omega) = g_s g_v e^4 v_F^2 (2\hbar \omega)^{-3}.
\]
Normal incidence $\omega$ and $2\omega$ beams are described in the following by $\mathbf{E}(\omega) = E_\omega e^{i\varphi_\omega} \hat{e}_\omega$ and $\mathbf{E}(2\omega) = E_{2\omega} e^{i\varphi_{2\omega}} \hat{e}_{2\omega}$, where $E_{\omega,2\omega}$ and $\varphi_{\omega,2\omega}$ are real amplitudes and phases of the fields, and $\hat{e}_{\omega,2\omega} = (\hat{x}_{\omega,2\omega} + i \hat{y}_{\omega,2\omega})/\sqrt{2}$ their polarizations. A configuration with co-circularly polarized beams ($\delta \varphi_\omega = \delta \varphi_{2\omega} = \pm \frac{\pi}{2}$) yields the current injection with the largest magnitude:

$$\mathbf{J} = 2\sqrt{2} \eta I(\omega) E_{\omega}^2 E_{2\omega} \mathbf{m}, \quad (6.17)$$

where $\mathbf{m} = \hat{x}_{2\omega} \sin(\Delta \varphi \pm 2\theta) \pm \hat{y}_{2\omega} \cos(\Delta \varphi \mp 2\theta)$. The phase-difference parameter $\Delta \varphi \equiv 2\varphi_\omega - \varphi_{2\omega}$ controls the direction of the current; $\theta$ is the angle that separates the polarization axes of the fundamental from those of the second harmonic: $\hat{x}_\omega = \hat{x}_{2\omega} \cos \theta + \hat{y}_{2\omega} \sin \theta$. Opposite-circular polarizations ($-\delta \varphi_\omega = \delta \varphi_{2\omega} = \pm \frac{\pi}{2}$) yield no net current injection, while linearly-polarized beams ($\delta \varphi_\omega = \delta \varphi_{2\omega} = 0$) yield

$$\mathbf{J} = 2\eta I(\omega) E_{\omega}^2 E_{2\omega} \sin(\Delta \varphi) \mathbf{n}, \quad (6.18)$$

where $\mathbf{n} = \hat{e}_{2\omega} \cos(2\theta) + \hat{e}_{2\omega}^\perp \sin(2\theta)$ and $\hat{e}_{2\omega}^\perp = \hat{z} \times \hat{e}_{2\omega}$. Here the angle $\theta$ between polarization axes controls the orientation of the current within the graphene plane, and $\Delta \varphi$ controls its magnitude. For co-linearly polarized and cross-polarized beams, the injected current is parallel with the direction of $\hat{e}_{2\omega}$, the polarization axis of the second harmonic. Conversely the injected current is perpendicular to $\hat{e}_{2\omega}$ when the polarization axes form an angle of $\theta = \frac{\pi}{4}$. Within this model, the orientation of the crystal axes has no influence on the current injection at normal incidence.

Graphene seems to be the first material that has been studied for which any value of $\theta$ is equally effective at injecting a current. This is a consequence of the ratio $d = \eta_{I}^{xyyx}/\eta_{I}^{xxxx}$ being $-1$ for graphene. In contrast, components of the current-injection tensor are found to satisfy $|\eta_{I}^{xyyx}| < |\eta_{I}^{xxxx}|$ for Ge [cf. Chapter 4], for GaAs [cf. Chapter 3, and References 20, 46, and 55], and for a number of zinc-blende materials [46]. In these materials a configuration with perpendicular polarization axes results in a significantly weaker current [cf. Chapter 3, Section 3.3.4]. The value of $d = -1$ for graphene is independent of frequency within the present model.

Figure 6.3 on page 104 shows the $k$-space distribution of the carrier-injection rate, $\dot{n}(k) = |\Omega_{cv}^{(1)}(2\omega, k) + \Omega_{cv}^{(2)}(\omega, k)|^2$, at $\omega_{cv}(k) = 2\omega$. Field amplitudes are chosen such that the integrated injection rates from one- and two-photon processes are balanced: $\dot{n}_1(2\omega) = \dot{n}_2(\omega)$. Opposite-circular polarization of the beams yield the nonpolar distribution in Figure 6.3(a) and no net current. In Figure 6.3(b) both components of the two-color field have the same circular polarization $\sigma^\pm$. The carrier distribution follows $\dot{n}(k) \propto$
Figure 6.3: The distribution $\dot{n}(\mathbf{k})$ of the carrier injection through reciprocal space under irradiation by an optical field with components $E(\omega)$ and $E(2\omega)$ satisfying $\Delta \varphi = \frac{\pi}{2}$. (a) Opposite-circular polarization ($-\delta \varphi_\omega = \delta \varphi_{2\omega} = \pm \frac{\pi}{2}$, $\theta = 0$). (b) Co-circular polarization ($\sigma^{\pm}$ light, $\delta \varphi_\omega = \delta \varphi_{2\omega} = \pm \frac{\pi}{2}$, $\theta = 0$). (c,d) Linear polarization ($\delta \varphi_\omega = \delta \varphi_{2\omega} = 0$) with $\hat{e}_{2\omega} = \hat{x}$ and $\hat{e}_\omega = \hat{x} \cos \theta + \hat{y} \sin \theta$; (c) $\theta = 0$ and (d) $\theta = \frac{\pi}{4}$. The distribution in (a) results in no net current; the asymmetric distributions (b), (c), and (d) result in net electrical currents injected in the graphene plane along $\hat{x}$ (b,c) or $\hat{y}$ (d).
\[ 1 + \sin(\Delta \varphi \pm \phi_k), \] where \( \phi_k = \tan^{-1}(k_y/k_x) \), resulting in the injection of the current given by Equation (6.17). The charge distribution and current rotate with \( \Delta \varphi \): clockwise for \( \sigma^+ \) and counterclockwise for \( \sigma^- \), when viewed from \( z > 0 \).

For linearly-polarized light, the phase-difference parameter is taken to be \( \Delta \varphi = \frac{\pi}{2} \). This maximizes both the cross-term in the \( k \)-dependent carrier density, \( \dot{n}(k) \propto |\sin \phi_k + ie^{-i\Delta \varphi} \sin(2\phi_k - 2\theta)|^2 \), and the resulting current, Equation (6.18). Without loss of generality, \( \hat{e}_{2\omega} \) is taken along the \( x \) axis: \( \hat{e}_{2\omega} = \hat{x} \) and \( \hat{e}_{\omega} = \hat{x} \cos \theta + \hat{y} \sin \theta \). The \( k \)-space distribution of the carrier-injection rate is shown for the angle \( \theta = 0 \) in Figure 6.3(c) and \( \theta = \frac{\pi}{4} \) in Figure 6.3(d). For co-linear polarization axes (\( \theta = 0 \)), the distribution is symmetric with respect to \( k_x \), while asymmetric and strongly enhanced towards positive \( k_x \), although with a node at \( \phi_k = 0 \). The excess of positive-\( k_x \) carriers gives rise to a net electric current along the \( x \) axis. As the polarization axis of the \( \omega \) component is rotated by the angle \( \theta \), carriers are redistributed towards positive \( k_y \). At \( \theta = \frac{\pi}{4} \), \( \dot{n}(k) \) is symmetric with respect to \( k_x \) and the net current is along the \( y \) axis.

### 6.3 Bilayer graphene

The chiral Hamiltonian for bilayer graphene, Equation (6.3), results in the same carrier and current injection as in the previous section with the substitutions \( \bar{\xi}_1 \rightarrow 2\bar{\xi}_1, \bar{\xi}_2 \rightarrow 8\hbar \omega \xi_2/\gamma_1 \), and \( \bar{\eta}_I \rightarrow 8\hbar \omega \bar{\eta}_I/\gamma_1 \); the velocity operator in the eigenstates basis takes the form of Equation (6.4) with \( v_F \rightarrow \hbar k/m \), and thus the symmetry properties of the injection tensors are unchanged. But such a treatment describes the carriers only near the K point for \( |v_F \hbar k| \ll \gamma_1 \) and leaves out important remote bands in the two-photon transition amplitude. A more accurate model is given by Equation (6.2), which is also valid for band energies on the order of \( \gamma_1 \). This \( 4 \times 4 \) Hamiltonian introduces two additional bands, one above and one below the Dirac point, shifted by an energy \( \gamma_1 \). More importantly, it gives the correct linear dispersion for larger values of \( k \). The band dispersion near K is shown in Figure 6.4 on page 107.

In this section the carrier- and current-injection tensors are calculated for the unbiased Bernal-stacked graphene bilayer according to the model Hamiltonian (6.2).
6.3.1 Carrier injection

One-photon carrier injection is obtained from Equation (6.12) by replacing $\sigma_0$ with the bilayer optical conductivity $\sigma$ from Abergel and Fal’ko [141].

\[
\xi_{xx}(\omega) = \bar{\xi}_1(\omega) \left( \frac{2\gamma_1 + \hbar \omega}{\gamma_1 + \hbar \omega} + \frac{2\gamma_1^2}{(\hbar \omega)^2} \Theta(\hbar \omega - \gamma_1) \right) + \frac{\hbar \omega - 2\gamma_1}{\hbar \omega - \gamma_1} \Theta(\hbar \omega - 2\gamma_1),
\]

(6.19)

where $\Theta(x)$ is the Heaviside step function.

Two-photon carrier injection is broken down into four distinct contributions. The first contribution (a) comes from absorption by the gapless doublet [leftmost transition, denoted GLT, in Figure 6.4 on page 107]. The second and third contributions arise from injection involving exactly one split-off band and contain either (b) only two-band or three-band amplitudes and no cross-term, or (c) cross-terms of two- and three-band amplitudes; two- and three-band amplitudes are denoted 2BT and 3BT in Figure 6.4. The fourth contribution (d) comes from absorption where initial and final states are split-off bands [SOT in Figure 6.4].

The nonzero tensor components are obtained from the symmetry of the matrix elements involved for each contribution, which yields:

\[
\xi_{xxxx}(\omega) = \bar{\xi}_{2a}(\omega) + \left[ 3\bar{\xi}_{2b}(\omega) + \bar{\xi}_{2c}(\omega) \right] \Theta(2\hbar \omega - \gamma_1) + \bar{\xi}_{2d}(\omega) \Theta(2\hbar \omega - 2\gamma_1),
\]

(6.20a)

\[
\xi_{xxyy}(\omega) = -\bar{\xi}_{2a}(\omega) + \left[ \bar{\xi}_{2b}(\omega) + 3\bar{\xi}_{2c}(\omega) \right] \Theta(2\hbar \omega - \gamma_1) - \bar{\xi}_{2d}(\omega) \Theta(2\hbar \omega - 2\gamma_1).
\]

(6.20b)

The matrix elements appearing in $\bar{\xi}_{2a}$ and $\bar{\xi}_{2d}$ have the same symmetry as those appearing in graphene. However, the contributions involving exactly one split-off band (b,c) differ from the graphene result of $\delta = -1$. Indeed, if one defines a partial linear-circular dichroism $\delta_i = \bar{\xi}_{xxyy}^{2i}/\bar{\xi}_{xxxx}^{2i}$ for each contribution $i \in \{a, b, c, d\}$, it follows that $\delta_a = -1$, $\delta_b = \frac{1}{3}$, $\delta_c = 3$ and $\delta_d = -1$. The total linear-circular dichroism depends on the relative strengths of the contributions $\bar{\xi}_{2a-d}$, which is addressed below.

In computing $\Omega_	ext{ec}^{(2)}(\omega, \mathbf{k})$ for the bilayer, a difficulty arises since it is possible for the energy denominator inside the sum in Equation (6.9) to become exactly zero. Take for example the top valence band as initial state $v$ and the second conduction band as final state $c$. When the intermediate state $m$ is the first conduction band, there exists a value
Chapter 6. Carrier and current injection in graphene and bilayer graphene

Figure 6.4: The band dispersion of bilayer graphene and the breakdown of the transition amplitudes for two-photon absorption into contributions of different symmetry. Bands $v_1$ and $v_2$ are valence bands and initially filled, $c_1$ and $c_2$ are initially empty conduction bands. Bands $v_2$ and $c_1$ form a gapless doublet touching at the K point; $c_2$ and $v_1$ are split-off bands shifted by an energy $\gamma_1$ above and below the gapless doublet, respectively. All bands are quadratic near K and linear at larger $k$. Transition amplitudes appear in four variants: i) the gapless term (GLT) between bands $v_2$ and $c_1$, ii) two- and iii) three-band terms involving exactly one split-off band (2BT and 3BT, respectively), and iv) the split-off term (SOT) between bands $v_1$ and $c_2$. The notation $\{\ldots\}$ next to a virtual state indicates that the sum in Equation (6.9) is restricted to $m \in \{\ldots\}$. Not shown are the 2BT and 3BT between bands $v_1$ and $c_1$. 

$\mathbf{v}_1 \mathbf{v}_2 \mathbf{c}_1 \mathbf{c}_2 \mathbf{K} (\mathbf{K}') \omega \omega \omega \omega \omega \omega \omega$
of \( k \) such that \( \hbar \omega_m(k) = \frac{1}{2} \gamma_1 \); at this \( k \) the intermediate state lies precisely in-between the initial and final states. This leads to a resonance in the calculated response functions at \( \hbar \omega = \gamma_1 \). To avoid this resonance, the substitution \( \omega_m \rightarrow \omega_m + i \Gamma / 2 \hbar \) is done in Equation (6.9). The linewidth \( \Gamma \) accounts phenomenologically for dephasing due to actual population of the intermediate state. Other linewidths could be added to describe the effects of disorder or interactions, but their inclusion does not significantly modify the injection process.

With \( \tilde{\xi}_2(\omega) \) given in Equation (6.13), the contributions to two-photon carrier injection are given by

\[
\begin{align*}
\tilde{\xi}_{2a}(\omega) &= \tilde{\xi}_2(\omega) \frac{2 \hbar \omega (2 \hbar \omega + 3 \gamma_1)^2}{(2 \hbar \omega + \gamma_1)(2 \hbar \omega + 2 \gamma_1)^2}, \\
\tilde{\xi}_{2b}(\omega) &= \tilde{\xi}_2(\omega) \frac{2 \gamma_1}{(2 \hbar \omega)^2} \frac{(2 \hbar \omega + \gamma_1)(2 \hbar \omega - \gamma_1)}{(2 \hbar \omega + 2 \gamma_1)^2} \\
&\quad \times \left( \frac{(2 \hbar \omega + 2 \gamma_1)^2}{(2 \hbar \omega)^2} + \frac{(2 \hbar \omega)^2 + \frac{1}{4} \Gamma^2}{(2 \hbar \omega - 2 \gamma_1)^2 + \Gamma^2} \right), \\
\tilde{\xi}_{2c}(\omega) &= -\tilde{\xi}_2(\omega) \frac{2 \gamma_1^3}{(2 \hbar \omega)^3} \frac{(2 \hbar \omega + \gamma_1)(2 \hbar \omega - \gamma_1)}{2 \hbar \omega + 2 \gamma_1} \\
&\quad \times \left( \frac{1}{2 \hbar \omega + 2 \gamma_1} + \frac{2 \hbar \omega - 2 \gamma_1}{(2 \hbar \omega - 2 \gamma_1)^2 + \Gamma^2} \right), \\
\tilde{\xi}_{2d}(\omega) &= \tilde{\xi}_2(\omega) \frac{2 \hbar \omega (2 \hbar \omega - \gamma_1)^2}{(2 \hbar \omega - \gamma_1)^3} \\
&\quad \times \left( 1 - \frac{\gamma_1^2}{(2 \hbar \omega - 2 \gamma_1)^2 + \Gamma^2} \right)^2.
\end{align*}
\]

In contrast to one-photon absorption, where the limits of the bilayer response function at low and high photon energies gave the graphene result times a factor of 2 [141], in two-photon absorption this “factor of 2” rule does not hold at low photon energy: \( \xi_{2\text{bilayer}} \rightarrow 9 \hbar \omega \xi_{2\text{graphene}} / 2 \gamma_1 \) in the limit \( \hbar \omega \ll \gamma_1 \). Further, using the \( 2 \times 2 \) Hamiltonian (6.3) instead yields \( \xi_{2\text{bilayer}} \rightarrow 8 \hbar \omega \xi_{2\text{graphene}} / \gamma_1 \) in the same limit. The derivation using the \( 4 \times 4 \) Hamiltonian (6.2) includes important three-band terms from the split-off bands in the two-photon transition amplitude, which are missing when using Equation (6.3). In the limit of high photon energy, \( \xi_{2\text{bilayer}} \rightarrow 2 \xi_{2\text{graphene}} \) as expected.

The individual contributions \( \tilde{\xi}_{2a-d} \) are shown in Figure 6.5(a) on the following page for a linewidth of \( \Gamma = 0.35 \gamma_1 \). The spectra of \( \tilde{\xi}_{2b-d} \) change quantitatively but not qualitatively when a different finite value is chosen for \( \Gamma \); \( \tilde{\xi}_{2a} \) is independent of \( \Gamma \). The components \( \xi_{2xxxx} \) and \( \xi_{2xxyy} \) of the two-photon carrier-injection tensor are shown in Figure 6.5(b).
Two features are apparent in the response tensor at the thresholds for absorption into the split-off bands. The first feature is a pronounced shoulder in both $\xi_{xxxx}$ and $\xi_{xxyy}$ at $2\hbar\omega = \gamma_1$ due to the onset of absorption involving one split-off band. The second feature is the resonance which occurs at $2\hbar\omega = 2\gamma_1$. There the contributions $\bar{\xi}_{2b}$ and $\bar{\xi}_{2c}$ approximate the real and imaginary parts of a complex Lorentzian function, and contribute to a peak in $\xi_{xxxx}$ and a change of sign in $\xi_{xxyy}$. The linear-circular dichroism $\delta$ is shown in Figure 6.5(c) for different values of $\Gamma$. The linewidth $\Gamma$ has very little effect on $\delta$. The graphene result of $\delta = -1$ is reproduced for $2\hbar\omega < \gamma_1$ and $2\hbar\omega \gtrsim 3\gamma_1$. For mid-frequencies, $\gamma_1 < 2\hbar\omega < 2\gamma_1$, the dichroism increases (decreases) sharply at the first (second) split-off band threshold; $\delta$ changes sign and has a maximum value $\sim 0.5$ near $2\hbar\omega = 1.5\gamma_1$. As a result the ratio of two-photon absorption for circularly-polarized light compared to linearly-polarized light, obtained from Equation (6.11), varies between 0.5 (when $\delta = 0.5$) and 2 (when $\delta = -1$).

6.3.2 Current injection

There are four contributions to the current-injection tensor in bilayer graphene, outlined in Figure 6.6 on page 110: The first (a) comes from absorption by the gapless doublet.
Figure 6.6: Diagrams of the contributions $\tilde{\eta}_{Ia}$, $\tilde{\eta}_{Ib}$, $\tilde{\eta}_{Ic}$, and $\tilde{\eta}_{Id}$ from Equation (6.23) to the current injection in bilayer graphene.
The second and third contributions arise from injection involving exactly one split-off band, with the second-order amplitude containing either (b) only two-band terms or (c) only three-band terms. Transitions involving only the split-off bands make up the fourth (d) contribution.

Each individual process involves matrix elements of varying symmetry, and they contribute differently to $\eta_{l}^{xxxx}$ and $\eta_{l}^{xyyx}$:

$$\eta_{l}^{xxxx}(\omega) = i\bar{\eta}_{la}(\omega) + [3i\bar{\eta}_{lb}(\omega) + i\bar{\eta}_{lc}(\omega)] \Theta(2\hbar\omega - \gamma_1)$$

$$+ i\bar{\eta}_{ld}(\omega) \Theta(2\hbar\omega - 2\gamma_1), \quad (6.22a)$$

$$\eta_{l}^{xyyx}(\omega) = -i\bar{\eta}_{la}(\omega) + [i\bar{\eta}_{lb}(\omega) + 3i\bar{\eta}_{lc}(\omega)] \Theta(2\hbar\omega - \gamma_1)$$

$$- i\bar{\eta}_{ld}(\omega) \Theta(2\hbar\omega - 2\gamma_1). \quad (6.22b)$$

The four contributions, taken individually, have dissimilar values of the parallel-perpendicular polarization disparity parameter: $d_a = -1$, $d_b = \frac{1}{3}$, $d_c = 3$, and $d_d = -1$. Recall that for graphene $d = -1$. Current injection in bilayer graphene differs from single-layer graphene due to the contributions of components $\bar{\eta}_{lb}$ and $\bar{\eta}_{lc}$.

The following magnitudes are obtained for the current-injection components:

$$\bar{\eta}_{la}(\omega) = \bar{\eta}_{l}(\omega) \frac{2\hbar\omega}{(2\hbar\omega + \gamma_1)^2} \frac{2\hbar\omega + 3\gamma_1}{2\hbar\omega + \gamma_1}, \quad (6.23a)$$

$$\bar{\eta}_{lb}(\omega) = \bar{\eta}_{l}(\omega) \frac{2\gamma_1^2}{(2\hbar\omega)^2} \frac{(2\hbar\omega + \gamma_1)(2\hbar\omega - \gamma_1)}{(2\hbar\omega)^2} \frac{2\hbar\omega - \gamma_1}{2\hbar\omega + \gamma_1}, \quad (6.23b)$$

$$\bar{\eta}_{lc}(\omega) = -\bar{\eta}_{l}(\omega) \gamma_1^2 \frac{2\hbar\omega + \gamma_1}{(2\hbar\omega)^3} \frac{(2\hbar\omega + \gamma_1)(2\hbar\omega - \gamma_1)}{(2\hbar\omega + \gamma_1)(2\hbar\omega - \gamma_1)}$$

$$\times \left( \frac{1}{2\hbar\omega + 2\gamma_1} + \frac{2\hbar\omega - 2\gamma_1}{(2\hbar\omega - 2\gamma_1)^2 + \Gamma^2} \right), \quad (6.23c)$$

$$\bar{\eta}_{ld}(\omega) = \bar{\eta}_{l}(\omega) \frac{2\hbar\omega}{(2\hbar\omega - \gamma_1)^3} \frac{2\hbar\omega - 2\gamma_1}{2\hbar\omega - \gamma_1}$$

$$\times \left( 1 - \frac{\gamma_1^2}{(2\hbar\omega - 2\gamma_1)^2 + \Gamma^2} \right), \quad (6.23d)$$

with $\bar{\eta}_{l}(\omega)$ given in Equation (6.16). In the high frequency limit, the current-injection tensor for the bilayer tends to $\bar{\eta}_{l(bilayer)}(\omega) \rightarrow 2\bar{\eta}_{l(graphene)}(\omega)$. In the low frequency limit, the $4 \times 4$ Hamiltonian (6.2) gives $\bar{\eta}_{l(bilayer)}(\omega) \rightarrow 6\hbar\omega \bar{\eta}_{l(graphene)}(\omega)/\gamma_1$, while the $2 \times 2$ Hamiltonian (6.3), which neglects three-band terms in the second-order amplitude, gives $\bar{\eta}_{l(bilayer)}(\omega) \rightarrow 8\hbar\omega \bar{\eta}_{l(graphene)}(\omega)/\gamma_1$.

The parameters $\bar{\eta}_{la-d}$ are plotted in Figure 6.7(a) on the next page. The two independent components of $\bar{\eta}_{l}$ in the isotropic model, $\eta_{l}^{xxxx}$ and $\eta_{l}^{xyyx}$, are plotted in Figure 6.7(b).
Figure 6.7: The current-injection tensor $\eta_I$ in bilayer graphene. (a) The contributions $\tilde{\eta}_{Ia}$ (plain red), $\tilde{\eta}_{Ib}$ (long-dashed blue), $\tilde{\eta}_{Ic}$ (short-dashed green), and $\tilde{\eta}_{Id}$ (dotted orange) from Equation (6.23), for an intermediate state linewidth $\Gamma/\gamma_1 = 0.25$. (b) The tensor components $\eta_I^{xxxx}$ (plain black) and $\eta_I^{yyxx}$ (dashed red). (c) The disparity parameter $d = \eta_I^{yyxx}/\eta_I^{xxxx}$ describing the asymmetry between parallel and perpendicular polarization axes, for $\Gamma/\gamma_1 = 0.15$ (dotted orange), 0.25 (short-dashed green), 0.35 (long-dashed blue), and 0.45 (plain red).

Figure 6.8: Current injection using linearly-polarized $\omega$ and $2\omega$ light in an isotropic medium. Polar plots of $f(\theta, d)$ and $g(\theta, d)$, the angular distributions of the projections of $\dot{J}$ parallel and perpendicular to $\hat{e}_{2\omega}$, as a function of the angle $\theta$ between the polarization vectors, for $d = -2$, $-1$, $-0.5$, 0, and 0.5. The shaded circles represent unit amplitude and dashed lines represent negative projections. The graphene prediction, $d = -1$, is highlighted.
A sharp increase occurs in $\eta_f$ at the first split-off band edge at $2\hbar\omega = \gamma_1$ and a sharp decrease at the second edge at $2\hbar\omega = 2\gamma_1$. Two features are manifest as a consequence of these split-off band edges: (i) In the region $\gamma_1 < 2\hbar\omega < 2\gamma_1$ the $\eta^{xyyx}_{f}$ component changes sign. (ii) For $2\hbar\omega \gtrsim 2\gamma_1$ the $\eta^{xxxx}_{f}$ component becomes very small. Figure 6.7(c) shows the frequency dependence of $d$ in bilayer graphene. The spectrum shows a constant $-1$ value from zero frequency until a sharp increase at the first split-off band edge at $2\hbar\omega = \gamma_1$; $d$ rises with photon energy and eventually switches sign. At the second split-off band edge at $2\hbar\omega = 2\gamma_1$, $d$ reverses sign abruptly. In the range $2\gamma_1 < 2\hbar\omega \lesssim 3\gamma_1$, $d$ takes on large negative values; as shown in Figure 6.7(b) $\eta^{xyyx}_{f}$ remains finite but $\eta^{xxxx}_{f}$ becomes small.

The value of $d$ tends to $-1$ at higher photon energy.

To consider current injection in bilayer graphene under irradiation by $\omega$ and $2\omega$ beams at normal incidence is considered, the electric fields $E(\omega)$ and $E(2\omega)$ are chosen as in the previous section. The current-injection rate is given for co-circular polarization of the beams ($\delta \varphi_\omega = \delta \varphi_{2\omega} = \pm \frac{\pi}{2}$) by

$$\dot{J} = (1 - d)\sqrt{2} \text{Im} [\eta^{xxxx}_{f}] E^2_\omega E_{2\omega} \hat{m} \quad (6.24)$$

and for opposite-circular polarization ($-\delta \varphi_\omega = \delta \varphi_{2\omega} = \pm \frac{\pi}{2}$) by $\dot{J} = 0$. In Equation (6.24), the disparity parameter $d$ only affects the magnitude of the current. In contrast, for linearly-polarized $\omega$ and $2\omega$ beams ($\delta \varphi_\omega = \delta \varphi_{2\omega} = 0$) forming an angle $\theta$ between their polarization axes, different values of $d$ lead to injected currents with different magnitudes but also with vastly dissimilar angular dependencies:

$$\dot{J} = 2 \text{Im} [\eta^{xxxx}_{f}] E^2_\omega E_{2\omega} \sin(\Delta \varphi) \left[ f(\theta, d) \hat{e}_{2\omega} + g(\theta, d) \hat{e}^\perp_{2\omega} \right], \quad (6.25)$$

where $f(\theta, d) = \cos^2 \theta + d \sin^2 \theta$ and $g(\theta, d) = \frac{1}{2} (1 - d) \sin 2\theta$. Thus, the current component that is parallel to $\hat{e}_{2\omega}$ has a nonseparable dependence on $\theta$ and $d$, whereas the perpendicular component always follows $\sin 2\theta$. Polar plots of the functions $f(\theta, d)$ and $g(\theta, d)$ are shown for $d = -2, -1, -0.5, 0, 0.5$ in Figure 6.8 on page 112. The value of $d = -1$ for graphene yields a clover-shaped angular distribution: the $\cos 2\theta$ dependence in Equation (6.18). For more (or less) negative values of $d$, the lobes around $\theta = \frac{\pi}{2}$ and $\frac{3\pi}{2}$ become more (or less) important. At $d = 0$, these two lobes vanish; any current injected with perpendicular $\omega$ and $2\omega$ polarization axes is completely perpendicular to $\hat{e}_{2\omega}$. For $d > 0$ there are no nodes in the angular distribution. For $|d| > 1$ the current parallel to $\hat{e}_{2\omega}$ is stronger for perpendicular polarization axes compared to parallel polarization axes. By scanning the photon energy in the range $\gamma_1 < 2\hbar\omega \lesssim 3\gamma_1$, the disparity parameter
\(d\) and thus the angular dependence of the current injection in bilayer graphene vary significantly, in contrast with the current injection in single-layer graphene. In particular, the sharp changes in the value of \(d\) near \(2\hbar\omega \approx \gamma_1\) and \(2\hbar\omega \approx 2\gamma_1\) would be perceived experimentally by rapid transitions in the angular dependence of the currents as the photon energy is scanned.

### 6.4 Conclusion

A number of differences occur between coherent current control in graphene and in conventional semiconductors. In two-color coherent control experiments in gapped semiconductors, the fields are typically chosen so that the semiconducting bandgap \(E_g\) lies between \(\hbar\omega < E_g < 2\hbar\omega\). Thus, one-photon absorption at the fundamental frequency is energetically forbidden. However, since the band dispersions of graphene and bilayer graphene are gapless, for a clean, unbiased sample there is a nonzero joint density of states down to zero frequency and one-photon absorption is always present. This is in contrast with typical two-color coherent control experiments, where the usual best practice is to have balanced absorption between the first-order process at \(2\omega\) and the second-order process at \(\omega\). However, this has not led to difficulties in observing the coherent current control in multilayer epitaxial graphene [72].

The results presented here hold for \(\hbar\omega > |E_F|\), where \(E_F\) is the Fermi energy. The linear absorption of the fundamental beam can be suppressed by taking advantage of Pauli blocking for a nonzero Fermi energy \(E_F\). In typical coherent control experiments with gapped semiconductors, the semiconducting bandgap \(E_g\) lies between \(\hbar\omega < E_g < 2\hbar\omega\), preventing one-photon absorption at \(\omega\). Restricting the fundamental and second harmonic beam to satisfy \(\hbar\omega/2 < |E_F| < \hbar\omega\) is a similarly equivalent condition for experiments in graphene, with the added advantage that the Fermi energy can be gate-controlled. Tunability in the Pauli blocking of the absorption could lead to novel electro-optical devices making use of coherent current control.

In summary, calculations of the response tensors for one- and two-photon carrier injection and two-color current injection in graphene and bilayer graphene have been presented. In single-layer graphene, a strong, frequency-independent linear-circular dichroism \(\delta = -1\) exists in the two-photon response. Using the optical coherent control technique, in-plane currents are generated for co-circularly polarized and linearly-polarized, \(\omega\) and \(2\omega\) beams. The ratio \(d\) of current injection for parallel and perpendicular polarizations of
linearly-polarized beams is independent of frequency at lowest order.

In bilayer graphene, both \( \delta \) and \( d \) display resonant features associated with interlayer coupling. The linear-circular dichroism \( \delta \) also equals \(-1\) when \( 2\hbar\omega < \gamma_1 \) or \( 2\hbar\omega \gtrsim 3\gamma_1 \), and changes sign when \( \gamma_1 < 2\hbar\omega \lesssim 3\gamma_1 \). The dependence on the angle \( \theta \) between linearly-polarized light components at \( \omega \) and \( 2\omega \), characterized by the parallel-perpendicular disparity \( d \), is strongly sensitive to the photon energy for \( \gamma_1 < 2\hbar\omega \lesssim 3\gamma_1 \).

A natural extension of the current model is to consider AB-stacked multilayer graphene samples. Koshino and Ando have shown that for \( n \) layers with \( n \) even, a unitary transformation decouples the Hamiltonian into \( n/2 \) bilayers (with \( n \) odd, \((n-1)/2\) bilayers and one decoupled single layer) \[142\]. Each bilayer pair has a reduced coupling strength \( \lambda_m \gamma_1 \) where \( \lambda_m = 2 \cos \kappa_m \) and \( \kappa_m \) is a wavevector in the stacking direction. The response of the multilayer system is the sum of the bilayer systems responses with detuned coupling strengths. In the limit of a high number of layers, the wavevector \( \kappa \) becomes a continuous variable and there is a continuous spectrum of resonances, smearing out the response tensor and eventually modeling the response of bulk graphite.
Chapter 7

Conclusion

The optical injection and coherent control of charge and spin in semiconductors are of fundamental and technological importance. The calculations of optical carrier, spin, current, and spin current injection offer a basis for understanding these phenomena and for experimental work on the materials GaAs, Ge, and graphene.

Calculations based on the $k \cdot p$ method rely on parameters that are not directly available from experiments. I obtained parameter sets describing Ge and GaAs that give the experimental effective masses and gyromagnetic factors at the $\Gamma$ point and the top-valence and lowest-conduction band energies at the edge of the Brillouin zone. I highlight that care must be taken in deriving $k \cdot p$ band parameters. All experimental data available must be taken into account in the fitting, especially the conduction-band gyromagnetic factor at the $\Gamma$ point. Exact diagonalization of the Hamiltonian is necessary to account for band mixing, which occurs even at the expansion point due to spin-orbit coupling.

Optical carrier, spin, current, and spin current injection processes by one- or two-color schemes are not exclusively band edge phenomena. Using a full-zone band structure model, I have calculated the injection rates over an energy range of 0–4 eV in GaAs and 0–3.5 eV in Ge. By comparison, previous studies were limited to a few hundred meV’s above the band edge. Anisotropic effects appear in the full-band structure calculations and are of interest for new experimental configurations. I find that injection at energies matching the $E_1$ resonance yields strong spin and current responses that are anisotropic in the nonlinear regime. For spin injection, the degree of spin polarization is 30% in one-photon absorption and 16% and 20% in two-photon absorption at respectively $\langle 001 \rangle$ and $\langle 111 \rangle$ incidence. For current injection, the anisotropy is $s \approx -0.5$ at the same energy, resulting
in a significant normal component of the current for \( \langle 111 \rangle \) incidence. The characteristic spin and current injection at the \( E_1 \) resonance results from the high joint density of states and the splitting in the valence bands in the \( \Gamma-L \) region of reciprocal space.

For Ge, I calculated the contributions of both electrons and holes to spin, current, and spin current injection processes related to even-order susceptibilities. As my calculations show, the electronic contribution does not behave qualitatively different between Ge and GaAs. Lighter effective masses and the smaller band gap in Ge yield larger magnitudes for the injection rates. At excess photon energy of 200 meV, injection rates for Ge and GaAs are in the ratio 2.5 : 1 for one-photon, 5 : 1 for two-color, and 10 : 1 for two-photon processes. The optical orientation of holes yields 83% spin polarization at the band edge. Injection rates for hole spin are higher than for electron spin within 80 meV of the band edge and are comparable for excess photon energy larger than 80 meV. Further, the average hole velocity contributes a significant anisotropic contribution to current and spin current injection in the two-color, \( \omega \) and \( 2\omega \) scheme. With its strong response, including electron and hole contributions, Ge is an interesting material for the experimental study of these optical effects.

Complicated carrier dynamics arises in Ge due to the indirect conduction-band minimum at the L point. The sidevalley scattering offers a relaxation process for injected electrons. The dynamics of the relaxation mechanism quickly leaves the holes as the only zone-center carriers. As a consequence, holes are more accessible and play a more important role in optical experiments in Ge than in GaAs. In the pump-probe scenario, carrier and spin injection affects the absorption and transmission of a probe beam. I calculated the change in linear optical absorption due to the injected electron population. Carrier cooling, spin relaxation, and sidevalley scattering are considered phenomenologically. For experiments sensitive to direct-gap absorption, the signature for spin injection relaxes on a much faster time scale in Ge than in GaAs due to the dynamics of fast electron intervalley scattering. Holes are thus of greater importance, and I presented an approach to include their dynamics and argued that instead of the usual Fermi filling factor, a density matrix treatment is necessary. Probing these effects in spin and current injection in Ge is a subject of ongoing experimental investigations.

For graphene in bilayer graphene, I calculated the response tensors for one- and two-photon absorption and two-color coherent current control within the tight-binding model. The two-photon absorption exhibits a strong linear-circular dichroism compared to the semiconductors GaAs and Ge. In single-layer graphene, the linear-circular dichroism
is $\delta = -1$ at all frequencies, and the two-photon absorption coefficient is twice as large for circularly-polarized light compared to linearly-polarized light. In bilayer graphene, this circular-linear dichroism $\delta$ varies between 0.5 and 2. The variation occurs as the excitation energy is tuned across a resonance in the two-photon absorption due to the interlayer coupling. Photocurrents are injected in single and bilayer graphene under linearly and co-circularly polarized two-color, $\omega$ and $2\omega$ light. Co-circular polarization yields the strongest current, while opposite-circular polarization yields no net current. For single-layer graphene, the magnitude of the current is unaffected by the rotation of linear-polarization axes, in contrast with the bilayer and conventional semiconductors such as GaAs and Ge. The dependence of the photocurrent on the linear-polarization axes is a clear and measurable signature of interlayer coupling in bilayer graphene. Thus, the angular dependence of the current injection can be used as a differentiation scheme between single-layer and bilayer graphene.
Appendix A

Conversion between systems of units

The tensors and pseudotensors used to describe the injection processes in Chapters 3 through 6 are introduced in the Gaussian \textit{cgs} system of quantities and units. In the Système International with \textit{mks} units, injection tensors are defined such that their defining equations retain their equality for both systems. However, even basic electromagnetic quantities are defined differently between Gaussian \textit{cgs} and International \textit{mks} systems. For example, the relation between an external electric field $\mathbf{E}$ and the polarization $\mathbf{P}$ has the form

$$\mathbf{P} = \chi \mathbf{E} + \chi^{(2)} \mathbf{E} \mathbf{E} + \ldots \quad \text{with} \quad \epsilon = 1 + 4\pi \chi \quad \text{in Gaussian \textit{cgs},}$$

and

$$\mathbf{P} = \epsilon_0 \left( \chi \mathbf{E} + \chi^{(2)} \mathbf{E} \mathbf{E} + \ldots \right) \quad \text{with} \quad \epsilon/\epsilon_0 = 1 + \chi \quad \text{in SI \textit{mks}.}$$

Table A.1 helps in the conversion of equations containing basic electromagnetic quantities from Gaussian \textit{cgs} to SI \textit{mks}. Table A.2 does the same for the various injection tensors, and lists their defining equation.
### Appendix A. Conversion between systems of units

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<th>SI mks</th>
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<td>( \chi^{(n)}\varepsilon_0/(4\pi\varepsilon_0)^{(n+1)/2} )</td>
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**Table A.1:** Conversion of basic electromagnetic quantities between the Gaussian system and Système International.

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</tr>
<tr>
<td>Two-color current injection control</td>
<td>( \eta_I )</td>
<td>( \eta_I/(4\pi\varepsilon_0)^{3/2} )</td>
<td>Equation (3.84)</td>
</tr>
<tr>
<td>One-photon spin current injection</td>
<td>( \mu_1 )</td>
<td>( \mu_1/4\pi\varepsilon_0 )</td>
<td>—</td>
</tr>
<tr>
<td>Two-photon spin current injection</td>
<td>( \mu_2 )</td>
<td>( \mu_2/(4\pi\varepsilon_0)^2 )</td>
<td>—</td>
</tr>
<tr>
<td>Two-color spin current injection control</td>
<td>( \mu_I )</td>
<td>( \mu_I/(4\pi\varepsilon_0)^{5/2} )</td>
<td>Equation (3.86)</td>
</tr>
</tbody>
</table>

**Table A.2:** Conversion of the various injection tensors between the Gaussian system and Système International.
Appendix B

Linear interpolation method

The computations of optical responses in \( n \) dimensions involve integrals of the form

\[
I = \int d^n r \ f(r) \ \delta(g(r)).
\] (B.1)

We use a coordinate transformation \( r \mapsto g(r), s(r) \) to rewrite this as

\[
I = \int dg \int \frac{d^{n-1}s}{|\nabla g|} \ f(r) \ \delta(g(r)),
\] (B.2)

where \( |\nabla g| \) is the Jacobian. Since the new coordinate \( g(r) \) is the argument to a delta function, we can readily evaluate the integration over this dimension. We obtain

\[
I = \left[ \frac{d^{n-1}s}{|\nabla g|} f(r) \right]_{g(r)=0},
\] (B.3)

with the integrand evaluated on the solution space \( g(r) = 0 \). Further, we assume that the integrand can be linearly interpolated within the solution space, and obtain

\[
I \approx \left\langle \frac{f}{|\nabla g|} \right\rangle \int_{g(r)=0} d^{n-1}s = \left\langle \frac{f}{|\nabla g|} \right\rangle V^{n-1}.
\] (B.4)

Thus, this reduces the problem to:

1. Finding \( \left\langle \frac{f}{|\nabla g|} \right\rangle \), the average of \( \frac{f(r)}{|\nabla g|} \) over the solution space to \( g(r) = 0 \).
2. Finding the volume \( V^{n-1} \) of the solution space to \( g(r) = 0 \).

B.1 Interpolation and integration in two dimensions

Linear interpolation over \( \mathbb{R}^2 \) involves three parameters: the \( x \) slope, the \( y \) slope, and the intercept. Solving for these parameters requires three equations, and thus three known
Appendix B. Linear interpolation method

$(x, y, f(x, y))$ triplets. For this reason, triangles are used for the linear interpolation; they are the simplest polygons with the required number of apex.

The solution to $g(r) = 0$ is a line through $\mathbb{R}^2$. Consider the triangular area element 1–2–3. Suppose the line segment cuts through the triangle on the edges 1–2 and 1–3, forming the intersection points A (along 1–2) and B (along 1–3). The apex of the triangle are at $r_1$, $r_2$ and $r_3$, and we know from discrete evaluations the values $f_1$, $f_2$, $f_3$ of $f(r)$ and $g_1$, $g_2$, $g_3$ of $g(r)$ at the apex. The function $g(r)$ within the triangle is linearly interpolated to

$$g(r) \approx g_1 + (g_2 a_{21} + g_3 a_{31}) \cdot (r - r_1).$$

The vectors $a_{21}$ and $a_{31}$ are given by

$$a_{21} = \hat{z} \times r_{31} / S,$$
$$a_{31} = \hat{z} \times r_{21} / S,$$

where $S = \hat{z} \cdot (r_{21} \times r_{31})$ is twice the area of the triangle, and we define the shorthands $g_{n1} \equiv g_n - g_1$ and $r_{n1} \equiv r_n - r_1$. Solving $g(r) = 0$ with $r = x_{21}r_{21} + x_{31}r_{31}$ yields for the components the relation

$$g_1 + g_{21}x_{21} + g_{31}x_{31} = 0 \Rightarrow \begin{pmatrix} x_{21} \\ x_{31} \end{pmatrix} = \begin{pmatrix} -g_1 / g_{21}(1-t) \\ -g_1 / g_{31}t \end{pmatrix}.$$  

Point A corresponds to $t = 0$ while point B to $t = 1$. Just like for $g(r)$, the linear interpolation for $f(r)$ within the triangle gives

$$f(r) \approx f_1 + (f_2 a_{21} + f_3 a_{31}) \cdot (r - r_1) = f_1 + x_{21}f_{21} + x_{31}f_{31}.$$ 

We can now provide answers to the last points from the previous section.

1. The average value of $f(r)$ on the line segment A–B is the value at the half-way point:

$$\langle f \rangle = [f]_{t=0.5} = f_1 - \frac{g_1}{2g_{21}}f_{21} - \frac{g_1}{2g_{31}}f_{31}.$$
2. The length of the line segment A–B can be found from the coordinates of A and B:

\[ \mathbf{r}_B - \mathbf{r}_A = (x_{21}(1) - x_{21}(0)) \mathbf{r}_{21} + (x_{31}(1) - x_{31}(0)) \mathbf{r}_{31} \]

\[ = \frac{g_1}{g_{21}} \mathbf{r}_{21} - \frac{g_1}{g_{31}} \mathbf{r}_{31}, \]

\[ |\mathbf{r}_B - \mathbf{r}_A|^2 = \frac{g_1^2}{g_{21}^2} \mathbf{r}_{21} \cdot \mathbf{r}_{21} + \frac{g_1^2}{g_{31}^2} \mathbf{r}_{31} \cdot \mathbf{r}_{31} - \frac{2g_1^2}{g_{21}g_{31}} \mathbf{r}_{21} \cdot \mathbf{r}_{31} \]

\[ = \frac{g_1^2}{g_{21}^2 g_{31}^2} \left( g_{31}^2 \mathbf{r}_{21} \cdot \mathbf{r}_{21} + g_{21}^2 \mathbf{r}_{31} \cdot \mathbf{r}_{31} - 2g_{21}g_{31} \mathbf{r}_{21} \cdot \mathbf{r}_{31} \right) \]

\[ = \frac{g_1^2}{g_{21}^2 g_{31}^2} |g_{31} \mathbf{r}_{21} - g_{21} \mathbf{r}_{31}|^2 \]

Compare with

\[ |\nabla g|^2 = |g_{21} \mathbf{a}_{21} + g_{31} \mathbf{a}_{31}|^2 \]

\[ = (g_{21} \mathbf{a}_{21} + g_{31} \mathbf{a}_{31}) \cdot (g_{21} \mathbf{a}_{21} + g_{31} \mathbf{a}_{31}) \]

\[ = g_{21}^2 \mathbf{a}_{21} \cdot \mathbf{a}_{21} + g_{31}^2 \mathbf{a}_{31} \cdot \mathbf{a}_{31} + 2g_{21}g_{31} \mathbf{a}_{21} \cdot \mathbf{a}_{31} \]

\[ = \left( g_{21}^2 \mathbf{r}_{31} \cdot \mathbf{r}_{31} + g_{31}^2 \mathbf{r}_{21} \cdot \mathbf{r}_{21} + 2g_{21}g_{31} \mathbf{r}_{21} \cdot \mathbf{r}_{31} \right) / S^2 \]

where we used \( \mathbf{a}_{21} \cdot \mathbf{a}_{21} = (\hat{z} \times \mathbf{r}_{31}) \cdot (\hat{z} \times \mathbf{r}_{31}) / S^2 = \mathbf{r}_{31} \cdot \mathbf{r}_{31} / S^2 \) and \( \mathbf{a}_{21} \cdot \mathbf{a}_{31} = (\hat{z} \times \mathbf{r}_{31}) \cdot (\hat{z} \times \mathbf{r}_{21}) / S^2 = \mathbf{r}_{21} \cdot \mathbf{r}_{31} / S^2 \). Recall \( S = 2s \) with \( s \) the area of the triangle.

We find

\[ |\mathbf{r}_B - \mathbf{r}_A| = 2s \left| \frac{g_1}{g_{21}g_{31}} \right| |\nabla g|. \]

Thus, we have

\[ I \approx 2s \left| \frac{g_1}{g_{21}g_{31}} \right| \left( f_1 - \frac{g_1}{2g_{21}} f_{21} - \frac{g_1}{2g_{31}} f_{31} \right). \]  \hspace{1cm} (B.5)

**B.2 Interpolation and integration in three dimensions**

In \( \mathbb{R}^3 \) the volume element used is the tetrahedron. The solution space for \( g(\mathbf{r}) \) is the surface of the intersection of a plane with the tetrahedron. Since there are different ways to cut a tetrahedron with a plane, there are different cases to consider. All three cases are covered in Blöchl et al. [143, Appendix C] and we give the result here:
Appendix B. Linear interpolation method

1. \( g_1 < g_2 < g_3 < g_4 \)

\[
I \approx 3v \left| \frac{g_1^2}{g_21g_31g_41} \right| \left( f_1 - \frac{g_1}{3g_21} f_{21} - \frac{g_1}{3g_31} f_{31} - \frac{g_1}{3g_41} f_{41} \right), \tag{B.6}
\]

where \( v \) is the volume of the tetrahedron.

2. \( g_1 < g_2 < 0 < g_3 < g_4 \)

\[
I \approx \frac{v}{g_31g_41} \left[ 3g_{21} - 6g_2 - 3\left( \frac{g_{31} + g_{42}}{g_{32}g_{42}} \right) \right] (f), \tag{B.7}
\]

3. \( g_1 < g_2 < g_3 < 0 < g_4 \)

\[
I \approx 3v \left| \frac{g_4^2}{g_{14}g_{24}g_{34}} \right| \left( f_4 - \frac{g_4}{3g_{14}} f_{14} - \frac{g_4}{3g_{24}} f_{24} - \frac{g_4}{3g_{34}} f_{34} \right). \tag{B.8}
\]
Appendix C

Irreducible adaptive grids

The computation of optical responses require numerically integrating expressions of the form of Equation (B.1). The integrand $f(\mathbf{k})$ and the isosurface $g(\mathbf{k}) = 0$ are evaluated numerically on a grid, and interpolated linearly, following Appendix B. The interpolation requires a dense grid if $f(\mathbf{k})$ and $g(\mathbf{k})$ have large curvature. Ge in particular has a small conduction-band effective mass, and thus a large curvature in its band dispersion near the $\Gamma$ point. The spectral features of the injection tensors require a significant number of $\mathbf{k}$ points in order to resolve them numerically. Efficient $\mathbf{k}$ point sampling becomes very important to minimize the computation time. The present work employs the reduction method of Blöchl et al. [143] and an adaptive refinement technique to produce an irreducible wedge covering the equivalent of the full Brillouin zone at various degrees of coarseness. Numerical integration is then performed by linearly interpolating integrands and energies over tetrahedral volume elements of various sizes. The number of volume elements is reduced by symmetry to cover only the irreducible Brillouin zone. The details of the refinement and reduction steps are described in Nastos et al. [36]. The resulting grid for GaAs uses 76,575 $\mathbf{k}$ points; the finest region, at the zone center, is covered by an effective $1280 \times 1280 \times 1280$ grid. For Ge, 90,124 $\mathbf{k}$ points are used for the same level of refinement.
Appendix D

Carrier and spin injection in Si

Si is an interesting material for spintronics applications due to its mature technology and long electron spin relaxation time [144]. A prerequisite for silicon-based spin devices is the effective injection of spins. The first spin injection experiment involved optical absorption across the indirect gap in Si [145, 146]. However, optical orientation in Si has since then mostly been abandoned for its apparent inefficiency. The necessary phonon mediation and the weak spin-orbit coupling have crippled interest, despite the lack of full-band structure calculations to address these points.

Si has also attracted widespread interest in photonics due to its potential application in ultracompact all-optical and opto-electronic devices, particularly for use at telecommunication wavelengths near 1.55\,\mu m. Many of these applications are based on the change in index of refraction with intensity, a third-order optical nonlinearity [147]. Two-photon absorption, which can plague optical devices because of both immediate nonlinear loss and subsequent loss due to free-carrier absorption, is also a third-order nonlinearity. However, in the interesting wavelength range of 1.2\,\mu m to 1.7\,\mu m the sum of energies from two photons is only sufficient to excite an electron across the indirect band gap, with the assistance of an absorbed or emitted phonon.

Spin injection by optical orientation in Si is described for direct transitions in Nastos, Rioux, Strimas-Mackey, Mendoza, and Sipe, Phys. Rev. B 76, 205113 (2007), and for indirect transitions in Cheng, Rioux, Fabian, and Sipe, Phys. Rev. B 83, 165211 (2011). Both publications give the selection rules for band-edge transitions, and numerically determine the degree of spin polarization for a range of photon energies above the band edge. We find that, despite weak spin-orbit coupling, carriers can be generated optically with a significant spin polarization, even at room temperature. For direct transitions,
there can be up to 30% spin polarization. For indirect transitions at 4 K, a maximum spin polarization of 25% is found at the band edge; at room temperature the polarization is still 15%. Such a robust optical spin orientation could be probed either electrically or optically.

Two-photon absorption in Si is described in Cheng, Rioux, and Sipe, Appl. Phys. Lett. 98, 131101 (2011). The full-band structure calculation uses a pseudopotential description of the electronic bands and an adiabatic bond charge model to describe phonon dispersion and polarization. We find that the two-photon indirect absorption coefficient is about 1 cm/GW at 1.55 μm and 300 K, in fair agreement with recent experimental results, and that the TA and TO phonon-assisted processes dominate the absorption.
Bibliography


