

UNIVERSITY OF THE BASQUE COUNTRY



Charge and spin photocurrents in topological systems, surfaces and unconventional magnets

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by

Javier Sivianes Castaño

Supervised by
Dr. Julen Ibañez Azpiroz
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Chapter 1

Introduction

The interplay of light and matter produces a wide variety of optical responses that are exploited for energy harvesting and information technology, in addition to more fundamental purposes such as probes of material symmetries. These responses range from elementary linear processes such as absorption and refraction to an extensive array of nonlinear phenomena whose sensitivity to symmetry and electronic structure makes them powerful probes of material properties. Among these, this thesis pays special attention to the bulk photovoltaic effect (BPVE)—a mechanism by which homogeneous non-centrosymmetric crystals generate a direct photocurrent under illumination. First discovered in the 1970s, early experiments confirmed the existence of the effect through anomalously large photovoltages that grow quadratically with the electric field of light. Despite the strong initial interest, the reported power conversion efficiencies remained very low, and the effect consequently lost relevance for practical applications.

Over roughly the past decade, the BPVE has undergone a pronounced resurgence, driven by both conceptual advances and the ability to compute and measure nonlinear photocurrents with quantitative accuracy. A central development has been the adaptation of the theory into a form directly compatible with first-principles electronic-structure methods. In particular, Young and Rappe [1] computed the shift current — one of the main contributions to the BPVE, formally introduced in Chapter 2 — in BaTiO_3 and managed to reproduce its key experimental features, that is, magnitude, spectral shape, and sign reversals of individual tensor components [1, 2]. Subsequent theoretical efforts have incorporated electron-phonon and electron-hole interactions into first-principles frameworks to clarify the ballistic contribution [3, 4]. Experimentally, BPVE detection has recently moved beyond wide-gap insulators into metallic systems, thanks to intense few-cycle pulses that enable time-resolved terahertz emission and photocurrent spectroscopy [5, 6].

Another major line of development has been the recognition of the BPVE as a manifestation of quantum geometry. The dependence of the effect on

the phase structure of Bloch states links it directly to the modern theory of polarization and to geometric and topological invariants of band structures [7–9]. This geometric perspective has been especially influential in the context of Weyl semimetals. For these systems, theory predicts that the injection current under circularly polarized light—the circular photogalvanic effect (CPGE)—can exhibit a quantized response determined by fundamental constants and the monopole charge of Weyl nodes [10, 11]. Experiments on Weyl semimetals such as TaAs have since reported giant photocurrents over wide frequency ranges, often exceeding by orders of magnitude the responses observed in conventional ferroelectrics [12–14]. Strong topological insulators similarly display enhanced photogalvanic effects at surfaces and interfaces due to their inverted band structures and robust spin-orbit coupling [15, 16]. These materials thus serve both as stringent tests of nonlinear optical theories grounded in quantum geometry and as promising platforms for high-sensitivity photodetection and optoelectronic functionality.

Two-dimensional (2D) materials have also emerged as a fertile platform for the BPVE, owing to their strong light-matter interactions and tunable properties. Noncentrosymmetric 2D crystals such as transition metal dichalcogenides and group-IV monochalcogenides exhibit sizable shift currents, with theoretical predictions indicating large effective three-dimensional shift currents in the visible spectrum [2]. These materials offer multiple degrees of freedom—including strain, gating, and stacking order—for engineering the photogalvanic response [17]. Spectrally, 2D materials are particularly attractive because van Hove singularities and other sharp features in the joint density of states amplify transition matrix elements, leading to pronounced photocurrent peaks. Since the band edge always induces a Van Hove singularity, low-dimensional materials naturally present stronger singularities, making them ideal for achieving large photoresponse peaks [18].

Magnetically ordered systems introduce yet another layer of richness to the phenomenology. In van der Waals magnets such as bilayer CrI_3 , the antiferromagnetic phase breaks both inversion and time-reversal symmetry while preserving their product, creating a symmetry environment in which injection-type currents can be generated even under linearly polarized light [19]. In such systems, the magnitude and direction of the photogalvanic response can be controlled by switching the magnetic configuration, providing an optoelectronic readout of magnetic states and suggesting potential applications in magneto-photovoltaic memory elements.

Despite these advances, leveraging the BPVE for practical energy harvesting remains challenging. While reports of local efficiencies exceeding the Shockley–Queisser limit exist under specialized conditions (e.g., tip-enhanced measurements on BaTiO_3 [20]), under standard illumination and geometries relevant for devices, current densities and efficiencies remain modest. The response peaks above the band gap—where solar flux is low—and its nonlinear nature complicates scaling. Nevertheless, multiple research directions are

actively working to bridge this gap, including the use of nanotubes [21, 22], strain engineering [23], ferroelectric nanostructures [24], and improved contact designs [25]. Consequently, the BPVE is currently better suited for specialized applications, such as probes of symmetry [26] and topology [27], where its unique features offer distinct advantages even without high efficiency.

Building on these developments, this thesis employs a combination of toy models and ab-initio methods to investigate the BPVE and related nonlinear optical responses in a variety of systems. Chapter 3 begins by exploring the shift photoconductivity in the Haldane model as a minimal theoretical setting where band topology directly affects the nonlinear optical response. A low-energy analytic treatment reveals that the shift current changes sign when the system undergoes a topological phase transition and exhibits an additional valley-opposed sign structure inside the topological phase. Exact numerical simulations using a continuum realization of the model confirm that the sign reversal at the transition is robust, pointing to its potential as a clear experimental signature for detecting topological phase transitions and other phenomena.

Chapter 4 turns to surface states as a generic route to bypass the inversion-symmetry constraint of the bulk photovoltaic effect. An extended Rashba model incorporating hexagonal warping is used to derive analytic expressions for the major contributions to the BPVE, which are benchmarked against first-principles calculations on the Au (111) surface, revealing the predictive power of the two-band picture. The focus then shifts to Tl/Si(111), which has a semiconducting bulk, a giant spin-orbit splitting of approximately ~ 0.6 eV, and a distinctive out-of-plane spin texture. Ab-initio results predict a shift photocurrent magnitude comparable to that of ferroelectrics, with a polarization-angle fingerprint that distinguishes it from competing mechanisms. The chapter further demonstrates that the same surface states support a tunable nonlinear spin photocurrent: by adjusting doping and light polarization, pure out-of-plane or in-plane spin-polarized currents can be generated, establishing surface-state engineering as a promising route for all-optical spintronics.

Finally, Chapter 5 examines how spin symmetries constrain the optical response of magnetic materials. The analysis is structured in two parts, each focused on a different class of unconventional magnets. Part I focuses on the newly introduced class of altermagnets. In these materials, the predictions of spin symmetries for linear dichroism and birefringence are studied using both a Lieb-lattice tight-binding model and first-principles calculations on the candidate compounds $\text{UCr}_2\text{Si}_2\text{C}$ and RbMnF_4 , which serve as strong and weak SOC limits, respectively. Additionally, the spin Hall effect in the noncollinear altermagnet ScMnO_3 is investigated. Part II turns to quadratic photocurrents in odd-parity magnets. There, the shift photoconductivity is examined in a minimal double-exchange model, exploring its dependence on magnetization and the role of spin symmetries in constraining the charge

and spin response. The material realization in Mn_5Si_3 is studied, where two competing non-collinear spin structures are compared to establish how spin symmetries predict distinct photocurrent characteristics that could be measured experimentally to distinguish between the two configurations.

Chapter 2

Theoretical framework

2.1 Methods for electronic structure of crystals

The central objective of this thesis is to investigate the optical responses of crystalline materials. Within the conventional framework of solid-state physics, such responses can be derived from the system's ground state quantities. Consequently, an accurate and efficient determination of the electronic structure is a prerequisite for any meaningful prediction of optical behavior. In this section, we describe the fundamental methods for computing the electronic band structure and related quantities employed throughout the thesis.

The starting point is the full many-body Hamiltonian for electrons and ions in a solid:

$$\begin{aligned}\hat{H} = & -\frac{\hbar^2}{2m_e} \sum_i \nabla_i^2 - \sum_{i,I} \frac{Z_I e^2}{|\mathbf{r}_i - \mathbf{R}_I|} + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} \\ & - \sum_I \frac{\hbar^2}{2M_I} \nabla_I^2 + \frac{1}{2} \sum_{I \neq J} \frac{Z_I Z_J e^2}{|\mathbf{R}_I - \mathbf{R}_J|},\end{aligned}\tag{2.1}$$

where lower-case indices i, j label electrons with coordinates $\mathbf{r}_i$ and mass m_e , and upper-case indices I, J label ions with coordinates $\mathbf{R}_I$, mass M_I , and nuclear charge $Z_I e$. The first and fourth terms represent the kinetic energy of electrons and ions, respectively; the second term is the electron–ion Coulomb interaction; the third is the electron–electron interaction; and the last term is the ion–ion Coulomb repulsion [28, 29].

Because ionic masses M_I are much larger than the electron mass m_e , the ion dynamics is typically much slower than the electronic dynamics. This separation of timescales underlies the Born–Oppenheimer (adiabatic) approximation, in which one first solves the electronic problem for fixed ionic positions and then treats the ions as moving on the resulting electronic energy surface [30]. Within this approximation, the Hamiltonian for the electronic

problem becomes

$$\hat{H}_e = -\frac{\hbar^2}{2m_e} \sum_i \nabla_i^2 - \sum_{i,I} \frac{Z_I e^2}{|\mathbf{r}_i - \mathbf{R}_I|} + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|}, \quad (2.2)$$

where the ionic coordinates $\{\mathbf{R}_I\}$ now enter as external parameters defining the crystal potential.

Even after this reduction, the problem remains a fully interacting many-electron problem. Formally, one must solve the stationary Schrödinger equation

$$\hat{H}_e \Psi(\{\mathbf{r}_i\}) = E \Psi(\{\mathbf{r}_i\}), \quad (2.3)$$

where $\Psi(\{\mathbf{r}_i\}) = \Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$ is a many-body wavefunction depending on the $3N$ electron coordinates and living in the antisymmetric N -electron Hilbert space. Direct solution is infeasible for realistic systems.

A standard simplification is the non-interacting (or effective single-particle) approximation, in which the many-electron state is approximated by an antisymmetrized product (Slater determinant) of single-particle orbitals $\{\psi_i(\mathbf{r})\}$. At the level of a simple Hartree(-like) picture, one may write schematically

$$\Psi(\{\mathbf{r}_i\}) \approx \prod_i \psi_i(\mathbf{r}_i), \quad (2.4)$$

understanding that in practice antisymmetry is enforced. Correspondingly, instead of solving the full many-body equation, one solves an effective one-particle Schrödinger equation

$$\hat{H}_{\text{eff}} \psi_i(\mathbf{r}) = \varepsilon_i \psi_i(\mathbf{r}), \quad (2.5)$$

with

$$\hat{H}_{\text{eff}} = -\frac{\hbar^2}{2m_e} \nabla^2 + V(\mathbf{r}). \quad (2.6)$$

Here $V(\mathbf{r})$ is an effective potential that incorporates, in an approximate way, the electron–ion interaction and the effects of electron–electron interactions. Different electronic-structure methods correspond to different approximations for V ; among these, Kohn–Sham density functional theory (DFT) is the most widely used in *ab initio* studies and will be described in detail in the next section [31, 32].

So far we have neglected relativistic effects. In materials with strong spin–orbit coupling (SOC), an additional term of the form

$$\hat{H}_{\text{SOC}} \propto \boldsymbol{\sigma} \cdot [\nabla V(\mathbf{r}) \times \mathbf{p}] \quad (2.7)$$

must be included, where $\boldsymbol{\sigma}$ are the Pauli matrices, $\mathbf{p}$ is the momentum operator, and $V(\mathbf{r})$ is the (scalar) potential. Inclusion of SOC does not alter the basic structure of the effective one-particle problem, but the single-particle

wavefunctions become two-component spinors and the Hamiltonian acquires a matrix structure in spin space.

In crystalline solids, the ions form a periodic lattice, and the corresponding crystal potential $U(\mathbf{r})$ satisfies

$$V(\mathbf{r} + \mathbf{R}) = V(\mathbf{r}), \quad (2.8)$$

for all lattice vectors $\mathbf{R} = n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3$ with integer n_i , where $\{\mathbf{a}_i\}$ are primitive lattice vectors. This lattice periodicity allows one to restrict the solution of the single-particle Schrödinger equation to a single unit cell, provided that appropriate boundary conditions—such as Born–von Karman boundary conditions—are imposed:

$$\psi(\mathbf{r} + N_i\mathbf{a}_i) = \psi(\mathbf{r}), \quad (2.9)$$

with N_i the number of unit cells along direction $\mathbf{a}_i$. In the thermodynamic limit, the details of these boundary conditions become unimportant, but they provide a convenient route to quantization of crystal momenta.

The translational symmetry implies that the effective Hamiltonian $\hat{H}_{\text{eff}}$ commutes with lattice-translation operators. As a consequence, its eigenstates can be chosen as simultaneous eigenstates of translation, leading to Bloch's theorem. Electronic eigenstates can be written as

$$\psi_{n\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} u_{n\mathbf{k}}(\mathbf{r}), \quad (2.10)$$

where n is a band index, $\mathbf{k}$ is the crystal momentum, and $u_{n\mathbf{k}}(\mathbf{r})$ is a cell-periodic function satisfying

$$u_{n\mathbf{k}}(\mathbf{r} + \mathbf{R}) = u_{n\mathbf{k}}(\mathbf{r}). \quad (2.11)$$

The vector $\mathbf{k}$ serves as a good quantum number associated with the translational symmetry of the crystal; distinct $\mathbf{k}$ -values label inequivalent irreducible representations of the translation group.

The periodicity of the direct lattice is conveniently encoded in the reciprocal lattice, defined by primitive reciprocal vectors $\{\mathbf{b}_i\}$ such that $\mathbf{a}_i \cdot \mathbf{b}_j = 2\pi\delta_{ij}$. Any reciprocal lattice vector $\mathbf{G}$ can be written as $\mathbf{G} = m_1\mathbf{b}_1 + m_2\mathbf{b}_2 + m_3\mathbf{b}_3$ with integers m_i . In reciprocal space, quantities such as the crystal potential and charge density are naturally represented by Fourier series over $\mathbf{G}$, and integrals over the Brillouin zone replace sums over lattice sites in real space [28].

Imposing Born–Von Karman boundary conditions on a finite crystal with N_i unit cells along each primitive direction quantizes the allowed $\mathbf{k}$ -points as

$$\mathbf{k} = \sum_i \frac{m_i}{N_i} \mathbf{b}_i, \quad m_i = 0, 1, \dots, N_i - 1. \quad (2.12)$$

In the thermodynamic limit, these discrete $\mathbf{k}$ -points become dense and effectively form a continuum over the first Brillouin zone. Each allowed $\mathbf{k}$ -point then occupies a volume

$$\Delta k = \frac{(2\pi)^3}{V}, \quad (2.13)$$

in reciprocal space, where V is the total crystal volume. In practical calculations, integrals over the Brillouin zone are approximated by finite $\mathbf{k}$ -point meshes with appropriate weighting factors.

The energy eigenvalues $\varepsilon_{n\mathbf{k}}$ associated with the Bloch states $\psi_{n\mathbf{k}}(\mathbf{r})$ form continuous functions of $\mathbf{k}$. For fixed band index n , the set $\{\varepsilon_{n\mathbf{k}}\}$ over the Brillouin zone defines an energy band. Thus, the central task of electronic-structure theory in crystalline solids is to compute Bloch eigenvalues and eigenstates $\{\varepsilon_{n\mathbf{k}}, u_{n\mathbf{k}}(\mathbf{r})\}$ for a given effective Hamiltonian $\hat{H}_{\text{eff}}$. In this thesis, we will obtain these quantities using two complementary approaches with different levels of approximation and computational cost: density functional theory (DFT) and tight-binding models, which are described in the following sections.

2.1.1 Tight-binding formalism

The tight-binding (TB) approximation models the electronic structure of crystals starting from a basis of localized atomic-like orbitals. The central assumption is that when atoms form a periodic lattice, their orbitals overlap only weakly, so that the crystal eigenstates can be represented as linear combinations of localized orbitals centered on each lattice site [28, 33, 34].

We introduce a localized orbital basis $\{|i\alpha\rangle\}$, where i labels the lattice site at position $\mathbf{R}_i$ and α labels the orbital type (e.g. $s, p_x, p_y, p_z, \dots$) on that site. In real space,

$$\langle \mathbf{r} | i\alpha \rangle = \phi_{i\alpha}(\mathbf{r}) = \phi_{\alpha}(\mathbf{r} - \mathbf{R}_i), \quad (2.14)$$

with ϕ_{α} a localized orbital centered at the origin. In this basis, the single-particle Hamiltonian is written as

$$\hat{H} = \sum_{i,j} \sum_{\alpha,\beta} H_{i\alpha,j\beta} |i\alpha\rangle \langle j\beta|, \quad (2.15)$$

where the matrix elements are

$$H_{i\alpha,j\beta} = \int d\mathbf{r} \phi_{\alpha}^*(\mathbf{r} - \mathbf{R}_i) \left[-\frac{\hbar^2}{2m_e} \nabla^2 + V(\mathbf{r}) \right] \phi_{\beta}(\mathbf{r} - \mathbf{R}_j). \quad (2.16)$$

Writing $\hat{H}$ in this form already implies an effective single-particle description: explicit many-body interactions would introduce higher-order terms such as $|i\alpha, i\alpha'\rangle \langle j\beta, j\beta'|$, which are absent in the simple TB Hamiltonian.

In the tight-binding spirit, the crystal potential is decomposed into contributions centered on each site,

$$V(\mathbf{r}) = \sum_i V_i(\mathbf{r} - \mathbf{R}_i), \quad (2.17)$$

so that the Hamiltonian matrix elements can be classified according to how many distinct centers (sites) are involved in the integrals. One distinguishes:

- One-center integrals ($i = j$): on-site terms, which define the orbital energies on a given atom.
- Two-center integrals ($i \neq j$ with two sites involved): hopping (or transfer) integrals, describing the amplitude for an electron to move between orbitals on neighboring sites.
- Three-center (and higher) integrals: involving the potential of a third site; these are typically neglected in standard TB parametrizations [33, 34].

Following the conventional tight-binding approach, we retain only one- and two-center contributions. The one-center integrals are referred to as on-site energies and parameterize the effective “atomic” energy levels in the crystal environment. The two-center integrals, or hopping parameters, control the strength and symmetry of the coupling between orbitals on different sites and thus largely determine the bandwidths and band dispersions.

A key practical feature of tight binding is that, rather than evaluating the above integrals explicitly, one parameterizes the Hamiltonian matrix elements $H_{i\alpha,j\beta}$ (often guided by symmetry and simple scaling rules) and treats them as phenomenological parameters. This allows one to capture the essential qualitative features of the band structure—and, for suitably chosen parameters, quantitative aspects as well—with relatively modest computational cost. It also makes TB models particularly useful for exploring trends, tuning parameters, and gaining physical intuition.

Throughout this thesis, we will use the second-quantized representation of tight-binding Hamiltonians. We introduce fermionic creation and annihilation operators $c_{i\alpha\sigma}^\dagger$ and $c_{i\alpha\sigma}$, which create and annihilate an electron with spin σ in the localized orbital $|i\alpha\rangle$. They can be related to the field operators $c_\sigma^\dagger(\mathbf{r})$ via

$$c_{i\alpha\sigma}^\dagger = \int d\mathbf{r} \phi_{i\alpha}(\mathbf{r}) c_\sigma^\dagger(\mathbf{r}). \quad (2.18)$$

In terms of these operators, the tight-binding Hamiltonian takes the general form

$$\hat{H} = \sum_{i\alpha,j\beta,\sigma} t_{i\alpha,j\beta} c_{i\alpha\sigma}^\dagger c_{j\beta\sigma} + \sum_{i\alpha,\sigma} \varepsilon_{i\alpha} c_{i\alpha\sigma}^\dagger c_{i\alpha\sigma}, \quad (2.19)$$

where

$$t_{i\alpha,j\beta} = \langle i\alpha | \hat{H} | j\beta \rangle \quad (2.20)$$

are the hopping (two-center) integrals and

$$\varepsilon_{i\alpha} = \langle i\alpha | \hat{H} | i\alpha \rangle \quad (2.21)$$

are the on-site (one-center) energies. In crystals with translational symmetry and equivalent sites, these parameters are usually independent of the site index i and depend only on orbital type and relative displacement between sites.

To obtain the band structure, it is convenient to transform from the localized (real-space) representation to the Bloch (reciprocal-space) representation. For a periodic system with N unit cells and sites related by lattice translations $\mathbf{R}_i$, we define

$$c_{\alpha\mathbf{k}\sigma} = \frac{1}{\sqrt{N}} \sum_i e^{-i\mathbf{k}\cdot\mathbf{R}_i} c_{i\alpha\sigma}, \quad (2.22)$$

with inverse

$$c_{i\alpha\sigma} = \frac{1}{\sqrt{N}} \sum_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{R}_i} c_{\alpha\mathbf{k}\sigma}. \quad (2.23)$$

Here $\mathbf{k}$ runs over the first Brillouin zone (or the discrete set of allowed $\mathbf{k}$ -points under Born–von Kármán boundary conditions). In this basis, the Hamiltonian becomes block-diagonal in $\mathbf{k}$:

$$\hat{H} = \sum_{\mathbf{k}\sigma} \sum_{\alpha,\beta} H_{\alpha\beta}(\mathbf{k}) c_{\alpha\mathbf{k}\sigma}^\dagger c_{\beta\mathbf{k}\sigma}, \quad (2.24)$$

with the Bloch Hamiltonian matrix

$$H_{\alpha\beta}(\mathbf{k}) = \sum_{\mathbf{R}} t_{\alpha\beta}(\mathbf{R}) e^{i\mathbf{k}\cdot\mathbf{R}}, \quad (2.25)$$

where $t_{\alpha\beta}(\mathbf{R})$ is the hopping amplitude between orbital β at a reference site and orbital α at a site displaced by $\mathbf{R}$.

For each $\mathbf{k}$, the matrix $H_{\alpha\beta}(\mathbf{k})$ is finite-dimensional (dimension equal to the number of orbitals per unit cell). Diagonalizing it yields the band energies $\varepsilon_{n\mathbf{k}}$ and eigenvectors $u_{n\alpha}(\mathbf{k})$ necessary to compute the optical properties of the model.

2.1.2 Density functional theory

Density functional theory (DFT) provides an *ab initio* framework for computing the ground-state electronic structure of many-electron systems at reasonable computational cost. Its formal foundation rests on the Hohenberg–Kohn theorems and the Kohn–Sham construction [31, 32].

The first Hohenberg–Kohn theorem states that, for a system of interacting electrons in an external scalar potential $v_{\text{ext}}(\mathbf{r})$, the ground-state electron density $n_0(\mathbf{r})$ uniquely determines $v_{\text{ext}}(\mathbf{r})$ up to an additive constant. Consequently, all ground-state properties are functionals of the density $n(\mathbf{r})$. The second theorem introduces a universal energy functional $E[n]$ such that the exact ground-state energy is obtained by minimizing $E[n]$ with respect to $n(\mathbf{r})$ under the constraint of fixed particle number:

$$E_0 = \min_n E[n], \quad \int d\mathbf{r} n(\mathbf{r}) = N. \quad (2.26)$$

In practice, instead of working directly with the unknown exact functional, Kohn and Sham proposed mapping the interacting system onto an auxiliary system of non-interacting electrons that reproduces the same ground-state density.

In the Kohn–Sham formulation, the total energy functional is written as

$$E[n] = T_s[n] + \int d\mathbf{r} v_{\text{ext}}(\mathbf{r}) n(\mathbf{r}) + \frac{1}{2} \int d\mathbf{r} d\mathbf{r}' \frac{n(\mathbf{r}) n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + E_{\text{XC}}[n], \quad (2.27)$$

where:

- $T_s[n]$ is the kinetic energy functional of a non-interacting reference system with density $n(\mathbf{r})$,
- the second term is the potential energy of the electrons in the external potential $v_{\text{ext}}(\mathbf{r})$ (typically the electron–ion potential),
- the third term is the classical Hartree (Coulomb) energy of the electron density,
- $E_{\text{XC}}[n]$ is the exchange–correlation (XC) functional, which accounts for all many-body effects beyond the non-interacting kinetic energy and the classical Coulomb repulsion.

The electron density is expressed in terms of single-particle Kohn–Sham orbitals $\{\varphi_i(\mathbf{r})\}$,

$$n(\mathbf{r}) = \sum_i^{\text{occ}} |\varphi_i(\mathbf{r})|^2, \quad (2.28)$$

where the sum runs over occupied orbitals. Minimization of $E[n]$ with respect to the orbitals, subject to orthonormality constraints, yields the Kohn–Sham equations:

$$\left[-\frac{\hbar^2}{2m_e} \nabla^2 + v_{\text{ext}}(\mathbf{r}) + v_H(\mathbf{r}) + v_{\text{XC}}(\mathbf{r}) \right] \varphi_i(\mathbf{r}) = \varepsilon_i \varphi_i(\mathbf{r}), \quad (2.29)$$

where

$$v_H(\mathbf{r}) = \int d\mathbf{r}' \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \quad (2.30)$$

is the Hartree potential and

$$v_{\text{XC}}(\mathbf{r}) = \frac{\delta E_{\text{XC}}[n]}{\delta n(\mathbf{r})} \quad (2.31)$$

is the exchange–correlation potential. The Kohn–Sham equations define an effective single-particle Hamiltonian

$$\hat{H}_{\text{KS}} = -\frac{\hbar^2}{2m_e} \nabla^2 + v_{\text{ext}}(\mathbf{r}) + v_H(\mathbf{r}) + v_{\text{XC}}(\mathbf{r}), \quad (2.32)$$

whose eigenvalues ε_i and eigenfunctions $\varphi_i(\mathbf{r})$ must be found self-consistently, since both v_H and v_{XC} depend on the density constructed from the φ_i . In practice, the atomic contribution to $v_{\text{ext}}(\mathbf{r})$ is modelled using pseudopotentials, which replace the strong ionic core potential with a softer, effective potential that acts on the valence electrons [35].

In crystalline solids, the external potential $v_{\text{ext}}(\mathbf{r})$ and, consequently, the Kohn–Sham potential are periodic with the lattice. The Kohn–Sham orbitals are therefore Bloch functions obeying Eq. (2.10), where the cell-periodic part satisfies for each crystal momentum $\mathbf{k}$

$$e^{-i\mathbf{k}\cdot\mathbf{r}} \hat{H}_{\text{KS}} e^{i\mathbf{k}\cdot\mathbf{r}} u_{n\mathbf{k}}(\mathbf{r}) = \varepsilon_{n\mathbf{k}} u_{n\mathbf{k}}(\mathbf{r}), \quad (2.33)$$

leading to a band structure $\varepsilon_{n\mathbf{k}}$ and corresponding Bloch states $u_{n\mathbf{k}}(\mathbf{r})$. The only approximation in practical Kohn–Sham DFT is the choice of the exchange–correlation functional $E_{\text{XC}}[n]$. Common approximations include the local density approximation (LDA) [32], generalized gradient approximation (GGA) [36], and more sophisticated hybrid or meta-GGA functionals [37]. While these functionals are approximate, they usually yield reasonably accurate band structures and wavefunctions for a wide range of materials, especially when the focus is on geometric quantities (e.g. Berry phases) rather than absolute band gaps.

Spin–orbit coupling can be included in the Kohn–Sham framework by adding a spin–orbit term to the effective Hamiltonian and treating the Kohn–Sham orbitals as two-component spinors. In practice, this spin–orbit term is often incorporated via fully relativistic pseudopotentials [38]. These Kohn–Sham bands and wavefunctions are the starting point for computing Berry connections, shift vectors, and nonlinear optical responses such as the BPVE.

2.1.3 Wannier interpolation

2.1.3.1 Construction of Wannier functions

In this section we describe the Wannier-interpolation technique used to compute band structures and optical response functions, including the BPVE, on dense $\mathbf{k}$ -point meshes at modest computational cost. The method exploits

the real-space localization of Wannier functions to construct an accurate tight-binding-like representation of the first-principles Hamiltonian, which can then be evaluated efficiently at arbitrary $\mathbf{k}$ [39–41].

The starting point is a DFT calculation on a coarse uniform $\mathbf{k}$ -point grid, which provides Bloch eigenstates (Eq. (2.11)) for bands n in an energy window of interest. From these states, one constructs Wannier functions $|\mathbf{R}n\rangle$ by applying a $\mathbf{k}$ -dependent unitary rotation within the chosen band subspace, followed by a Fourier transform over the Brillouin zone:

$$|\mathbf{R}n\rangle = \frac{V}{(2\pi)^3} \int_{\text{BZ}} d\mathbf{k} e^{-i\mathbf{k}\cdot\mathbf{R}} \sum_m U(\mathbf{k})_{mn} |\psi_{m\mathbf{k}}\rangle, \quad (2.34)$$

where V is the unit-cell volume, and $U(\mathbf{k})$ is a unitary matrix acting in the Bloch subspace at each $\mathbf{k}$. The matrices $U(\mathbf{k})$ encode the gauge freedom in the choice of Bloch basis; different choices of $U(\mathbf{k})$ produce different, but physically equivalent, sets of Wannier functions spanning the same subspace.

A common strategy is to exploit this gauge freedom to obtain maximally localized Wannier functions (MLWFs). This is achieved by minimizing the total quadratic spread of the Wannier functions [39],

$$\Omega = \sum_n \left[\langle \mathbf{0}n | \mathbf{r}^2 | \mathbf{0}n \rangle - |\langle \mathbf{0}n | \mathbf{r} | \mathbf{0}n \rangle|^2 \right], \quad (2.35)$$

with respect to the unitary matrices $U(\mathbf{k})$. Here $\mathbf{r}$ is the position operator and $|\mathbf{0}n\rangle$ are Wannier functions in the home unit cell. The minimization is performed iteratively, typically starting from a physically motivated initial guess for the gauge.

To avoid convergence to poor local minima, it is standard to construct these initial guesses from projected Bloch-like orbitals. One introduces a set of localized trial orbitals $g_n(\mathbf{r})$ (e.g. atomic or molecular orbitals) and projects them onto the Bloch manifold:

$$|\phi_{n\mathbf{k}}\rangle = \mathcal{N}_n(\mathbf{k}) \sum_m |\psi_{m\mathbf{k}}\rangle \langle \psi_{m\mathbf{k}} | g_n \rangle, \quad (2.36)$$

where $\mathcal{N}_n(\mathbf{k})$ is a normalization factor (often obtained via Löwdin orthonormalization). The corresponding cell-periodic functions are

$$|u_{n\mathbf{k}}^{(0)}\rangle = e^{-i\mathbf{k}\cdot\mathbf{r}} |\phi_{n\mathbf{k}}\rangle, \quad (2.37)$$

and serve as an initial gauge, which is subsequently refined during the spread minimization.

The localization procedure can, in general, break some of the intrinsic crystal symmetries at the level of individual Wannier functions, because the spread functional does not explicitly enforce point-group or crystalline symmetries [40, 42]. There exist symmetry-adapted Wannier constructions

that explicitly constrain the gauge $U(\mathbf{k})$ to preserve the desired symmetry operations (e.g. site symmetry, point-group symmetry) during localization [43]. In practice, an alternative strategy is to skip the spread minimization step altogether. Using the projected Wannier functions directly then naturally preserves the symmetries encoded in the initial Bloch manifold and the chosen trial orbitals. If the initial projected Wannier functions are already well localized, this approach generally leads to an accurate interpolation.

2.1.3.2 Interpolation of matrix elements

The Hamiltonian matrix in the Wannier gauge at any arbitrary $\mathbf{k}$ -point is obtained by Fourier transform of the real-space Hamiltonian matrix elements between Wannier functions:

$$H_{nm}^{(W)}(\mathbf{k}) = \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}} \langle \mathbf{0}n | \hat{H} | \mathbf{R}m \rangle, \quad (2.38)$$

where the superscript (W) denotes the Wannier gauge. Because the Wannier functions are short-ranged, only a modest number of $\mathbf{R}$ vectors is needed. The real-space matrix elements $H_{nm}(\mathbf{R}) = \langle \mathbf{0}n | \hat{H} | \mathbf{R}m \rangle$ are computed once in the DFT grid.

Diagonalizing the Hamiltonian $H^{(W)}(\mathbf{k})$ at any $\mathbf{k}$ yields the interpolated band energies $\varepsilon_{n\mathbf{k}}^{(H)}$ and the unitary transformation $U(\mathbf{k})$ that rotates from the Wannier gauge to the Hamiltonian (eigenstate) gauge denoted by superscript (H):

$$U^\dagger(\mathbf{k}) H^{(W)}(\mathbf{k}) U(\mathbf{k}) = H^{(H)}(\mathbf{k}). \quad (2.39)$$

Evaluating $H(\mathbf{k})$ on a dense $\mathbf{k}$ -mesh and diagonalizing it is computationally inexpensive, because the real-space $H_{mn}(\mathbf{R})$ has already been constructed and is short-ranged. This Fourier-based Wannier interpolation enables accurate calculation of band energies $\varepsilon_{n\mathbf{k}}$ and Bloch states on arbitrarily dense $\mathbf{k}$ -point grids, which is crucial for converging Brillouin-zone integrals appearing in nonlinear optical coefficients, including the BPVE.

The Wannier interpolation strategy extends straightforwardly to other operators that can be represented in the Wannier basis, such as the position operator, velocity operator, and their derivatives with respect to $\mathbf{k}$. Of particular importance for the BPVE is the Berry connection (or, equivalently, the interband position matrix elements) in the Hamiltonian gauge. The matrix elements of the position operator between Wannier-gauge Bloch states define a Berry connection in this gauge,

$$A_{mn}^{a(W)}(\mathbf{k}) = i \langle u_{m\mathbf{k}}^{(W)} | \partial_{k_a} u_{n\mathbf{k}}^{(W)} \rangle, \quad (2.40)$$

which can be efficiently obtained from real-space matrix elements $\langle \mathbf{0}m | \mathbf{r} | \mathbf{R}n \rangle$ via Fourier transforms, in close analogy with the Hamiltonian [40].

The Berry connection in the Hamiltonian gauge is related to the Wannier-gauge connection by the $\mathbf{k}$ -dependent unitary transformation

$$A^{a(H)}(\mathbf{k}) = U^\dagger(\mathbf{k}) A^{a(W)}(\mathbf{k}) U(\mathbf{k}) + i U^\dagger(\mathbf{k}) \partial_{k_a} U(\mathbf{k}). \quad (2.41)$$

This can be written in shorthand as

$$\mathbf{A}^{(H)} = \mathbf{A}^{(W)} + i\mathbf{D}, \quad (2.42)$$

where the second term $D^a = (U^\dagger \partial_{k_a} U)_{nm}$ can be expressed directly in terms of the Hamiltonian matrix in the Wannier gauge as [44]

$$D_{nm}^a(\mathbf{k}) = \frac{\partial_{k_a} H_{nm}^{(H)}}{\varepsilon_m - \varepsilon_n} \quad (n \neq m). \quad (2.43)$$

The diagonal elements $\mathbf{D}_{nn}(\mathbf{k}) = i\mathbf{A}_{nn}^{(H)}(\mathbf{k})$ entering Eq. (2.42) are purely imaginary and correspond to the Berry connection of the individual bands which depends on the choice of gauge [45].

Another essential quantity for evaluating optical responses is the velocity matrix element, which in the Hamiltonian gauge takes the form

$$v_{nm}^a(\mathbf{k}) = \frac{1}{\hbar} \langle \psi_n^{(H)}(\mathbf{k}) | \partial_{k_a} H^{(H)} | \psi_m^{(H)}(\mathbf{k}) \rangle. \quad (2.44)$$

The relationship between the $\mathbf{k}$ -derivatives in the two gauges is given by

$$\partial_{k_a} H^{(H)} = U^\dagger (\partial_{k_a} H^{(W)}) U + [H^{(H)}, U^\dagger \partial_{k_a} U]. \quad (2.45)$$

Because $H^{(H)}$ is diagonal, the commutator contributes only off-diagonal elements $(\varepsilon_n - \varepsilon_m)\mathbf{D}_{nm}$. The derivatives of the Wannier-interpolated Hamiltonian are obtained from the Fourier representation:

$$\partial_{k_a} H^{(W)}(\mathbf{k}) = \sum_{\mathbf{R}} i R_a e^{i\mathbf{k} \cdot \mathbf{R}} H(\mathbf{R}). \quad (2.46)$$

Substituting Eq. (2.45) and (2.46) into Eq. (2.44) yields a relation expressed entirely in terms of Wannier-gauge quantities, which can be evaluated efficiently. From the velocity matrix elements one then obtains the off-diagonal position matrix elements via $r_{nm}^a = v_{nm}^a / i\omega_{nm}$, with $\omega_{nm} = (\varepsilon_n - \varepsilon_m) / \hbar$.

Thus, once the real-space Wannier matrix elements of the Hamiltonian and the position operator are known, all quantities required for optical response calculations—energies, velocities, Berry connections, and their derivatives—can be obtained on dense $\mathbf{k}$ -meshes through efficient Fourier interpolation. This makes Wannier interpolation an ideal tool for converging the Brillouin-zone integrals that appear in the shift- and injection-current formulas presented in the following sections [46].

2.2 Optical responses in crystals

Knowledge of the electronic structure provides the foundation for computing a wide range of physical observables. Among these, this section focuses on photocurrents, that is, electrical and spin currents generated by the interaction of electronic states in solids with time-dependent electromagnetic radiation. At the microscopic level, the coupling of electrons to a classical external electromagnetic field is conveniently described directly in the length gauge. In this gauge the vector potential is set to zero, and a uniform electric field is introduced through the scalar potential $\phi(\mathbf{r}, t) = -\mathbf{E}(t) \cdot \mathbf{r}$, yielding the Hamiltonian [47, 48]

$$H(t) = -\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r}) + e\mathbf{E}(t) \cdot \mathbf{r}, \quad (2.47)$$

where $V(\mathbf{r})$ is the periodic crystal potential, and $e > 0$ is the magnitude of the electron charge. In the optical regime, the dominant interaction is typically the electric-dipole coupling, while magnetic dipole and higher multipole couplings are suppressed by small parameters of order v/c and (a/λ) , where v is a characteristic electronic velocity, a the lattice constant, and λ the optical wavelength [47, 49–51]. Therefore, we focus in what follows on the electric-field-driven contribution to the photocurrent.

Under an applied electric field, the induced current density $\mathbf{J}$ is related to the field $\mathbf{E}$ by a nonlocal, frequency-dependent conductivity tensor. In reciprocal space, the constitutive relation at linear order in the electric field reads [47–50]

$$J^a(\omega, \mathbf{q}) = \sigma^{ab}(\omega, \mathbf{q}) E^b(\omega, \mathbf{q}), \quad (2.48)$$

where a, b label Cartesian components, $\mathbf{q}$ is the wavevector of the incident field, and $\sigma^{ab}(\omega, \mathbf{q})$ is the full optical conductivity tensor, which in general is complex and encodes both dissipative and reactive responses.

When the wavevector $\mathbf{q}$ is small compared to the inverse lattice constant a^{-1} , spatial dispersion can be neglected to leading order. Expanding the total conductivity around $\mathbf{q} = 0$ gives

$$J^a(\omega, \mathbf{0}) = \sigma^{ab}(\omega, \mathbf{0}) E^b(\omega, \mathbf{0}) + \mathcal{O}(q), \quad (2.49)$$

so that, to zeroth order in $\mathbf{q}$, the response is effectively local in space. Physically, the condition $|\mathbf{q}| \ll a^{-1}$ corresponds to $\lambda \gg a$, implying that the electric field is approximately constant over a unit cell. This is the long-wavelength, or electric-dipole, approximation, equivalent to truncating the multipole expansion of the light–matter interaction at the dipole term [49, 51]. While this approximation excludes certain optical effects, such as natural optical activity and various magnetoelectric phenomena that rely on spatial dispersion or magnetic-dipole/quadrupole contributions [49, 51, 52], it is

adequate for the optical phenomena considered in this thesis. Henceforth, we suppress the explicit $\mathbf{q}$ -dependence in the response functions.

In this long-wavelength context we refer to $\sigma^{ab}(\omega)$ as the linear conductivity tensor. It describes the conventional linear optical and transport response, in which the induced current oscillates at the same frequency as the driving field. This contribution is typically the largest and underlies standard photovoltaic operation, where light absorption and subsequent carrier transport occur essentially in the linear regime [53–55]. However, under uniform monochromatic illumination, the linear response alone cannot generate a steady (DC) current, because $J^a(\omega)$ oscillates at the driving frequency and averages to zero over an optical cycle. Conventional photovoltaic devices therefore rely on additional macroscopic asymmetries, such as built-in electric fields in p – n junctions or Schottky barriers, to separate photoexcited electron–hole pairs and thereby rectify the oscillating photocurrent into a net DC output [53–55].

Besides the linear contribution described by Eq. (2.49), the photocurrent is also affected by nonlinear contributions in the applied electric field. Here we pay special attention to the quadratic piece, which reads [7, 49, 50, 56]:

$$J^a(\omega) = \sigma^{abc}(\omega; \omega', \omega'') E^b(\omega') E^c(\omega''), \quad (2.50)$$

where $\sigma^{abc}(\omega; \omega', \omega'')$ is the second-order (quadratic) photoconductivity tensor, which encodes a nonlinear response. It couples pairs of field components at frequencies ω' and ω'' to a current at frequency $\omega = \omega' + \omega''$, giving rise to a variety of second-order nonlinear optical phenomena [7, 49, 50, 56, 57]. Depending on the frequency content of the driving fields, this quadratic photoconductivity can generate both DC and AC currents with frequencies different from those of the incident light.

A crucial symmetry constraint follows directly from this tensorial relation. Importantly, in a centrosymmetric crystal, the current density $\mathbf{J}$ and the electric field $\mathbf{E}$ both change sign under spatial inversion, while the second-order conductivity tensor σ^{abc} , if inversion symmetry is present, must remain invariant. The equation can then only be satisfied if $\sigma^{abc} = 0$ identically. Consequently, any DC photocurrent arising from the quadratic response requires broken inversion symmetry as a necessary condition.

For a single monochromatic source of angular frequency ω_0 , i.e. for $E^b(t) \propto e^{-i\omega_0 t} + \text{c.c.}$, the second-order current contains two particularly important contributions:

- A rectified DC photocurrent arising from the “difference-frequency” channel with $\omega' = \omega_0$ and $\omega'' = -\omega_0$:

$$J^a(0) = \sigma^{abc}(0; \omega_0, -\omega_0) E^b(\omega_0) E^c(-\omega_0). \quad (2.51)$$

In noncentrosymmetric crystals, this DC response is known as the **bulk photovoltaic effect** [1, 11, 54, 57, 58]. In contrast to conventional

junction-based photovoltaics, the BPVE can produce a DC current in a homogeneous crystal under uniform illumination, solely as a consequence of broken inversion symmetry and the associated second-order photoconductivity.

- A current oscillating at twice the driving frequency, associated with the “sum-frequency” channel with $\omega' = \omega_0$ and $\omega'' = \omega_0$:

$$J^a(2\omega_0) = \sigma^{abc}(2\omega_0; \omega_0, \omega_0) E^b(\omega_0) E^c(\omega_0). \quad (2.52)$$

This is the familiar second harmonic generation (SHG) process. In bulk media, SHG is allowed only in the absence of inversion symmetry (apart from surface and interface contributions), and it serves as a standard probe of noncentrosymmetric and polar order [7, 49, 50, 56, 59].

Experimentally, these quadratic contributions can, in principle, be separated from the linear response by analyzing the different Fourier components of the photocurrent at n integer multiples of the fundamental frequency ω_0 . In the monochromatic case, this corresponds to isolating the DC component ($n = 0$) and the $2\omega_0$ component ($n = 2$) from the fundamental response at $n = 1$.

When two distinct monochromatic sources with frequencies ω_1 and ω_2 are applied simultaneously, the same second-order tensor $\sigma^{abc}(\omega; \omega', \omega'')$ enables additional processes [7, 49, 50, 56]:

- A current at the sum frequency $\omega = \omega_1 + \omega_2$, known as sum frequency generation (SFG), arising from products of the form $E^b(\omega_1)E^c(\omega_2)$.
- Currents at the difference frequencies $\omega = \omega_1 - \omega_2$ and $\omega = \omega_2 - \omega_1$, referred to as difference frequency generation (DFG).

These are standard manifestations of second-order nonlinear optics [7, 49, 50, 56, 57] and provide additional channels for generating AC and, in suitable limits (e.g. $\omega_1 \rightarrow \omega_2$), quasi-DC photocurrents. In this thesis, we will focus on the microscopic mechanisms and symmetry constraints governing both the linear conductivity $\sigma^{ab}(\omega)$ of Eq. (2.49) and the quadratic photoconductivity $\sigma^{abc}(0; \omega', \omega'')$ of Eq. (2.51) underlying the BPVE.

2.2.1 Linear response tensor $\sigma^{ab}(\omega)$

Before examining the nonlinear mechanisms that govern the BPVE, it is instructive to review the phenomenology of the linear optical response. In the linear regime, the current induced in a material by an optical field is proportional to the field itself (Eq. (2.49)). This tensor governs familiar phenomena such as absorption, reflection, and transmission, and its properties are well described within equilibrium linear response theory [47, 48, 60, 61].

At the same time, linear response is subject to several fundamental constraints that sharply distinguish it from the nonlinear BPVE and that historically motivated the search for intrinsically nonlinear photocurrent mechanisms.

In conventional junction-based photovoltaics, the photovoltage is described within a quasi-equilibrium, linear-response picture: illumination generates excess carriers that are separated by a built-in electric field and an open-circuit voltage V_{oc} (or a short-circuit current) is generated. Because photogenerated carriers rapidly thermalize to states near the band extrema, excess photon energy $\hbar\omega - E_g$ (E_g is the gap energy) is dissipated as heat on ultrafast timescales [54, 62]. As a result, the open-circuit photovoltage V_{oc} is effectively bounded by the band gap as $eV_{oc} \lesssim E_g$ [54, 55, 63–65]. Thus, within linear-response photovoltaics, above-gap photons can increase the generated current but cannot be converted into proportionally larger steady-state photovoltages.

A second key feature of linear response is that, for a fixed material and light polarization aligned with a principal axis, the absorptive response does not reverse sign as a function of photon energy in an equilibrium, nonmagnetic, time-reversal-symmetric system. This is because optical absorption is governed by the real part of the conductivity, which in the principal-axis channel is built from squared current matrix elements and therefore contributes nonnegatively. Varying ω changes the magnitude of $\text{Re } \sigma^{aa}(\omega)$ and can introduce resonances, but it cannot induce a sign flip for that fixed polarization configuration.

With this phenomenological background established, we now turn to the microscopic theory. Within the independent-particle approximation, the optical conductivity is commonly formulated using the Kubo–Greenwood expression [60, 61],

$$\sigma^{ab}(\omega) = \frac{ie^2}{\hbar V N_{\mathbf{k}}} \sum_{\mathbf{k}} \sum_{n,m} f_{mn} A_{nm}^a(\mathbf{k}) A_{mn}^b(\mathbf{k}) \frac{\varepsilon_{m\mathbf{k}} - \varepsilon_{n\mathbf{k}}}{\varepsilon_{m\mathbf{k}} - \varepsilon_{n\mathbf{k}} - \hbar\omega - i\eta}, \quad (2.53)$$

where V is the crystal volume, $N_{\mathbf{k}}$ is the number of $\mathbf{k}$ -points sampling the Brillouin zone, $\varepsilon_{n\mathbf{k}}$ are the band energies, $\hbar\omega$ is the photon energy, $\eta > 0$ is a broadening parameter, and a, b denote Cartesian coordinates. In semiconductors this interband response fully accounts for the optical conductivity. The quantity $f_{mn} = f_m - f_n$ represents the difference in occupation factors, with $f_n = f(\varepsilon_{n\mathbf{k}})$ given by the Fermi–Dirac distribution

$$f(E) = \frac{1}{1 + \exp[(E - \mu)/k_B T]}. \quad (2.54)$$

Here μ is the chemical potential, T the temperature, and k_B the Boltzmann constant. The occupation difference ensures that only transitions between occupied and unoccupied states contribute to the conductivity.

Applying the Sokhotski–Plemelj relation,

$$\lim_{\eta \rightarrow 0^+} \frac{1}{x - i\eta} = \mathcal{P} \left(\frac{1}{x} \right) + i\pi\delta(x), \quad (2.55)$$

where $\mathcal{P}$ denotes the Cauchy principal value, the conductivity can be decomposed into Hermitian (reactive) and anti-Hermitian (absorptive) parts [47]. The anti-Hermitian part, proportional to $\delta(\varepsilon_{m\mathbf{k}} - \varepsilon_{n\mathbf{k}} - \hbar\omega)$, enforces energy conservation and describes real interband transitions that dissipate energy. The Hermitian part, associated with the principal value, accounts for off-resonant virtual transitions and can remain finite even for photon energies below the band gap.

The DC limit ($\omega \rightarrow 0$) of the antisymmetric part of $\sigma^{ab}(\omega)$ yields the intrinsic anomalous Hall conductivity in magnetic systems [66, 67]. In two-dimensional Chern insulators, the anomalous Hall conductivity becomes quantized and is directly related to the Chern number of the occupied bands [68, 69].

In metallic systems, where the Fermi surface cuts through partially filled bands, additional intraband contributions become essential for describing the DC transport and low-frequency response. The intraband optical conductivity, termed the Drude conductivity, can be written as

$$\sigma_{Drude}^{ab}(\omega) = \frac{e^2}{\hbar V} \sum_{kn} f_{n\mathbf{k}} \left(i \frac{\partial_a \partial_b \omega_{n\mathbf{k}}}{\omega} - \varepsilon^{cab} \Omega_{n\mathbf{k}}^c \right), \quad (2.56)$$

where $\varepsilon^{cab} \Omega_{n\mathbf{k}}^c = \partial_a A_{nn}^b - \partial_b A_{nn}^a$ is the Berry curvature of band n .

2.2.2 Bulk Photovoltaic Effect

2.2.2.1 Early phenomenology

The BPVE was first identified experimentally in the late 1960s and early 1970s, notably through photocurrent and photovoltage measurements under uniform illumination. Researchers observed anomalously large open-circuit voltages in polar materials like $\text{SbSI}_x\text{Br}_{1-x}$ and BaTiO_3 that exceeded the band gap by factors of several, sometimes reaching hundreds to thousands of volts across macroscopic samples [70–72]. Such above band-gap photovoltages go beyond conventional junction-based mechanisms, where the voltage is limited by quasi-Fermi level splitting, indicating a fundamentally different process.

A defining feature of this new effect is its occurrence in homogeneous, single-phase crystals lacking inversion symmetry, with no built-in junctions or compositional gradients. Unlike conventional solar cells that rely on internal fields at interfaces to separate carriers, materials like BaTiO_3 and LiNbO_3 generated steady-state photocurrents and large photovoltages under uniform illumination, even after minimizing extrinsic asymmetries at contacts [72, 73]. This established the BPVE as a genuine bulk property: the oscillating optical field in a noncentrosymmetric medium can produce direct current without an internal bias.

Definitive proof came from Glass [73], who measured a DC current in iron-doped LiNbO_3 that scaled linearly with light intensity. Since the optical field amplitude E scales as $\sqrt{I}$, this linear intensity dependence implies a current quadratic in E ($j \propto |E|^2$), characteristic of a second-order nonlinear response. These results ruled out contact rectification and confirmed an intrinsic bulk photovoltaic mechanism.

Systematic studies by Koch and co-workers on BaTiO_3 in the mid-1970s established key phenomenological hallmarks of the BPVE [72]. They demonstrated that large photovoltages arise uniformly throughout the crystal, not at interfaces, distinguishing it from conventional effects. Polarization-resolved measurements mapped the second-order response tensor, revealing a sign reversal of the zzz component near 390 nm, showing that photocurrent direction can be tuned by photon energy. They also confirmed the quadratic scaling with the optical field, consistent with second-order nonlinear optics.

The early phenomenological description of the BPVE relied heavily on symmetry arguments and nonlinear response theory [71, 74–76]. As introduced above in Eq. (2.51), for a monochromatic optical field, the DC photocurrent can be expressed as a second-order response to the electric field amplitudes at ω_0 and $-\omega_0$, and it is only nonzero in the absence of inversion symmetry. This last observation has two important consequences. First, it reinforces the identification of polar, ferroelectric, and generally noncentrosymmetric materials as natural hosts for the BPVE. Second, it suggests that the BPVE could serve as a sensitive probe of structural phase transitions involving inversion-symmetry breaking, since the onset or disappearance of a nonzero σ^{abc} is directly tied to the symmetry of the underlying crystal phase [57, 70].

Early theoretical work in the 1970s and 1980s separated the BPVE into distinct microscopic contributions: the shift current, arising from a real-space displacement of charge during an optical transition; the ballistic current, arising from a nonequilibrium asymmetric distribution of photoexcited carriers in momentum space together with their subsequent band transport over a finite lifetime; and the injection current, describing the rate of change of the photocurrent, with the resulting current buildup ultimately limited by relaxation. Disentangling these coexisting mechanisms experimentally remains challenging, but ongoing research continues to make progress toward this goal [77].

2.2.2.2 Overview of the microscopic description

We now turn to the microscopic theory of the BPVE. In the clean limit where scattering is weak, the intrinsic quadratic response reduces to the shift and injection currents. For the purposes of this work, we focus on this clean-limit response and do not consider scattering-assisted (ballistic) contributions [75]. To describe nonlinear optical phenomena in periodic solids in a systematic and gauge-invariant way, several theoretical frameworks have been developed.

Here we briefly summarize the perturbative approach introduced by Sipe and Shkrebtii [50], which provides a general formalism for calculating the second-order conductivity $\sigma^{abc}(0; \omega, -\omega)$ for clean semiconductors within the independent-particle approximation [7, 50].

The starting point is the dipole (length-gauge) Hamiltonian for an electron in a spatially uniform, time-dependent electric field:

$$H_{\text{dip}}(t) = -e\mathbf{r} \cdot \mathbf{E}(t), \quad (2.57)$$

where $\mathbf{r}$ is the position operator. In a periodic crystal, the position operator $\mathbf{r}$ is not well-defined between Bloch states, so its matrix elements must be treated carefully. Blount's prescription [7, 78] provides a gauge-invariant definition by expressing them in terms of derivatives with respect to crystal momentum and Berry connections, ensuring that all physical quantities remain invariant under phase transformations of the Bloch functions. Specifically, the matrix elements of the position operator between Bloch states can be written as

$$\langle \phi_{n\mathbf{k}} | \mathbf{r} | \phi_{m\mathbf{k}'} \rangle = i\delta_{nm} \nabla_{\mathbf{k}} \delta(\mathbf{k} - \mathbf{k}') + \delta(\mathbf{k} - \mathbf{k}') \langle u_{n\mathbf{k}} | i\nabla_{\mathbf{k}} | u_{m\mathbf{k}} \rangle, \quad (2.58)$$

For $n \neq m$ and $\mathbf{k} = \mathbf{k}'$, the first term vanishes, making the position matrix element reduce precisely to the off-diagonal Berry connection $A_{nm}(\mathbf{k})$. This relation together with the length gauge Hamiltonian makes explicit the geometric character of interband optical matrix elements.

The nonlinear optical response is obtained by solving the dynamical evolution of the single-particle density matrix elements [7, 50]:

$$c_{nm}(\mathbf{k}, t) = \langle a_n^\dagger(\mathbf{k}) a_m(\mathbf{k}) \rangle \quad (2.59)$$

perturbatively in powers of the electric field $\mathbf{E}(t)$, with $a_n^\dagger(\mathbf{k})$ a field operator that creates an electron in the state characterized by band n and wave-vector $\mathbf{k}$. Within the independent-particle approximation, retaining terms up to second order in the field yields closed-form expressions for the second-order polarization and current, and hence for the conductivity σ^{abc} , which naturally separates into purely interband and intraband terms. This decomposition forms the standard starting point for modern first-principles calculations of the BPVE.

Complementary formulations based on nonequilibrium density-matrix techniques and diagrammatic (Green's-function) approaches lead to equivalent gauge-invariant expressions [79, 80]. Non-perturbative methods—such as Floquet theory, which treats the periodic drive non-perturbatively, and real-time simulations within time-dependent density functional theory—have also been employed to study strong-field regimes and ultrafast dynamics beyond the strictly perturbative limit [81, 82].

2.2.2.3 Classification of the responses

Within these theoretical descriptions, the quadratic DC photocurrent generated by monochromatic light is conventionally decomposed into two main contributions: the shift current and the injection current. Each mechanism reflects a distinct aspect of carrier dynamics following optical excitation and responds differently to light polarization and to symmetry constraints [11, 50]. More recently, Wang and Qian [83] have provided a systematic symmetry-based classification of these contributions, showing that both shift and injection currents can be further subdivided into normal and magnetic types according to their behavior under time-reversal symmetry.

Consider a monochromatic electric field of frequency ω written as

$$E^b(t) = E^b(\omega)e^{-i\omega t} + E^b(-\omega)e^{i\omega t}, \quad (2.60)$$

with $E^b(-\omega) = E^{b*}(\omega)$ ensuring that $\mathbf{E}(t)$ is real. In the clean limit and within second-order response theory, the DC photocurrent can be written as

$$J^a(0) = \sigma_T^{abc}(0; \omega, -\omega)E^b(\omega)E^c(-\omega) + \sigma_T^{abc}(0; -\omega, \omega)E^b(-\omega)E^c(\omega), \quad (2.61)$$

where $\sigma_T^{abc}(0; \omega, -\omega)$ is the total third-rank second-order conductivity tensor, which encompasses all the individual contributions. Reality of the current imposes the constraint

$$\sigma_T^{abc}(0; -\omega, \omega) = [\sigma_T^{acb}(0; \omega, -\omega)]^*, \quad (2.62)$$

so only half of the tensor components are independent [50, 83].

To make the dependence on light polarization explicit, it is convenient to separate the products of field components into real and imaginary parts:

$$E^b(\omega)E^c(-\omega) = \text{Re}(E^bE^c) + i\text{Im}(E^bE^c), \quad (2.63)$$

$$E^b(-\omega)E^c(\omega) = \text{Re}(E^bE^c) - i\text{Im}(E^bE^c). \quad (2.64)$$

Substituting Eqs. (2.64) into Eq. (2.61), one obtains

$$J^a = [\sigma_T^{abc}(0; \omega, -\omega) + \sigma_T^{abc}(0; -\omega, \omega)] \text{Re}(E^bE^{c*}) + \quad (2.65)$$

$$i[\sigma_T^{abc}(0; \omega, -\omega) - \sigma_T^{abc}(0; -\omega, \omega)] \text{Im}(E^bE^{c*}). \quad (2.66)$$

Following Wang and Qian [83], the photoconductivity tensor for each light polarization can be decomposed into four distinct contributions: the shift σ^{abc} , magnetic shift σ_M^{abc} , injection η^{abc} , and magnetic injection η_M^{abc} photoconductivities, organized compactly as

$$J^a = (\sigma^{abc} + \eta_M^{abc}) \text{Re}(E^bE^c) + i(\sigma_M^{abc} + \eta^{abc}) \text{Im}(E^bE^c), \quad (2.67)$$

where the total photocurrent J^a separates into shift- and injection-type contributions, each further divided into normal and magnetic components.

The normal shift current σ^{abc} and the magnetic injection current η_M^{abc} couple to the real part of the bilinear product $E^b E^c$, making them responsive to linearly polarized light, whereas the magnetic shift current σ_M^{abc} and the normal injection current η^{abc} couple to the imaginary part and are therefore activated by circularly or elliptically polarized light. This separation into four terms is motivated by their distinct behavior under time-reversal symmetry $\mathcal{T}$: the normal terms σ^{abc} and η^{abc} are even under $\mathcal{T}$, while the magnetic terms σ_M^{abc} and η_M^{abc} are odd under $\mathcal{T}$ and require broken time-reversal symmetry, appearing only in magnetic or $\mathcal{T}$ -breaking systems [83]. By disentangling the photocurrent into components with well-defined symmetry properties and polarization dependencies, this formalism provides a transparent framework for identifying which microscopic mechanisms are symmetry-allowed in a given material.

Having reviewed this general formalism and symmetry classification, we now turn to the explicit expressions and physical interpretations of the shift and injection currents within the independent-particle approximation.

Shift current The shift current is a coherent, second-order photocurrent that arises from a real-space displacement of electronic charge during interband optical transitions. In a noncentrosymmetric crystal, the centers of charge associated with valence and conduction bands generally do not coincide; when an electron is excited from one band to another, the center of its wavepacket undergoes a finite shift in real space. This geometric displacement, accumulated over all allowed optical transitions, gives rise to a DC current under uniform illumination [7, 50, 71].

Within the independent-particle framework and in the clean limit, the shift photoconductivity tensors can be written in a compact, gauge-covariant form using the generalized derivative of the interband Berry connection. Defining

$$r_{nm}^{b;a} \equiv \partial_{k_a} r_{nm}^b - i(A_{nn}^a - A_{mm}^a)r_{nm}^b, \quad (2.68)$$

the normal shift current σ^{abc} and the magnetic shift current σ_M^{abc} become [83]

$$\sigma^{abc} = -\frac{i\pi e^3}{4\hbar^2} \int \frac{d\mathbf{k}}{(2\pi)^3} \sum_{mn} f_{nm} \left(r_{mn}^b r_{nm}^{c;a} + r_{mn}^c r_{nm}^{b;a} \right) \times \\ (\delta(\omega_{nm} - \omega) + \delta(\omega_{mn} - \omega)), \quad (2.69)$$

$$\sigma_M^{abc} = -\frac{i\pi e^3}{4\hbar^2} \int \frac{d\mathbf{k}}{(2\pi)^3} \sum_{mn} f_{nm} \left(r_{mn}^b r_{nm}^{c;a} - r_{mn}^c r_{nm}^{b;a} \right) \times \\ (\delta(\omega_{nm} - \omega) + \delta(\omega_{mn} - \omega)). \quad (2.70)$$

A key property of the shift current is its independence from scattering times: it is determined at the instant of photoexcitation by the quantum geometry of the Bloch states and does not rely on subsequent carrier drift or

diffusion. In this sense, the shift current is an intrinsically dissipation-free geometric response that is fully specified by the band structure and optical matrix elements throughout the Brillouin zone [1, 7, 11].

Injection current The injection current is a second-order photocurrent arising from an asymmetric photoexcited carrier distribution in momentum space, which produces a net current through the carriers' group velocities. Unlike the shift current, the injection current is typically described as an optically induced current injection rate whose DC steady-state value under continuous illumination is set by the balance between asymmetric photoexcitation and momentum-relaxing scattering processes [11, 50, 76].

Within the independent-particle framework and using a phenomenological scattering time τ , the normal and magnetic injection conductivities are given by [83]

$$\eta^{abc} = \tau \frac{\pi e^3}{\hbar^2} \int \frac{d\mathbf{k}}{(2\pi)^3} \sum_{n,m} f_{nm} \Delta v_{nm}^a \text{Im}[r_{nm}^b r_{mn}^c] \delta(\omega_{nm} - \omega), \quad (2.71)$$

$$\eta_M^{abc} = \tau \frac{\pi e^3}{\hbar^2} \int \frac{d\mathbf{k}}{(2\pi)^3} \sum_{n,m} f_{nm} \Delta v_{nm}^a \text{Re}[r_{nm}^b r_{mn}^c] \delta(\omega_{nm} - \omega). \quad (2.72)$$

Here $\Delta v_{nm}^a = v_{nn}^a - v_{mm}^a$ is the group-velocity difference, and the remaining notation follows that of the shift current expressions above. The roles of these two contributions under time reversal and their coupling to light polarization follow directly from the symmetry classification discussed earlier [83]: η is even under $\mathcal{T}$ and couples to circularly polarized light (via $\text{Im}[r_{nm}^b r_{mn}^c]$), while η_M is odd under $\mathcal{T}$ and couples to linearly polarized light (via $\text{Re}[r_{nm}^b r_{mn}^c]$).

Microscopically, the injection current arises from an asymmetric $\mathbf{k}$ -space distribution of excited carriers: when an electron transitions from band m to band n , its group velocity changes by Δv_{nm}^a . If the transition rates are unbalanced in $\mathbf{k}$ -space, a net current emerges. Because this asymmetric population grows linearly with time in the absence of scattering, the steady-state current is proportional to the relaxation time τ , distinguishing injection from the scattering-independent shift current [50].

2.2.2.4 Realistic estimation of photocurrents

The picture that the photocurrent depends only on the photoconductivity as in Eq. (2.67) is a practical simplification. A realistic estimate of the photocurrent needs to take into account several additional factors, such as the reflectivity and the competition between the linear and quadratic effects. To estimate the generated photocurrent, we consider the standard expression for a sample of thickness d illuminated by a laser with spot width w [21, 84]:

$$J^a(0) = G^{abb}(\omega) \cdot (1 - R(\omega))(1 - e^{-\alpha^{bb \cdot d}}) \cdot w \cdot I^b. \quad (2.73)$$

Here, $I^b = c\epsilon_0(E^b)^2/2$ is the incident light intensity for an applied electric field E^b , $R(\omega)$ is the reflectivity, and $\alpha^{bb}(\omega) = \sqrt{2\frac{\omega}{c}}\sqrt{|\epsilon^{bb}| - \text{Re}(\epsilon^{bb})}$ is the absorption coefficient, involving the dielectric function $\epsilon^{ab}(\omega)$. The Glass coefficient,

$$G^{abb}(\omega) = \frac{2\sigma^{abb}(\omega)}{c\epsilon_0\sqrt{\epsilon_r(\omega)} \cdot \alpha^{bb}(\omega)}, \quad (2.74)$$

quantifies the bulk photocurrent generation efficiency by accounting for absorption [58, 73]. The reflectivity is calculated as:

$$R(\omega) = \left| \frac{\sqrt{\epsilon(\omega)} - 1}{\sqrt{\epsilon(\omega)} + 1} \right|^2. \quad (2.75)$$

As the reflectivity is sensitive to transitions between bands as well as to intraband processes, metallic contributions such as the Drude conductivity described in Sec. 2.2.1 have to be included.

2.2.3 Spin currents

Alongside the generation of charge currents, the interaction of light with matter can also induce spin currents, that is, flows of spin angular momentum. The theoretical foundation of such spin currents dates back to 1971, when Dyakonov and Perel [85] first predicted that an electric current in a semiconductor could produce a transverse spin imbalance, a phenomenon later recognized as the spin Hall effect. Though the idea was initially overlooked, it was taken up independently by Hirsch in 1999, who not only coined the term Spin Hall Effect but also sparked widespread theoretical interest in spin current phenomena [86]. The experimental detection of spin currents was achieved through techniques such as Kerr rotation microscopy, which directly confirmed the existence of pure spin transport in semiconductors [87]. These advances motivated the development of the field of spintronics, in which information is carried not by the charge of electrons but by their spin angular momentum, enabling functionalities beyond conventional electronics. Today, spin currents play an important role in the ongoing development of next generation technologies including magnetic random access memory [88], spin torque oscillators [89], and low dissipation logic devices [90]. Their ability to transport information without significant Joule heating offers a promising path toward faster and more energy efficient computing, addressing fundamental limits faced by conventional electronics.

In analogy with the constitutive relation for the charge current, the spin current density $J^{s,a}(\omega)$ induced by an electric field can be expanded in powers of the field amplitude. Here, $J^{s,a}$ denotes the spin current polarized along the spin direction s and flowing in the spatial direction a . The linear response is governed by the spin Hall conductivity tensor $\sigma^{s,ab}(\omega)$:

$$J^{s,a}(\omega) = \sigma^{s,ab}(\omega)E^b(\omega). \quad (2.76)$$

This linear effect, known as the spin Hall effect (SHE), describes the generation of a transverse spin current from a longitudinal charge current in the presence of spin-orbit coupling.

At second order, a DC spin current can arise from the quadratic coupling to the electric field, analogous to the bulk photovoltaic effect for charge. This phenomenon is termed the spin bulk photovoltaic effect (SBPVE). For a monochromatic field of frequency ω , the DC spin current is given by

$$J^{s,a}(0) = \sigma^{s,abc}(0; \omega, -\omega) E^b(\omega) E^c(-\omega), \quad (2.77)$$

where $\sigma_s^{abc}(0; \omega, -\omega)$ is the second-order spin photoconductivity tensor.

2.2.3.1 Spin Hall conductivity

The microscopic description of the spin Hall conductivity (SHC) within the independent-particle framework can be formulated using a Kubo-Greenwood formalism [91]. The frequency-dependent SHC is given by

$$\sigma^{s,ab}(\omega) = \frac{e}{\hbar V N_{\mathbf{k}}} \sum_{\mathbf{k}} \sum_{n,m \neq n} \frac{f_{nm} \text{Im} [j_{mn}^{s,a}(\mathbf{k}) v_{nm}^b(\mathbf{k})]}{(\varepsilon_{n\mathbf{k}} - \varepsilon_{m\mathbf{k}})^2 - (\hbar\omega + i\eta)^2}, \quad (2.78)$$

where $\sigma_s^{ab}(\omega)$ is the spin Hall conductivity tensor and $\eta > 0$ a broadening parameter. The spin current operator $j^{s,a}$ is defined as the symmetrized product of the velocity operator v^a and the spin operator S^s [92]:

$$j^{s,a} = \frac{1}{2} \{v^a, S^s\}. \quad (2.79)$$

Here, $\mathbf{S} = \hbar \boldsymbol{\sigma}/2$, with $\boldsymbol{\sigma} = (\sigma_x, \sigma_y, \sigma_z)$ the vector of Pauli matrices. This symmetrization ensures the Hermiticity of the spin current operator, a necessary condition for physical observability.

Using the relation $v_{mn}^b(\mathbf{k}) = (i/\hbar)(\varepsilon_{m\mathbf{k}} - \varepsilon_{n\mathbf{k}})A_{mn}^b(\mathbf{k})$ for $n \neq m$, where $A_{mn}^b(\mathbf{k})$ is the Berry connection, Eq. (2.78) can be rewritten in a form that is convenient for numerical implementation:

$$\sigma^{s,ab}(\omega) = -\frac{e}{\hbar V N_{\mathbf{k}}} \sum_{\mathbf{k}} \sum_{n,m \neq n} \frac{f_{nm} \text{Re} [j_{mn}^{s,a}(\mathbf{k}) A_{nm}^b(\mathbf{k})]}{\varepsilon_{m\mathbf{k}} - \varepsilon_{n\mathbf{k}} - (\hbar\omega + i\eta)}. \quad (2.80)$$

This expression is used in modern first-principles codes such as Wannier-Berri [93] to compute the SHC from electronic structure calculations.

2.2.3.2 Shift and injection spin photoconductivities

Having introduced the linear spin Hall conductivity, we now turn to the second-order spin photoconductivity $\sigma^{s,abc}(\omega; \omega', \omega'')$, which governs the SBPVE and related quadratic spin responses. In analogy with the charge case, the

second-order spin photocurrent can be decomposed into shift and injection contributions, each with distinct physical origins and symmetry properties. Within the independent-particle approximation and the length-gauge formalism, these contributions are expressed in terms of the band structure and the matrix elements of the velocity and spin-current operators.

Similar to the charge case of Eq. (2.67), the quadratic spin photocurrent can be expressed as the sum of four contributions, the spin shift $\zeta^{s,abc}$, magnetic spin shift $\zeta_M^{s,abc}$, spin injection $\xi^{s,abc}$, and magnetic spin injection $\xi_M^{s,abc}$ photoconductivities, organized compactly as

$$J^{s,a} = (\zeta_M^{s,abc} + \xi^{s,abc}) \text{Re}(E^b E^c) + i(\zeta^{s,abc} + \xi_M^{s,abc}) \text{Im}(E^b E^c), \quad (2.81)$$

where the total spin photocurrent $J^{s,a}$ separates into shift- and injection-type contributions, each further divided into normal and magnetic components.

Spin shift photoconductivity The normal and magnetic spin shift photoconductivity are given by [94]

$$\zeta^{s,abc} = \frac{\pi q^3}{2\hbar^2 V \omega^2} \sum_{\mathbf{k}, m, n} f_{mn} \text{Re}(I_{mn}^{s,abc}(\mathbf{k}) - I_{mn}^{s,acb}(\mathbf{k})) \delta(\omega + \omega_{mn}) \quad (2.82)$$

$$\zeta_M^{s,abc} = \frac{-\pi q^3}{2\hbar^2 V \omega^2} \sum_{\mathbf{k}, m, n} f_{mn} \text{Im}(I_{mn}^{s,abc}(\mathbf{k}) + I_{mn}^{s,acb}(\mathbf{k})) \delta(\omega + \omega_{mn}), \quad (2.83)$$

with $I_{mn}^{s,abc}(\mathbf{k}) = d_{mn}^{s,ba} v_{nm}^c - d_{nm}^{s,ca} v_{mn}^b$ the associated transition matrix element, $d^{s,ba} = j_{mn}^{s,ab} + \sum_{p \neq m} \frac{j^{s,a} v_{pn}^b}{\omega_{mp}} + \sum_{p \neq n} \frac{v_{mp}^b j_{pn}^{s,a}}{\omega_{np}}$, $j^{s,ab} = \frac{1}{2} \langle u_m | \{S^s, \partial^a \partial^b H\} | u_n \rangle$ and $j^{s,a} = \frac{1}{2} \langle u_m | \{S^s, v^a\} | u_n \rangle$. Under time reversal, the normal spin shift current $\zeta^{s,abc}$ is even and couples to circularly polarized light, while the magnetic spin shift current $\zeta_M^{s,abc}$ is odd and couples to linearly polarized light.

Spin injection photoconductivity The spin injection photoconductivity, also from Ref. [94], reads:

$$\begin{aligned} \xi^{s,abc}(\omega) = & -\tau \frac{\pi e^3}{\hbar^2 \omega^2 V} \sum_{\mathbf{k}} \sum_{n, m} f_{nm} \Delta j_{nm}^{s,a}(\mathbf{k}) \text{Re}(v_{mn}^b(\mathbf{k}) v_{nm}^c(\mathbf{k}) \\ & + v_{mn}^c(\mathbf{k}) v_{nm}^b(\mathbf{k})) \delta(\omega + \omega_{nm}), \end{aligned} \quad (2.84)$$

$$\begin{aligned} \xi_M^{s,abc}(\omega) = & -\tau \frac{\pi e^3}{\hbar^2 \omega^2 V} \sum_{\mathbf{k}} \sum_{n, m} f_{nm} \Delta j_{nm}^{s,a}(\mathbf{k}) \text{Im}(v_{mn}^b(\mathbf{k}) v_{nm}^c(\mathbf{k}) \\ & - v_{mn}^c(\mathbf{k}) v_{nm}^b(\mathbf{k})) \delta(\omega + \omega_{nm}), \end{aligned} \quad (2.85)$$

where $\Delta j_{nm}^{s,a}(\mathbf{k}) = j_{mm}^{s,a}(\mathbf{k}) - j_{nn}^{s,a}(\mathbf{k})$ is the difference in the expectation values of the spin-current operator between bands m and n . Under time reversal, the

normal spin injection current $\xi^{s,abc}$ is even and couples to linearly polarized light, while the magnetic spin injection current $\xi_M^{s,abc}$ is odd and couples to circularly polarized light.

Chapter 3

Shift photoconductivity in the Haldane model

3.1 Introduction

The introduction of topology and differential geometry into condensed matter physics profoundly changed how electronic phases of matter are understood. A key milestone was the work of Thouless, Kohmoto, Nightingale, and den Nijs (TKNN) in 1982, who related the quantized Hall conductance in two-dimensional electron gases under strong magnetic fields to a topological invariant, the Chern number [68]. In this framework, the Hall conductance is expressed in terms of an integer invariant defined over the Brillouin zone, showing that the precision and robustness of the integer quantum Hall effect originate from the global topology of the Bloch wavefunctions in momentum space, rather than from microscopic details. This perspective led to the broader realization that band structures can carry nontrivial topological invariants even in the absence of external magnetic fields, giving rise to topological insulators: materials that are insulating in the bulk but host robust, symmetry-protected conducting states at their boundaries, in sharp contrast to conventional band insulators [95].

The influence of geometric ideas is not limited to the classification of equilibrium phases. It also appears prominently in nonlinear optical and transport phenomena, where the response of a material can be governed by the geometry of its Bloch states rather than by band dispersions alone [11, 96]. For instance, certain second-order photocurrents in noncentrosymmetric crystals, including the shift current, can be traced directly to geometric properties of the wavefunctions and their intracell positions [50]. In this way, nonlinear optical responses offer an experimentally accessible window into the underlying geometric structure of electronic states in momentum space.

This deep connection between nonlinear responses and quantum geometry suggests that the shift current, and related phenomena, can be significantly

enhanced in the vicinity of band degeneracies and topological phase transitions, where geometric quantities like the Berry curvature and quantum metric exhibit strong variations [9, 11, 97, 98]. For instance, shift currents are often pronounced around Dirac points or Weyl nodes, where the quantum metric and Berry curvature can become singular [10, 12, 99–102]. A concrete demonstration of this principle was provided by the work of Tan and Rappe [27], who showed that the shift current is enhanced near a topological phase transition. They studied materials such as BiTeI and CsPbI₃, which undergo transitions between distinct topological phases (from a trivial to a $\mathbb{Z}_2$ topological insulator phase) as a function of lattice constant, a parameter effectively tunable via hydrostatic pressure. In BiTeI, they demonstrated that the shift current exhibits a pronounced peak near a critical lattice constant of $a = 4.13 \text{ \AA}$, precisely where the band gap closes, signaling the topological phase transition. Remarkably, the sign of the shift current reverses across this critical point, providing a direct link between the topological invariant of the bulk band structure and the sign of a nonequilibrium, experimentally measurable photocurrent. This establishes the shift current as a sensitive geometric probe of the electronic structure, capable of diagnosing subtle topological changes that may be invisible to linear response.

Given the established role of quantum geometry in nonlinear responses and its pronounced sensitivity to topological transitions, the well-known Haldane model emerges as an ideal theoretical testbed for a detailed investigation. First, it provides the paradigmatic description of a Chern insulator, exhibiting a topological phase transition (TPT) between trivial and topological insulating phases with Chern numbers $C = 0$ and $C = \pm 1$ [69]. This allows one to directly probe the geometric consequences of a changing bulk topological invariant. Secondly, its inherent breaking of inversion symmetry—a necessary condition for a non-zero shift current—makes it a minimal platform for studying this geometric photocurrent [50]. Finally, its simple two-band structure permits an analytic and transparent analysis of the relationship between band topology, quantum geometry, and the shift current, offering clear insights into phenomena such as the sign reversal effect and its regime of validity.

This chapter pursues a twofold objective. First, to analytically study, within the tight-binding Haldane model, the sign reversal of the shift current across the topological phase transition. This is presented in Sec. 3.2, where we discuss the role of the topological phase transition and the $\mathbf{k} \rightarrow -\mathbf{k}$ asymmetry in the band structure. Second, to computationally simulate this effect in a continuum version of the Haldane model, an approach that, unlike its tight-binding counterpart, enables a proper description of the off-diagonal position operator matrix elements. This is carried out in Sec. 3.3, where we analyze the quantitative importance of those off-diagonal elements not included in the tight-binding model. Finally, we provide conclusions and outlook.

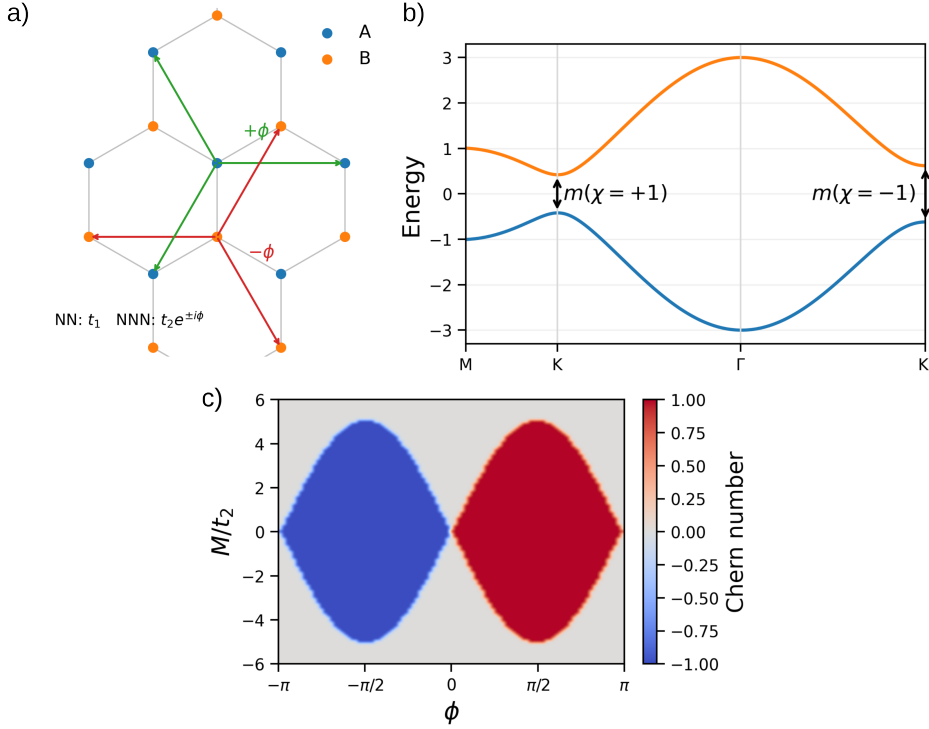


Figure 3.1: (a) Lattice, (b) band structure and (c) phase diagram of the Haldane model.

3.2 Shift current in the Haldane model

3.2.1 Review of the model

The Haldane model occupies a central place in the theory of topological phases because it established that quantized Hall responses and nontrivial Chern numbers can arise purely from the band structure of a lattice system, without Landau levels or a net magnetic field [69]. In its standard formulation, the Haldane model is defined on a two-dimensional honeycomb lattice, which consists of a triangular Bravais lattice with a two-atom basis, forming two inequivalent sublattices denoted A and B (see Fig. 3.1 a). The geometry is characterized by the primitive lattice vectors

$$\mathbf{a}_1 = \frac{a}{2}(\sqrt{3}, 3), \quad \mathbf{a}_2 = \frac{a}{2}(\sqrt{3}, -3), \quad (3.1)$$

the nearest-neighbor displacement vectors (from an A site to its three adjacent B sites)

$$\boldsymbol{\delta}_1 = (0, a), \quad \boldsymbol{\delta}_2 = \frac{a}{2}(-\sqrt{3}, -1), \quad \boldsymbol{\delta}_3 = \frac{a}{2}(\sqrt{3}, -1), \quad (3.2)$$

and the next-nearest-neighbor vectors (connecting sites on the same sublattice)

$$\mathbf{v}_1 = (-\sqrt{3}a, 0), \quad \mathbf{v}_2 = \frac{a}{2}(\sqrt{3}, 3), \quad \mathbf{v}_3 = \frac{a}{2}(\sqrt{3}, -3). \quad (3.3)$$

Here, a is the lattice constant. The system is described by a tight-binding Hamiltonian with three essential ingredients:

- Staggered on-site energies $\pm M$ for sublattices A and B , respectively, which break inversion symmetry.
- Real nearest-neighbor hopping with amplitude t_1 .
- Complex next-nearest-neighbor hopping $t_2 e^{\pm i\phi}$, where the $+$ ($-$) sign applies to hopping processes on the A (B) sublattice.

The corresponding real-space tight-binding Hamiltonian can be written as

$$\hat{H} = \sum_{\langle i,j \rangle} t_1 \hat{c}_i^\dagger \hat{c}_j + \sum_{\langle\langle i,j \rangle\rangle} t_2 e^{i\phi_{ij}} \hat{c}_i^\dagger \hat{c}_j + M \sum_{i \in A} \hat{c}_i^\dagger \hat{c}_i - M \sum_{i \in B} \hat{c}_i^\dagger \hat{c}_i, \quad (3.4)$$

where $\hat{c}_i^\dagger$ ($\hat{c}_i$) creates (annihilates) an electron at site i , $\langle i, j \rangle$ denotes summation over all nearest-neighbor pairs, and $\langle\langle i, j \rangle\rangle$ denotes summation over all next-nearest-neighbor pairs. The phase ϕ_{ij} is $+\phi$ if the hopping from site j to i occurs in the counterclockwise direction with respect to the center of the hexagonal lattice, and $-\phi$ for the clockwise direction.

The crucial phase ϕ represents a periodic, staggered magnetic flux pattern with zero net flux per unit cell. Consequently, any closed loop formed solely by nearest-neighbor hops encloses no net flux, leaving t_1 real. In contrast, a next-nearest-neighbor hop, combined with a nearest-neighbor return path, encloses a single plaquette and thus acquires the phase factor $e^{\pm i\phi}$. This complex hopping explicitly breaks time-reversal symmetry $\mathcal{T}$ while preserving the translational symmetry of the lattice, realizing the conditions for a Chern insulator without an external magnetic field.

To analyze the model's spectral and topological properties, we need the Bloch Hamiltonian in momentum space, which takes the form [103]

$$\mathcal{H}(\mathbf{k}) = \sum_i f_i(\mathbf{k}) \sigma_i, \quad (3.5)$$

with

$$\begin{aligned}
f_0 &= 2t_2 \cos \phi \left[\sum_{i=1}^3 \cos(\mathbf{k} \cdot \mathbf{v}_i) \right], \\
f_1 &= t_1 \sum_i \cos(\mathbf{k} \cdot \mathbf{e}_i), \\
f_2 &= t_1 \sum_i \sin(\mathbf{k} \cdot \mathbf{e}_i), \\
f_3 &= M - 2t_2 \sin \phi \sum_i \sin(\mathbf{k} \cdot \mathbf{v}_i).
\end{aligned} \tag{3.6}$$

The energy dispersion is given by $\epsilon_{\pm}(\mathbf{k}) = \pm \sqrt{\sum_i f_i^2(\mathbf{k})}$. The band structure along the high-symmetry path $M \rightarrow K \rightarrow \Gamma \rightarrow K'$ is plotted in Fig. 3.1 b. Expanding the Hamiltonian near these points yields a massive Dirac Hamiltonian, where the band gap $\Delta(\mathbf{k})$ at the two valleys is

$$\Delta(\chi) = 2 \left(M + \chi 3\sqrt{3}t_2 \sin \phi \right) \equiv 2m(\chi), \tag{3.7}$$

where $\chi = -1$ ($+1$) refers to the K (K') point, and $m(\chi)$ is the Dirac mass term. Equation (3.7) shows that the valley gaps depend on the tight-binding parameters and, for $t_2 \sin \phi \neq 0$, they differ in magnitude at K and K' . A band inversion occurs when $m(\chi) < 0$, signaling a change in the topological character of the system.

The topological order of the Haldane model is characterized by the Chern number C of the lowest band. It can be computed as the integral of the Berry curvature over the Brillouin zone, which for the two-level Hamiltonian $\hat{H}(\mathbf{k}) = \mathbf{f}(\mathbf{k}) \cdot \boldsymbol{\sigma}$ takes the compact form

$$C = \frac{1}{4\pi} \int_{\text{BZ}} \frac{\mathbf{f}}{\|\mathbf{f}\|^3} \cdot \left(\frac{\partial \mathbf{f}}{\partial k_x} \times \frac{\partial \mathbf{f}}{\partial k_y} \right) dk_x dk_y. \tag{3.8}$$

The resulting topological phase diagram is shown in Fig. 3.1 c. The system exhibits three distinct regimes [104]:

- $|M| = 3\sqrt{3}|t_2 \sin \phi|$: The bulk gap closes, and the system is a semimetal.
- $|M| > 3\sqrt{3}|t_2 \sin \phi|$: The system is a trivial insulator with Chern number $C = 0$.
- $|M| < 3\sqrt{3}|t_2 \sin \phi|$: The system is a topological Chern insulator with Chern number $C = \pm 1$, where the sign is determined by the sign of $t_2 \sin \phi$.

The phase boundaries are thus defined by the condition $m(\chi) = 0$. Notably, the lowest energy band-edge gap changes sign precisely upon crossing the

topological phase transition. Another crucial observation for the subsequent analysis is that the mass terms $m(\chi)$ acquire opposite signs at the two valleys only in the topological insulator phase ($C = \pm 1$), whereas in the trivial phase ($C = 0$) they share the same sign.

3.2.2 Band-edge shift current: sign change at the TPT

To derive an analytical expression for the shift current near the band edges, we employ a simplified formulation for the transition matrix elements valid for generic two-band models, as presented in Ref. [18]. For a Hamiltonian $H(\mathbf{k}) = \mathbf{f}(\mathbf{k}) \cdot \boldsymbol{\sigma}$, the relevant tensor component can be expressed as

$$I_{12}^{abb} = \sum_{ijm} \frac{1}{4\epsilon^3} \left(f_m f_{i,b} f_{j,ab} - f_m f_{i,b} f_{j,a} \frac{\epsilon_{i,b}}{\epsilon} \right) \epsilon_{ijm}, \quad (3.9)$$

where subscripts 1, 2 are the bottom and top bands respectively, $\epsilon(\mathbf{k}) = |\mathbf{f}(\mathbf{k})|$ is the band dispersion, $f_{i,a} \equiv \partial f_i / \partial k_a$, $f_{j,ab} \equiv \partial^2 f_j / \partial k_a \partial k_b$, and ϵ_{ijm} is the Levi-Civita symbol.

Given our focus on the low-energy response near the band extrema, we expand the Bloch Hamiltonian $\mathbf{f}(\mathbf{k})$ to second order in momentum around the Dirac points $\mathbf{K}$ and $\mathbf{K}'$. This order is necessary because the expression in Eq. (3.9) involves second derivatives $f_{j,ab}$. Performing a Taylor expansion of the tight-binding Hamiltonian Eq. (3.5) around $\mathbf{k} = \chi \mathbf{K}$ (with $\chi = \pm 1$) yields the low-energy form:

$$f_1(\mathbf{q}) = \frac{3}{2} t_1 \left(\chi q_x a - \frac{1}{4} q_y^2 a^2 + \frac{1}{4} q_x^2 a^2 \right), \quad (3.10)$$

$$f_2(\mathbf{q}) = \frac{3}{2} t_1 \left(q_y a - \frac{1}{2} \chi q_x q_y a^2 \right), \quad (3.11)$$

$$f_3(\mathbf{q}) = m(\chi) + \chi \frac{9\sqrt{3}}{4} t_2 \sin \phi (q_x^2 a^2 + q_y^2 a^2), \quad (3.12)$$

where $\mathbf{q} = \mathbf{k} - \chi \mathbf{K}$ is the momentum measured from the valley center (either K or K' depending on χ), $m(\chi) = M + \chi 3\sqrt{3} t_2 \sin \phi$ is the Dirac mass defined in Eq. (3.7), and a is the lattice constant. A possible constant term $f_0(\mathbf{q})$, proportional to the identity matrix, has been omitted as it does not affect the interband matrix elements entering Eq. (3.9).

For incident photon energies near the fundamental absorption edge, i.e., $\hbar\omega \approx 2|m(\chi)|$, the shift current conductivity formula in Eq. (2.69) can be factorized into a geometric part and a spectral part, following the treatment in Ref. [18]:

$$\sigma^{abb}(\omega) = -\frac{\pi e^3}{4\hbar^2} I_{12}(\omega) N(\omega). \quad (3.13)$$

Here, $I_{12}(\omega)$ is the frequency-dependent geometric factor defined in Eq. (3.9), which encapsulates the transition matrix elements and their momentum-space

derivatives, and

$$N(\omega) = \int_{\text{BZ}} \frac{d^2q}{(2\pi)^2} \delta(2\omega_{12}(\mathbf{q}) - \hbar\omega) \quad (3.14)$$

is the joint density of states (JDOS) for vertical interband transitions, where $2\omega_{12}(\mathbf{q}) = E_1(\mathbf{q}) - E_2(\mathbf{q})$ is the energy difference between the conduction and valence bands. This factorization separates the purely geometric contribution to the nonlinear response, contained in $I_{12}(\omega)$, from the spectral availability of states for optical excitation, given by $N(\omega)$.

Evaluating the geometric factor $I_{12}^{ab}(\omega)$ defined in Eq. (3.9) using the low-energy Hamiltonian in Eqs. (3.10)–(3.12) yields, to leading order in momentum $\mathbf{q}$, the following expressions at the χ valley:

$$I_{12}^{yyy}(\omega) = \frac{9a^3t_1^2\text{sign}[m(\chi)]}{8(\hbar\omega)^2} + \mathcal{O}(q), \quad (3.15)$$

$$I_{12}^{xyy}(\omega) = -\frac{9a^3t_1^2\text{sign}[m(\chi)]}{8(\hbar\omega)^2} + \mathcal{O}(q). \quad (3.16)$$

Notably, the results are independent of the next-nearest-neighbor parameters t_2 and ϕ at this order, depending only on the nearest-neighbor hopping t_1 , the lattice constant a , and—crucially—the sign of the Dirac mass $m(\chi)$. The $\mathcal{O}(q)$ corrections arise from higher-order terms in the $\mathbf{k} \cdot \mathbf{p}$ expansion and become negligible for photon energies close to the band edge.

The symmetry properties of these components are consistent with the C_{3v} point group of the Haldane model, which contains a threefold rotational axis and vertical mirror planes. Under this symmetry, the second-order conductivity tensor must satisfy $\sigma^{yyy} = -\sigma^{yxx}$, as is indeed reflected in the relations $I_{12}^{yyy} = -I_{12}^{xyy}$ obtained above. All other independent tensor components vanish by symmetry, confirming the consistency of our low-energy calculation with the lattice symmetry.

To evaluate the joint density of states $N(\omega)$ near the band edge, we expand the energy difference between the valence and conduction bands, $2\omega_{12}(\mathbf{q})$, to second order in the relative momentum $\mathbf{q}$. Writing the expansion in polar coordinates (q, θ) yields

$$\hbar\omega_{12}(q) \approx 2|m(\chi)| + \frac{\hbar^2q^2}{M'(\chi)}, \quad (3.17)$$

where the inverse effective mass parameter is

$$\frac{\hbar^2}{M'(\chi)} = \frac{9a^2t_1^2 - 18\sqrt{3}a^2m(\chi)t_2\chi\sin\phi}{4|m(\chi)|}. \quad (3.18)$$

The linear term in q vanishes due to the isotropic form of the low-energy dispersion at this order. Substituting this parabolic approximation into the definition of the JDOS, the integral can be performed analytically, giving

$$N(\omega) = \frac{\hbar\omega\Theta(\hbar\omega - 2|m(\chi)|)}{18\pi a^2t_1^2|\eta(\chi)|}, \quad (3.19)$$

with the dimensionless factor

$$\eta(\chi) = 1 - \frac{2\sqrt{3}|m(\chi)|t_2 \sin \phi}{t_1^2}. \quad (3.20)$$

The Heaviside step function Θ enforces the threshold condition for optical absorption. Notably, for $t_2 \neq 0$, the factors $\eta(\chi)$ differ between the K and K' valleys, implying an asymmetry in the JDOS and the optical absorption between the two valleys.

Finally, inserting the geometric factor $I_{12}^{yyy}(\omega)$ from Eq. (3.15) and the JDOS from Eq. (3.19) into the factorized conductivity formula Eq. (3.13), we obtain the leading-order shift current conductivity at the band edge for the χ valley:

$$\sigma^{yyy}(\omega) = -\frac{e^3 a}{4\hbar^3 \omega |\eta(\chi)|} \text{sign}[m(\chi)] = -\sigma^{yxx}(\omega). \quad (3.21)$$

The result inherits the symmetry relation $\sigma^{yyy} = -\sigma^{yxx}$ from the geometric factor I_{12} , as required by the C_{3v} point group. The conductivity exhibits a characteristic $1/\omega$ frequency dependence near the gap and, most importantly, depends explicitly on the sign of the Dirac mass $m(\chi)$.

A crucial aspect of the result in Eq. (3.21) is its explicit dependence on the sign of the Dirac mass, $\text{sign}[m(\chi)]$, which changes as the system crosses the TPT. Our analytic model thus directly reproduces the sign reversal of the shift current across a TPT predicted by DFT calculations in materials like BiTeI and CsPbI₃ [27] and in agreement with [105]. A second feature emerges from the valley dependence of the mass term $m(\chi)$. In the topological insulating phase ($C = \pm 1$), $m(K)$ and $m(K')$ have opposite signs. Consequently, Eq. (3.21) implies that the shift current contributions from the two valleys are opposite in sign. This valley opposition suggests that the total band-edge photoconductivity could exhibit an additional sign reversal as a function of frequency. Specifically, as the frequency of the external radiation is tuned from the smaller to the larger of the two valley gaps, the dominant contribution may switch from one valley to the other, potentially inverting the sign of the net current.

In the following section, we move beyond the low-energy approximation to examine these two key features, that is, the topological sign reversal at the TPT and the valley-induced sign structure within the topological phase, through an exact numerical evaluation of the shift current in the full tight-binding model.

3.3 Testing model predictions

The low-energy analytic results of the previous section provide a clear conceptual picture linking the shift current to the sign of the Dirac mass and the valley topology. To assess the robustness and quantitative accuracy of

these predictions, we now perform an exact numerical calculation of the shift current using a continuum realization of the Haldane model. This approach serves two primary purposes: first, to verify the validity of the simplified two-band expression in Eq. (3.21) beyond the $\mathbf{k} \cdot \mathbf{p}$ approximation, and second, to investigate the role of position-operator matrix elements that are not fully captured in the minimal tight-binding formulation.

We employ the numerical scheme of Ref. [46], which allows for an exact evaluation of nonlinear optical responses from a continuum Hamiltonian. In a full quantum-mechanical treatment, the shift current depends explicitly on both the Hamiltonian matrix elements and the matrix elements of the position operator $\hat{\mathbf{r}}$. Standard tight-binding models, including the one in Sec. 3.2.1, account for the Hamiltonian's matrix structure through inter-site hopping parameters. However, they typically treat the position operator as diagonal in the Wannier basis, an approximation that can miss important contributions from intra-cell electron motion.

To examine this point systematically, we consider the representation of the position operator in a basis of localized Wannier functions $|\mathbf{R}, m\rangle$, where $\mathbf{R}$ is a lattice vector and m is a band index [42]. Its matrix elements can be decomposed as

$$\langle \mathbf{0}n | \hat{\mathbf{r}} | \mathbf{R}m \rangle = \tau_m \delta_{\mathbf{0}\mathbf{R}} \delta_{nm} + \mathbf{d}_{nm}(\mathbf{R}), \quad (3.22)$$

where τ_m is the intracell coordinate of the Wannier center for orbital m , and $\mathbf{d}_{nm}(\mathbf{R})$ represents inter-site dipole couplings that are generally non-zero for $n \neq m$ or $\mathbf{R} \neq \mathbf{0}$. The standard tight-binding approximation retains only the diagonal term τ_m , while the full continuum treatment includes the term $\mathbf{d}_{nm}(\mathbf{R})$.

In Eq. (3.22), the term $\tau_m \delta_{\mathbf{0}\mathbf{R}} \delta_{nm}$ corresponds to the diagonal (onsite) part of the position operator, which depends only on the Wannier center of each orbital. The term $\mathbf{d}_{nm}(\mathbf{R})$ represents the off-diagonal (inter-site) position matrix elements, which describe couplings between different sites or bands. In the standard Haldane tight-binding model and its low-energy $\mathbf{k} \cdot \mathbf{p}$ reduction, these off-diagonal terms are implicitly neglected by setting $\mathbf{d}_{nm} = 0$ [106–108]. Consequently, the analytic expression for the shift current in Eq. (3.21) includes only contributions from the Hamiltonian and the diagonal part of the position operator.

The importance of these off-diagonal dipole terms in optical responses has been recognized in several contexts. Early works assessed their impact on linear conductivity in simplified models [109, 110]. More recently, studies have shown that for nonlinear responses like the shift current, the contribution of $\mathbf{d}_{nm}$ can be comparable in magnitude to that of the Hamiltonian matrix elements [46, 111]. Notably, this effect is particularly pronounced in two-band systems [112]. This raises a critical question regarding the predictions derived from our simplified model: to what extent do the topological sign reversals and valley-dependent sign structure predicted by Eq. (3.21) survive when the

full position operator, including off-diagonal couplings, is taken into account?

Therefore, the main purpose of the remainder of this work is to numerically test the robustness of the model's predictions. Using a continuum version of the Haldane model that allows for an exact treatment of all matrix elements, we will compute the shift current across the topological phase transition and within the topological phase. This will allow us to determine whether the sign reversal at the TPT and the potential additional sign reversal due to valley opposition are fundamental geometric signatures of the topology, or if they are qualitatively altered by the detailed microscopic dipole couplings omitted in the minimal model.

3.3.1 Continuum Haldane Model

To perform an exact numerical test of the tight-binding predictions, we employ a continuum realization of the Haldane model originally proposed for cold atoms in optical lattices [113]. This model provides a smooth, microscopic potential landscape from which the effective tight-binding parameters emerge, and it allows for a complete quantum-mechanical treatment of all matrix elements, including the off-diagonal dipole terms $\mathbf{d}_{nm}(\mathbf{R})$ discussed in the previous section.

The model is defined on a two-dimensional honeycomb lattice with primitive vectors

$$\mathbf{a}_1 = \frac{2\pi}{3k_L} (\mathbf{e}_x - \sqrt{3}\mathbf{e}_y), \quad \mathbf{a}_2 = \frac{2\pi}{3k_L} (\mathbf{e}_x + \sqrt{3}\mathbf{e}_y), \quad (3.23)$$

where k_L is the laser wave vector that sets the lattice scale. The single-particle Hamiltonian is of the minimal coupling form

$$\mathcal{H} = \frac{1}{2m} [\mathbf{p} - \mathbf{A}(\mathbf{r})]^2 + VL(\mathbf{r}), \quad (3.24)$$

where m is the particle mass, $\mathbf{p}$ is the momentum operator, and $V_L(\mathbf{r})$ and $\mathbf{A}(\mathbf{r})$ are periodic scalar and vector potentials, respectively.

The scalar potential $V_L(\mathbf{r})$ generates the underlying honeycomb lattice and includes a sublattice-staggering term that breaks inversion symmetry:

$$V_L(\mathbf{r}) = 2sE_R \left\{ \cos[(\mathbf{b}_1 - \mathbf{b}_2) \cdot \mathbf{r}] + \cos\left(\mathbf{b}_1 \cdot \mathbf{r} - \frac{\pi}{3}\psi\right) + \cos(\mathbf{b}_2 \cdot \mathbf{r}) \right\}, \quad (3.25)$$

where $E_R = \hbar^2 k_L^2 / 2m$ is the recoil energy, s controls the overall lattice depth, $\mathbf{b}_i$ are reciprocal lattice vectors satisfying $\mathbf{a}_i \cdot \mathbf{b}_j = 2\pi\delta_{ij}$, and ψ is a phase that introduces an energy offset between the two sublattices, thereby mimicking the staggered mass M .

Time-reversal symmetry is broken by the periodic vector potential

$$\mathbf{A}(\mathbf{r}) = \alpha \hbar k_L \left[\left\{ \sin [(\mathbf{b}_2 - \mathbf{b}_1) \cdot \mathbf{r}] + \frac{1}{2} \sum_{i=1}^2 (-1)^i \sin (\mathbf{b}_i \cdot \mathbf{r}) \right\} \mathbf{e}_x - \frac{\sqrt{3}}{2} \sum_{i=1}^2 \sin (\mathbf{b}_i \cdot \mathbf{r}) \mathbf{e}_y \right] \quad (3.26)$$

whose amplitude α controls the strength of time-reversal-symmetry breaking. This vector potential gives rise to complex next-nearest-neighbor hoppings with a phase ϕ in the tight-binding limit, without introducing a net magnetic flux per unit cell.

In the deep-lattice limit ($s \gg 1$), the continuum Hamiltonian Eq. (3.24) maps onto the Haldane tight-binding model [114]. The effective parameters t_1 , t_2 , ϕ , and M become smooth functions of the continuum parameters (s, ψ, α) . By tuning these parameters, we can explore both trivial and topological phases, as well as the transition between them, within a framework that retains the full quantum-mechanical structure of the position operator. This allows us to assess whether the predictions of the simplified tight-binding analysis—in particular, the sign reversals of the shift current—persist when all matrix elements are treated exactly.

3.3.2 Calculation Details

The numerical evaluation of the shift current from the continuum Hamiltonian proceeds by combining exact diagonalization, Wannierization, and post-processing via Wannier interpolation as detailed in section 2.1. First, we obtain the Bloch eigenvalues $E_{n\mathbf{k}}$ and eigenfunctions $\psi_{n\mathbf{k}}(\mathbf{r})$ of the continuum Hamiltonian $\mathcal{H}$ in Eq. (3.24) by solving the stationary Schrödinger equation on a plane-wave basis. This is performed using the method described in Refs. [115, 116], which exploits the periodicity of the potentials $V_L(\mathbf{r})$ and $\mathbf{A}(\mathbf{r})$ to cast the problem into a matrix eigenvalue equation in momentum space.

From the Bloch eigenfunctions we then construct a set of maximally localized Wannier functions (MLWFs) using the Wannier90 software package [117]. This step provides a real-space representation of the electronic states and, crucially, yields the complete matrix elements of the position operator $\hat{\mathbf{r}}$ in the Wannier basis, including both diagonal (τ_n) and off-diagonal ($\mathbf{d}_{nm}(\mathbf{R})$) contributions defined in Eq. (3.22). Finally, we compute the shift current conductivity $\sigma^{ab}(\omega)$ using the Wannier interpolation technique detailed in Sec. 2.1.3.2.

The continuum model parameters (s, ψ, α) are chosen according to the mapping described in Refs. [114, 116] to reproduce the desired tight-binding regime. For the Wannierization, we use a uniform 15×15 $\mathbf{k}$ -point grid in

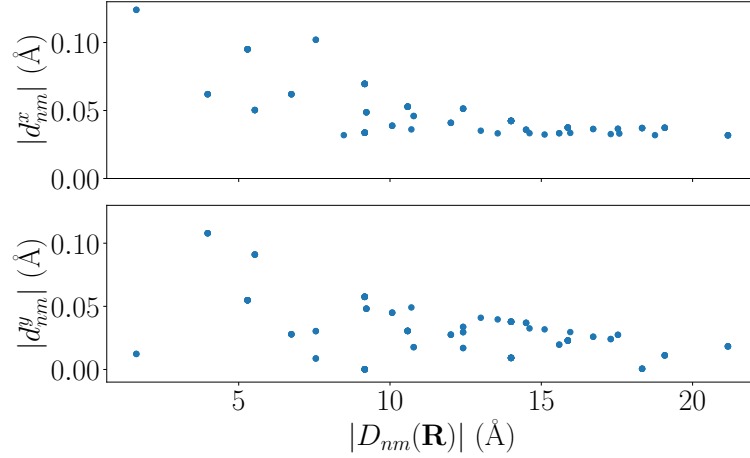


Figure 3.2: Cartesian components of off-diagonal matrix elements of the position operator as a function of the distance between Wannier orbitals. Employed parameters are $s = 0.70$, $\psi = 1.5 \cdot 10^{-3}$ and $\alpha = 0.27$.

the Brillouin zone as the initial basis for constructing the MLWFs. The shift current integration is then performed via Wannier interpolation on a much finer 2000×2000 $\mathbf{k}$ -point mesh to ensure convergence of the Brillouin-zone integrals.

3.3.3 Matrix elements of the position operator

We begin our analysis by quantifying the magnitude and spatial decay of the off-diagonal position matrix elements $\mathbf{d}_{nm}(\mathbf{R})$ defined in Eq. (3.22), as these terms are neglected in the standard tight-binding approximation. First, we establish the real-space scale of the system. In our numerical implementation, we set the laser wave vector to $k_L = 0.78 \text{ \AA}^{-1}$, which yields primitive lattice vectors $\mathbf{a}_{1,2} = (2.65, \mp 4.58) \text{ \AA}$, a corresponding lattice constant $a = |\mathbf{a}_1| \approx 3.05 \text{ \AA}$, and Wannier centers located at $\boldsymbol{\tau}_{1,2} = (1.40, \mp 0.81) \text{ \AA}$. This choice produces a lattice geometry with dimensions comparable to those of real two-dimensional monolayers [118], such as monolayer BC_2N studied in Ref. [112], providing a physically relevant reference scale.

Figure 3.2 shows the Cartesian components of $\mathbf{d}_{nm}(\mathbf{R})$ as a function of the real-space distance between orbital centers,

$$D_{nm}(\mathbf{R}) = |\boldsymbol{\tau}_n - \boldsymbol{\tau}_m + \mathbf{R}|, \quad (3.27)$$

where $\mathbf{R}$ is a lattice vector. The data are calculated for a parameter set corresponding to a relatively shallow optical lattice ($s = 0.70$), with broken inversion symmetry ($\psi = 1.5 \times 10^{-3}$) and broken time-reversal symmetry ($\alpha = 0.27$). This regime is intentionally chosen to maximize the relative

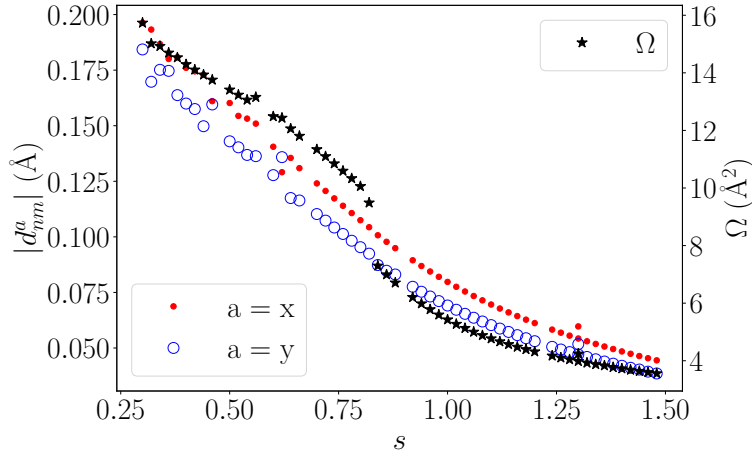


Figure 3.3: Cartesian components of the dominant off-diagonal matrix elements of the position operator as a function of s and its correlation to the spread of the Wannier functions. Employed parameters are $\psi = 1.5 \cdot 10^{-3}$ and $\alpha = 0.27$.

importance of off-diagonal dipole couplings, as shallow potentials lead to more extended Wannier functions and thus larger inter-site matrix elements. The plot illustrates the magnitude and spatial decay of $\mathbf{d}_{nm}(\mathbf{R})$, providing a direct measure of the terms omitted in the simplified tight-binding description.

The results in Fig. 3.2 reveal the spatial structure and relative magnitude of the off-diagonal dipole matrix elements. For the x -component d_{nm}^x , the largest contribution originates from nearest-neighbor (nn) pairs within the unit cell, corresponding to a separation $D_{nm} \sim 1.6 \text{ \AA}$. However, matrix elements for pairs as distant as $10 \text{ \AA}$ remain substantial, retaining approximately half the peak magnitude. The y -component d_{nm}^y is dominated by next-nearest-neighbor (nnn) couplings at $D_{nm} \sim 4.0 \text{ \AA}$, with a spatial decay profile similar to that of d_{nm}^x . Both the hierarchy of couplings and their absolute scale trends are consistent with the position-operator matrix elements computed for real two-band materials such as monolayer BC_2N [112], confirming that our continuum model captures realistic dipole characteristics.

To systematically assess the dependence of these matrix elements on the lattice potential depth, Fig. 3.3 shows the dominant (maximum magnitude) values of d_{nm}^x and d_{nm}^y as a function of the parameter s , together with the corresponding Wannier spread Ω defined in Eq. (2.35). A clear correlation is observed: as s decreases (shallower lattice), the Wannier functions become more delocalized, leading to a sharp increase in both Ω and the magnitude of $\mathbf{d}_{nm}$. This demonstrates that the parameter s effectively tunes the importance of off-diagonal position-matrix elements in the model. Notably, in the low- s regime the computed $\mathbf{d}_{nm}$ values are comparable in magnitude to those found

in ab initio calculations for real 2D materials like BC_2N [112]. This regime is therefore particularly relevant for testing the tight-binding predictions against a more realistic, full quantum-mechanical treatment of the position operator.

3.3.4 Numerical Evaluation of the Shift Current

3.3.4.1 Deep Tight-Binding Regime

We now proceed to test the predictions of the analytic tight-binding model of Sec. 3.2.2 by numerically evaluating the shift current. We begin with the deep tight-binding regime (large s), where the continuum model maps accurately onto the Haldane tight-binding Hamiltonian. We select two specific parameter sets, corresponding to a trivial insulator ($C = 0$) and a topological Chern insulator ($C = 1$), as determined by the mapping procedure of Ref. [114].

First, we examine the momentum-resolved geometric factor $I_{12}^{yyy}(\mathbf{k}, \omega)$ near the band edge, shown in Fig. 3.4. The response is strongly localized around the K and K' valleys, validating the $\mathbf{k} \cdot \mathbf{p}$ expansion employed in Sec. 3.2.2. Moreover, the sign of I_{12}^{yyy} at each valley precisely matches the prediction of Eq. (3.15), namely $\text{sign}[m(\chi)]$, for both topological phases. This confirms that the low-energy Hamiltonian correctly captures the geometric origin of the response.

The computed shift current conductivity $\sigma^{yyy}(\omega)$ for both phases is presented in Fig. 3.5. The key features predicted by the analytic model are clearly observed:

1. The band-edge response reverses sign between the trivial ($C = 0$) and topological ($C = 1$) phases. For the $C = 0$ case shown, the gaps at the two valleys are equal, resulting in a single sign for the lowest-energy peak.
2. In the topological phase ($C = 1$), a second sign reversal occurs at the frequency corresponding to the larger of the two valley gaps. This is a direct consequence of the opposite signs of I_{12}^{yyy} at the K and K' valleys [cf. Fig. 3.4(b)], as anticipated from the valley-dependent mass term in Eq. (3.7).

These observations are in agreement with the low-energy expression in Eq. (3.21), demonstrating that the two-band model correctly captures the essential spectral and topological signatures of the shift current near the absorption edge.

Finally, we examine the frequency dependence of the response. Figure 3.5 includes, for the $C = 0$ case, a fit of the low-energy peak to the $1/\omega$ decay predicted by Eq. (3.21). The fit reproduces the numerical data well immediately above the band edge but gradually underestimates the conductivity at higher photon energies, where the parabolic band approximation and the neglect of higher-order terms in the $\mathbf{k} \cdot \mathbf{p}$ expansion become less accurate.

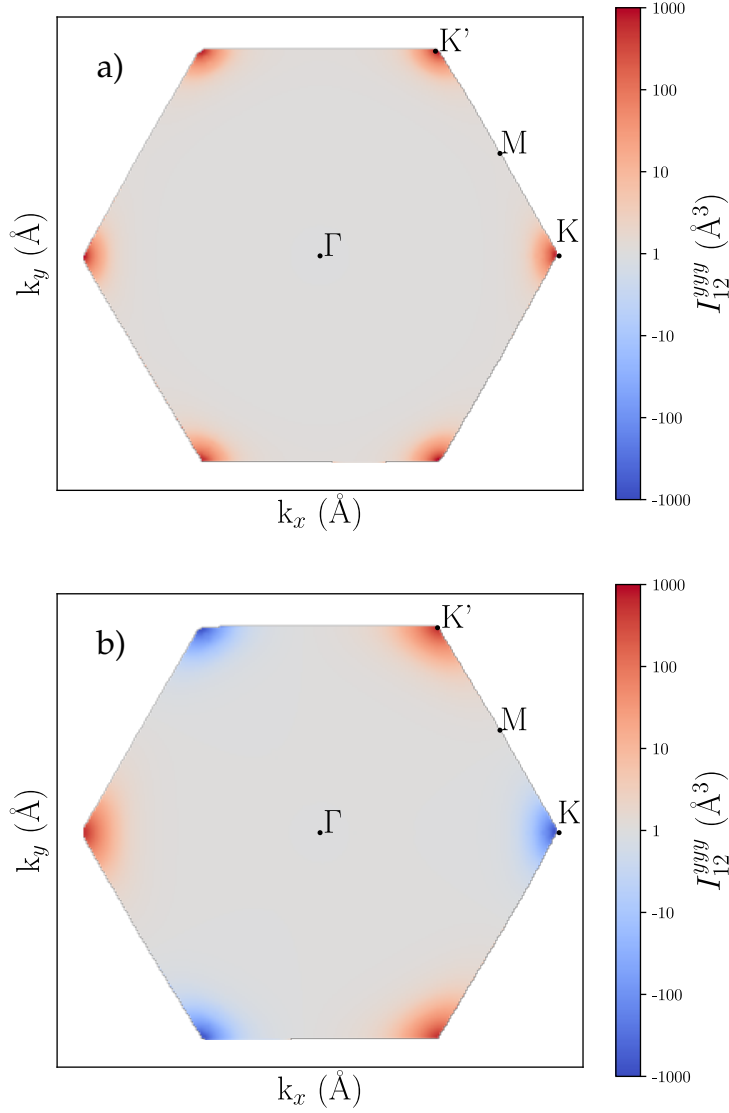


Figure 3.4: Representation of I_{12}^{yyy} in the BZ for the (a) $C = 0$ and (b) $C = 1$ phases obtained with parameters $\alpha = 0.0$, $\psi = 1.5 \cdot 10^{-3}$, $s = 2.5$ and $\alpha = 0.13$, $\psi = 1.5 \cdot 10^{-3}$, $s = 2.5$, respectively.

3.3.4.2 Limits of the Tight-Binding Description

Having established the agreement in the deep tight-binding regime, we now investigate the limits of the model's validity by exploring shallower lattice potentials. We compute the shift current conductivity $\sigma^{yyy}(\omega)$ as a function of the potential depth parameter s , which directly controls the importance of off-diagonal position matrix elements (see Sec. 3.3.3). The results for three

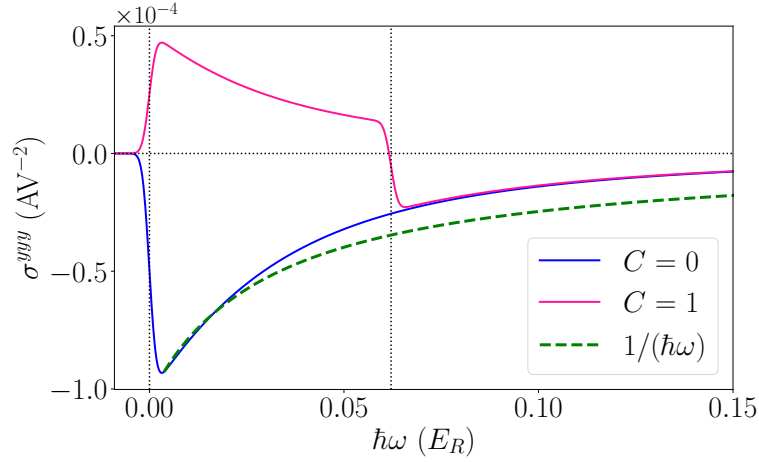


Figure 3.5: Shift photoconductivity $\sigma^{yyy}(\omega)$ of the trivial (blue) and topological (magenta) systems described in Fig. 3.4. The energy is measured with respect to each one's first band-gap and vertical lines mark the gaps at the band-edges of the topological insulator. A $1/\hbar\omega$ decay for the $C = 0$ case is also included (green dashed line).

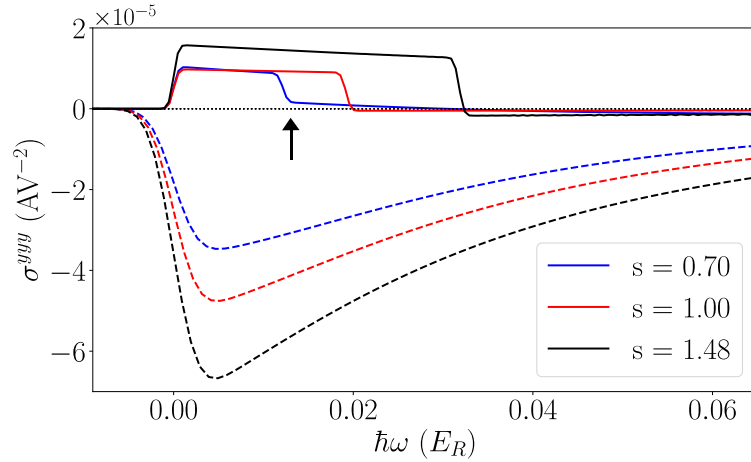


Figure 3.6: Shift photoconductivity $\sigma^{yyy}(\omega)$ in the continuum Haldane model for three values of s . For each value of s a trivial insulator (dashed) and a topological insulator (solid) is represented, with parameters $\alpha = 0.0$, $\psi = 1.5 \cdot 10^{-3}$ and $\alpha = 0.27$, $\psi = 1.5 \cdot 10^{-3}$, respectively. For $s = 0.70$, the sign at the second band-edge is not reversed, a feature that is marked by the arrow.

representative values of s are shown in Fig. 3.6. A key finding is that the sign reversal of the band-edge response across the TPT persists for all values

of s , including the shallow-potential regime ($s = 0.70$) where off-diagonal dipole matrix elements are significant. This demonstrates that the sign change driven by the inversion of the Dirac mass $m(\chi)$ is a robust geometric signature of the change in bulk topology, largely independent of the detailed treatment of the position operator. In contrast, the second sign reversal within the topological phase predicted to occur between the two valley gaps exhibits a strong dependence on the model details. As seen in Fig. 3.6, this feature is clearly present in the deep tight-binding regime ($s = 2.0$) but vanishes for shallower potentials ($s = 0.70$, indicated by the arrow). The disappearance of this sign inversion indicates that the valley-opposed response is more sensitive to the specific form of the wavefunctions and the inclusion of full position-matrix elements, which can alter the relative weight and phase of contributions from the K and K' points. Thus, while the topological sign reversal at the TPT is a universal consequence of the band inversion, the valley-induced sign structure in the topological phase is a more delicate property that may not survive in materials where Wannier functions are significantly delocalized and off-diagonal dipole couplings are important.

To understand the disappearance of the second sign reversal in the shallow-potential regime, we analyze in detail the transition matrix element $I_{12}^{yyy}(\mathbf{k}, \omega)$ near the band edge. Figure 3.7 shows I_{12}^{yyy} along the high-symmetry path K – M – K' – Γ for the topological phase ($C = 1$) with $s = 0.70$. We compare the full numerical result with a tight-binding-like calculation in which the off-diagonal position matrix elements are artificially set to zero ($\mathbf{d}_{nm} = 0$). This comparison isolates the specific contribution of $\mathbf{d}_{nm}$. The difference between the two calculations is maximal at the Γ point but remains substantial at the K and K' valleys. Crucially, the effect of $\mathbf{d}_{nm}$ is valley-asymmetric. In the full calculation, the magnitudes at the two valleys differ significantly:

$$|I_{12}^{yyy}(K)| = 35.7 \text{ \AA}, \quad (3.28)$$

$$|I_{12}^{yyy}(K')| = 31.8 \text{ \AA}. \quad (3.29)$$

In contrast, the tight-binding-like result ($\mathbf{d}_{nm} = 0$) yields nearly equal magnitudes (28.68 $\text{\AA}$ at K and 28.01 $\text{\AA}$ at K'), as expected from the low-energy model Eq. (3.15), given the similar valley gaps $\Delta(K') \approx 1.02\Delta(K)$. The observed asymmetry in the full calculation, where $|I_{12}^{yyy}(K)| > |I_{12}^{yyy}(K')|$, explains the absence of the sign reversal at the second gap in Fig. 3.6. Because the response from the K valley dominates over that from K' , the total conductivity does not change sign when the photon energy crosses the larger gap.

This result provides a clear and quantitative demonstration that off-diagonal position matrix elements $\mathbf{d}_{nm}$ can qualitatively alter model predictions. While the tight-binding description correctly captures the sign structure of the geometric factor at each valley, it misses the valley-dependent renormalization of their magnitudes induced by the full quantum-mechanical

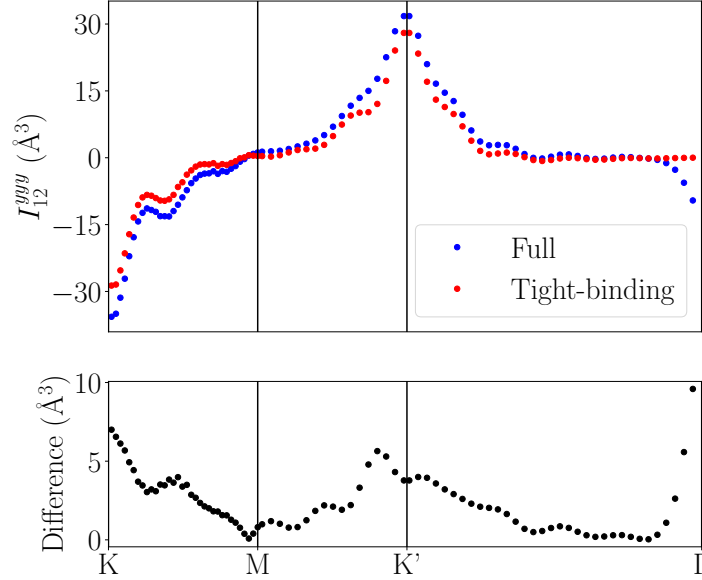


Figure 3.7: Top: tight-binding and full matrix element I_{12}^{yyy} along the high symmetry line K-M-K'-Γ. Bottom: the difference between the two data sets, which accounts for the contribution from $\mathbf{d}_{mn}$ to I_{12}^{yyy} .

position operator. Consequently, phenomena that rely on a precise balance between valley contributions—such as the secondary sign reversal in the topological phase—may not be robust in real materials where such matrix elements are significant.

3.4 Conclusions

In summary, we have investigated topological signatures of the shift current in the paradigmatic Haldane model. Using a low-energy $\mathbf{k} \cdot \mathbf{p}$ expansion, we derived an analytic expression for the band-edge shift photoconductivity which shows that the sign of the response is governed by the Dirac mass term $m(\chi)$. This led to two key results: a sign reversal of the current when the system undergoes a topological phase transition (TPT), and a secondary sign reversal within the topological phase arising from the competition between valleys with opposite mass signs. As further demonstrated in Appendix 3.4, the sign reversal at the TPT persists even when the transition occurs between non-trivial phases with higher Chern numbers, such as between $C = \pm 1$ and $C = \mp 2$, reinforcing the generality of this behavior. To test the robustness of

these predictions, we performed exact numerical calculations on a continuum version of the model that includes the full position operator, notably the off-diagonal matrix elements $\mathbf{d}_{nm}$ neglected in tight-binding approaches. We found that the sign reversal at the TPT is remarkably robust, persisting even in shallow-potential regimes where $\mathbf{d}_{nm}$ are significant, suggesting it is a fundamental geometric signature of the band inversion. In contrast, the secondary sign reversal within the topological phase is not always present in these regimes, as the off-diagonal matrix elements introduce a valley asymmetry that disrupts the precise balance of contributions required for a net sign change. Consequently, the shift current serves as a potent optical probe of band topology, with the sign reversal across a topological transition representing a robust and experimentally accessible signature for diagnosing topological phases via nonlinear optics.

Appendix: Higher Chern number phase transitions

In this appendix, we build upon the results of Sec. 3.2.2 by analyzing a topological phase transition occurring between non-trivial phases. Within the Haldane framework, a phase carrying a Chern number $|C| = 2$ becomes possible when third-nearest-neighbor hopping t_3 is included, following the proposal in Ref. [119]. This extended model permits transitions between the $C = \pm 1$ and $C = \mp 2$ phases, as illustrated in the phase diagram of Ref. [119]. Our goal here is to examine how the shift current behaves across such transitions.

The third-nearest-neighbor hopping connects A and B sublattices, thereby introducing additional contributions to the Hamiltonian terms proportional to the Pauli matrices σ_1 and σ_2 :

$$f'_1 = f_1 + t_3 \sum_i^3 \cos(\mathbf{k} \cdot \mathbf{c}_i) \quad (3.30)$$

$$f'_2 = f_2 + t_3 \sum_i^3 \sin(\mathbf{k} \cdot \mathbf{c}_i) \quad (3.31)$$

Here $\mathbf{c}_i$ denote the vectors to third-nearest neighbors [119].

A notable departure from the conventional Haldane model is that the band gap closes not exactly at the K or K' point, but instead at three distinct points surrounding it. One such gap-closing point is described by

$$\tilde{K}^{(\prime)} = K^{(\prime)} + \chi \delta k(1, 0), \quad (3.32)$$

with δk a small shift. The remaining two points follow from applying the C_3 symmetry operation.

Expanding the Hamiltonian around $\tilde{K}^{(\prime)}$ leads to cumbersome expressions for the modified coefficients f'_i . For our purposes, the key modification occurs in the f_3 term, which contains the mass term. This term becomes

$$m'(\chi) = m(\chi) + \frac{9\sqrt{3}a^2\delta k^2 t_2 \sin(\phi)}{4} + \mathcal{O}(\delta k^3) \quad (3.33)$$

The topological phase transition is driven by a sign reversal of this effective mass term.

Using Eq. (3.9), the shift-current transition matrix element I_{12}^{yyy} for the modified model evaluates to

$$I_{12}^{yyy} \simeq \frac{a^3(9t_1^2 + 18t_1t_3 - 36t_3^2)}{8\hbar^2\omega^2} \text{sign}[m'(\chi)]. \quad (3.34)$$

Analogous to Eq. (3.15) for the original Haldane model, Eq. (3.34) depends solely on the sign of the modified mass term. This dependence arises because the band-edge contribution to I_{12}^{abb} originates from the terms $f_3 f_{1,b} f_{2,ab}$ and $f_3 f_{2,b} f_{1,ab}$ in Eq. (3.9), each containing the mass term linearly. Hence, Eq. (3.34) demonstrates that the band-edge shift current also flips sign at the TPT connecting the $C = \pm 1$ and $C = \mp 2$ nontrivial phases. This finding is consistent with the more general argument presented in Ref. [105].

Chapter 4

Surface-state engineering for nonlinear charge and spin photocurrent generation

4.1 Introduction

The requirement for inversion symmetry breaking is a fundamental constraint on the BPVE, as it directly limits the pool of candidate materials to the subset of noncentrosymmetric crystals [57, 71]. Structurally, 21 of the 32 crystallographic point groups lack an inversion center. While this includes important families like ferroelectrics, piezoelectrics, and certain topological semimetals, these materials are significantly outnumbered in nature and synthesis by their centrosymmetric counterparts, which constitute the majority of known, high-symmetry compounds [120]. This scarcity presents a major bottleneck in the search for materials with strong, tunable BPVE responses.

This symmetry constraint, however, can be circumvented by exploiting the inherent structural asymmetry at material surfaces [121]. At any crystal boundary, inversion symmetry is generically broken due to the termination of the periodic lattice. Crucially, this symmetry reduction is not limited to the surface-normal direction; in many cases, the effective two-dimensional point group describing the surface layer is itself noncentrosymmetric, thereby enabling specific in-plane nonlinear optical selection rules forbidden in the bulk. A clear illustration of this principle is provided by the termination of a face-centered cubic lattice along the (111) plane: the loss of translational symmetry along the surface-normal direction ($\hat{z}$) renders every atomic position in the surface layer inequivalent, and the in-plane arrangement of these inequivalent sites reduces the surface symmetry from the bulk cubic point group to the noncentrosymmetric point group $3m$. Consequently, the symmetry reduction that takes place at the surface of any material dramatically expands the material landscape for photocurrent generation far beyond the limited set of

intrinsically acentric bulk crystals, making surfaces a generic and versatile platform for realizing nonlinear optical phenomena.

Following from the discussion of universal symmetry breaking at surfaces, it is crucial to consider the electronic states that emerge specifically in this region. The breakdown of periodicity at a free surface not only alters the symmetry but also has profound consequences for the electronic structure. At the interface of a semiconductor or metal, electronic surface states can arise, which are spatially bound to the surface and possess energies that lie within the forbidden bulk band gap [121, 122]. These states exist because the termination of the lattice violates the periodic boundary conditions required by Bloch's theorem. In the bulk, Bloch states are described by purely real wave vectors $\mathbf{k}$. At a surface, however, the wave vector can acquire an imaginary component, leading to solutions of the Schrödinger equation of the form

$$\psi(\mathbf{r}) = e^{i\mathbf{k}_{\parallel} \cdot \mathbf{r}_{\parallel}} u(\mathbf{r}) e^{-\kappa z}, \quad (4.1)$$

where κ quantifies the exponential decay of the wave function into the bulk, localizing it near the surface [121].

In addition to the emergence of localized electronic states, surfaces host other characteristic phenomena, most notably spin-orbit splitting of electronic bands [123, 124]. To explore spin-split surface states, it is essential to understand the symmetry constraints that govern the spin-orbit coupling Hamiltonian. The general form of the SOC Hamiltonian is given by

$$\hat{H}_{\text{SOC}} = \frac{\hbar}{4m^2c^2} \boldsymbol{\sigma} \cdot (\nabla V(\mathbf{r}) \times \mathbf{p}), \quad (4.2)$$

where $\boldsymbol{\sigma}$ is the vector of Pauli matrices, $V(\mathbf{r})$ is the crystal potential, and $\mathbf{p}$ is the momentum operator [123]. Under time-reversal symmetry (TRS), both $\boldsymbol{\sigma}$ and $\mathbf{p}$ change sign, leaving $\hat{H}_{\text{SOC}}$ invariant. This imposes a fundamental constraint on the band structure:

$$E(\mathbf{k}, \uparrow) = E(-\mathbf{k}, \downarrow). \quad (4.3)$$

If the system additionally possesses inversion symmetry, a separate condition holds. Under inversion, $\mathbf{k} \rightarrow -\mathbf{k}$ while the spin orientation remains unchanged, leading to

$$E(\mathbf{k}, \uparrow) = E(-\mathbf{k}, \uparrow), \quad (4.4)$$

$$E(\mathbf{k}, \downarrow) = E(-\mathbf{k}, \downarrow). \quad (4.5)$$

When both time-reversal and inversion symmetries are present, these conditions combine to yield

$$E(\mathbf{k}, \uparrow) = E(\mathbf{k}, \downarrow), \quad (4.6)$$

demonstrating that even in the presence of SOC, a centrosymmetric non-magnetic material exhibits no net spin splitting, as all states remain at least two-fold degenerate (Kramers degeneracy) [123].

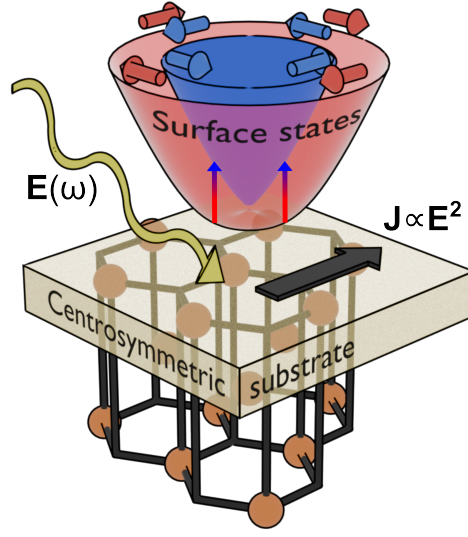


Figure 4.1: Illustration of the chapter’s main concept: light illuminates a centrosymmetric substrate with a pair of surface states, driving a current through the BPVE.

Therefore, in non-magnetic systems, spin-split bands require the breaking of inversion symmetry. This breaking can occur via two distinct mechanisms: Bulk Inversion Asymmetry (BIA), which gives rise to Dresselhaus-type spin-orbit coupling [125], or Structural Inversion Asymmetry (SIA), which is the focus of this chapter [123, 124]. SIA arises naturally at surfaces or interfaces, where the crystal potential gradient normal to the interface defines an effective internal electric field,

$$\mathbf{E}_{\text{SIA}} = -\frac{1}{e} \frac{\partial V}{\partial z} \hat{\mathbf{z}}, \quad (4.7)$$

with z denoting the surface-normal direction, V the crystal potential, and e the elementary charge. This broken symmetry at the interface is the fundamental origin of SIA-induced spin-orbit effects, most notably the Rashba effect, which gives rise to momentum-dependent spin-split surface states [124].

In this scenario, the nonlinear response is expected to be most pronounced in states highly localized near the surface, particularly in electronic transitions that involve surface states. In this chapter, we explore how SIA can be used to generate photocurrents at a surface. Fig. 4.1 illustrates the concept: light-induced transitions between spin-split surface states drive a current via the BPVE. The notion of exploiting surface states to produce currents has been examined previously. Earlier theoretical studies have investigated shift and ballistic photocurrents in topological surface states using the Rashba model [126, 127], quadratic photocurrents in metallic surface alloys via a nonequilibrium Keldysh framework [128, 129], including recent work on orbital

contributions [130], and the BPVE originating from surface Fermi arcs in Weyl semimetals [131–133]. Taken together, these studies lay important groundwork, yet they highlight that the potential to harness spin–orbit physics through nonlinear charge and spin responses at surfaces remains a largely open and underexplored field.

This chapter presents a systematic investigation of nonlinear photocurrents arising from spin-orbit-split surface states. The work is structured as follows: first, analytical expressions for the quadratic shift and injection photoconductivities are derived within an extended Rashba model that incorporates hexagonal warping. Second, first-principles density functional theory (DFT) calculations are performed for the prototypical Rashba system Au(111), and the results are compared both qualitatively and quantitatively with the analytical model to assess its validity and limitations. Third, to bridge theory with experiment, the focus shifts to the Tl/Si(111) surface. This system is more experimentally tractable due to its semiconducting bulk and giant spin-orbit splitting; here, realistic estimates are provided for the magnitude and angular dependence of the surface-state charge photocurrent. Finally, the analysis is extended to the spin degree of freedom in Tl/Si(111), demonstrating how its distinctive out-of-plane spin polarization enables the generation of tunable, nonlinear spin-polarized currents.

4.2 Proof of principle in Rashba surface states

4.2.1 Overview of the Rashba model

As the focus of this chapter is the study of nonlinear optical responses in spin-split surface states, the Rashba model serves as the most prominent and widely adopted minimal theoretical framework. This model describes the effective spin-orbit coupling arising from SIA at surfaces or interfaces. Substituting the internal electric field from SIA into the general spin-orbit Hamiltonian, and using $p = \hbar k$, yields the simplified Rashba form:

$$H_R = \alpha_R \boldsymbol{\sigma} \cdot (\hat{\mathbf{z}} \times \hbar \mathbf{k}), \quad (4.8)$$

where α_R is the Rashba parameter encapsulating the strength of the interaction. In two-dimensional polar coordinates (ρ, ϕ) describing the surface, where $\mathbf{k} = \rho(\cos \phi, \sin \phi, 0)$, this Hamiltonian can be expressed as:

$$H_R(\rho, \phi) = \alpha_R \rho \begin{pmatrix} 0 & -ie^{-i\phi} \\ ie^{i\phi} & 0 \end{pmatrix}. \quad (4.9)$$

Diagonalizing this operator yields the well-known linear-in-momentum dispersion in addition to the kinetic energy:

$$E_{\pm}(\rho) = \frac{\hbar^2 \rho^2}{2m^*} \pm \alpha_R \hbar \rho, \quad (4.10)$$

where the $\pm$ sign corresponds to the two spin-split bands. This is the original Rashba Hamiltonian. It describes two energy paraboloids (conical in the vicinity of the Γ point) with opposite-rotating in-plane spin projections, creating a characteristic linear splitting in momentum space around the Brillouin zone center (see Fig. 4.1).

The standard Rashba dispersion derived above is isotropic in the surface plane. However, real material surfaces possess specific crystal symmetries described by two-dimensional point groups. To accurately describe the electronic structure of a surface, the Rashba Hamiltonian must be extended to include higher-order contributions that respect the relevant point group symmetry. In this chapter we will focus on systems that belong to the $3m$ point group. For such $3m$ symmetric surfaces, the effective low-energy Hamiltonian becomes [134]:

$$H = \frac{\hbar^2 k^2}{2m^*} \mathcal{I} - (\alpha + \gamma k^2) \hbar k \sin(\phi) \sigma_x + (\alpha + \gamma k^2) \hbar k \cos(\phi) \sigma_y + \beta k^3 \cos(3\phi) \sigma_z. \quad (4.11)$$

Here, $\mathcal{I}$ is the 2×2 identity matrix, and the k -dependent term $\frac{\hbar^2 k^2}{2m^*}$ represents the isotropic parabolic dispersion. The Hamiltonian includes the isotropic linear Rashba term characterized by the coupling constant α , a third-order isotropic correction with coefficient γ , and a crucial third-order term proportional to β . This final term, originally described by Fu in the context of topological insulators [135], is known as hexagonal warping. The inclusion of hexagonal warping is essential, as it captures the anisotropy imposed by the underlying threefold (C_3) crystal symmetry. This term distorts the otherwise circular constant-energy contours into a hexagonal, snowflake-like shape. This symmetry breaking is not merely cosmetic; it has profound physical consequences. Most importantly for this work, the hexagonal warping term is essential to enable a finite bulk photovoltaic effect at the surface. In the isotropic Rashba model, symmetry forbids a net in-plane DC photocurrent. The introduction of the warping term β , which respects the $3m$ point group, breaks this prohibition and allows the nonlinear shift and injection currents to manifest, making it a critical ingredient for surface-state photocurrent engineering.

4.2.2 Analytic calculation of transition matrix elements

To quantitatively analyze the nonlinear photoresponse in spin-split surface states, we begin by describing the two primary quadratic contributions to the bulk photovoltaic effect. Under illumination by a monochromatic light field $\mathbf{E}(t) = \mathbf{E}(\omega)e^{i\omega t} + \mathbf{E}(-\omega)e^{-i\omega t}$, the generated DC charge photocurrent described in Eq. (2.67) can be simplified in a time-reversal invariant material to

$$J^a(0) = \sigma^{abc} \text{Re}[E^b(\omega)E^c(-\omega)] + \tau \cdot \eta^{abc} \text{Im}[E^b(\omega)E^c(-\omega)], \quad (4.12)$$

Table 4.1: Independent components of the integrated charge (abc) and spin (s, abc) shift and injection photoconductivity tensors under linearly (LPL) and circularly (CPL) polarized light that contribute to in-plane photocurrents for the $3m$ point group describing Au(111) and Tl/Si(111) surfaces.

	LPL	CPL
Charge shift	yyy, xxz	—
Charge injection	—	xxz
Spin shift	—	$x, xxy; x, xxz; z, xyz$
Spin injection	$x, xxy; x, xxz; x, yyy$ $x, yzz; z, xxx; z, xyz$	—

where σ and η are the shift and injection photoconductivities described in Chapter 2. Table 4.1 displays the permitted (independent) components which can generate current under linearly polarized light and circularly polarized light by the shift and injection mechanisms in a $3m$ surface, respectively.

In this section, these general formulas are applied analytically to the specific extended Rashba Hamiltonian for a surface with $3m$ symmetry. This allows us to derive explicit $\mathbf{k}$ -dependent expressions for the shift and injection transition matrix elements, elucidating their functional dependence on momentum, polarization angle, and the model parameters, most notably the hexagonal warping strength β .

Since in real materials' surface states the generalized Rashba model is only valid within a small region close to the $\bar{\Gamma}$ point in the surface Brillouin zone, the $\mathcal{O}(\rho^3)$ terms are treated as a perturbation to the isotropic Rashba Hamiltonian H_0 . Up to first order in this perturbation, the eigenstates of the total Hamiltonian $H = H_0 + V$ are given by:

$$|+\rangle = \begin{bmatrix} -\frac{\sqrt{2}i(2\alpha+\beta\rho^2\cos(3\phi))e^{-i\phi}}{\frac{4\alpha}{\sqrt{2}\cdot(2\alpha-\beta\rho^2\cos(3\phi))}} \\ \frac{4\alpha}{\sqrt{2}\cdot(2\alpha-\beta\rho^2\cos(3\phi))} \end{bmatrix}, \quad (4.13)$$

$$|-\rangle = \begin{bmatrix} \frac{\sqrt{2}i(2\alpha-\beta\rho^2\cos(3\phi))e^{-i\phi}}{\frac{4\alpha}{\sqrt{2}\cdot(2\alpha+\beta\rho^2\cos(3\phi))}} \\ \frac{4\alpha}{\sqrt{2}\cdot(2\alpha+\beta\rho^2\cos(3\phi))} \end{bmatrix}, \quad (4.14)$$

and the energy separation between the two bands is:

$$\omega_{-+} = 2\rho(\alpha + \gamma\rho^2). \quad (4.15)$$

Using these eigenstates and energies, the expressions for the linear and second-order photoconductivity tensors are solved (Eqs. (2.69) and (2.71) for the shift and injection currents, respectively). This results in the following $\mathbf{k}$ -dependent tensor components for the shift current (σ^{abc}):

$$\sigma^{xxx}(\mathbf{k}) = \frac{3\beta \sin(2\phi)}{2\alpha\rho}, \quad (4.16)$$

$$\sigma^{xxy}(\mathbf{k}) = \frac{\beta (16 \sin^6(\phi) + 12 \sin^4(\phi) - 35 \sin^2(\phi) - \sin(\phi) \sin(5\phi) - 16)}{16\alpha\rho}, \quad (4.17)$$

$$\sigma^{xyy}(\mathbf{k}) = \frac{\beta (-16 \sin^5(\phi) - 12 \sin^3(\phi) + 27 \sin(\phi) + \sin(5\phi)) \cos(\phi)}{8\alpha\rho}, \quad (4.18)$$

$$\sigma^{yxx}(\mathbf{k}) = \frac{\beta (16 \sin^6(\phi) - 52 \sin^4(\phi) + 21 \sin^2(\phi) - \sin(\phi) \sin(5\phi) - 8)}{8\alpha\rho}, \quad (4.19)$$

$$\sigma^{yyx}(\mathbf{k}) = \frac{\beta (-16 \sin^5(\phi) + 52 \sin^3(\phi) - 13 \sin(\phi) + \sin(5\phi)) \cos(\phi)}{16\alpha\rho}, \quad (4.20)$$

$$\sigma^{yyy}(\mathbf{k}) = \frac{3\beta \cos^2(\phi)}{\alpha\rho}. \quad (4.21)$$

For the injection current (η^{abc}), we obtain:

$$\eta^{xxy}(\mathbf{k}) = \frac{-2\beta \cos(\phi) \cos(3\phi)}{4\rho^2 (\alpha^2 + 4\alpha\gamma\rho^2)}, \quad (4.22)$$

$$\eta^{yyx}(\mathbf{k}) = \frac{-2\beta \sin(\phi) \cos(3\phi)}{4\rho^2 (\alpha^2 + 4\alpha\gamma\rho^2)}. \quad (4.23)$$

Note the intrinsic symmetry properties of these tensors. The shift photoconductivity σ^{abc} is symmetric with respect to interchange of the last two indices ($b \leftrightarrow c$), implying that $\sigma^{xyx}(\mathbf{k}) = \sigma^{xxy}(\mathbf{k})$ and $\sigma^{yyx}(\mathbf{k}) = \sigma^{xyy}(\mathbf{k})$. Conversely, the injection photoconductivity η^{abc} is antisymmetric under the same interchange, leading to $\eta^{xyx}(\mathbf{k}) = -\eta^{xxy}(\mathbf{k})$ and $\eta^{yyx}(\mathbf{k}) = -\eta^{xyy}(\mathbf{k})$.

4.2.3 *Ab-initio* calculation in Au(111) surface

Having established the analytical framework for nonlinear photoresponse within the extended Rashba model, the next step is to evaluate its accuracy against a realistic material system. For this purpose, we turn to the Au(111) surface, a paradigmatic system for studying spin-orbit-split surface states. Following the seminal work by LaShell et al., which first reported evidence of spin-split surface states driven by spin-orbit coupling on Au(111) [136], this system has become a standard realization of the Rashba two-dimensional electron gas [137–139]. Unlike bulk Au, which is centrosymmetric, the

Au(111) surface belongs to the noncentrosymmetric point group $3m$, enabling symmetry-allowed quadratic optical responses.

We first computed the ground state using **Quantum ESPRESSO** [140, 141] with PBE pseudopotentials [36] as an approximation for the exchange-correlation term. The slab employed to simulate the surface consisted of 7 unit cells, with an energy cutoff of 45 Ry and a Monkhorst-Pack grid of $8 \times 8 \times 1$ k-points. Subsequently, we constructed a MLWF model using **Wannier90**. A selective disentanglement approach was employed, isolating only the two spin-orbit-coupled surface states crossing the Fermi level, while excluding all other bands. As initial projections for the Wannierization procedure, we used spinor p_z orbitals centered on the position of the top-most Au atom [142]. The resulting Wannier-interpolated band structure, shown in Figure 4.3a, successfully reproduces the electronic dispersion near the $\bar{\Gamma}$ point where the spin-split surface states can be clearly distinguished from the continuum of the bulk bands.

The qualitative features of the nonlinear response are illustrated in Fig. 4.2, which presents k-resolved maps of the calculated transition probabilities around the $\bar{\Gamma}$ point. The colormaps correspond to the ab initio results for the Au(111) surface, while the overlaid lines represent iso-value contours obtained from the analytical Rashba model. The figure reveals structured, anisotropic patterns for both the shift and injection photoconductivity components, reflecting the underlying $3m$ crystal symmetry. For the injection photocurrents following Eqs. (4.22) and (4.23) [Figs. 4.2a,b], the ab-initio results align remarkably well with the model predictions, accurately reproducing the multi-lobe pattern and the sign distribution. In contrast, the Rashba model provides a less accurate qualitative description of the shift photocurrent expressions of Eqs. (4.21) and (4.19), as shown in Figs. 4.2c,d. This discrepancy can be attributed to the sensitivity of the shift mechanism to the quantum-geometric properties of the Bloch wavefunctions—specifically, the generalized derivative of the Berry connection—which enters the expression for σ^{abc} [50]. Such details are not fully captured by simplified two-band models [112, 143].

A more quantitative test is provided by comparing the frequency-dependent shift current conductivity spectra from ab initio calculations with the predictions of the fitted Rashba model. To obtain quantitative results from the model, its parameters are first fit to reproduce the ab initio energy dispersion of the Au(111) surface states around $\bar{\Gamma}$, as shown in Fig. 4.3b. The resulting parameters are:

$$\alpha = 0.54 \text{ eV}\text{\AA}, \quad \beta = -3.57 \text{ eV}\text{\AA}^3, \quad \gamma = -6.57 \text{ eV}\text{\AA}^3, \quad \frac{\hbar^2}{2m^*} = 16.0 \text{ eV}\text{\AA}^2. \quad (4.24)$$

The shift photoconductivity spectrum is then calculated using the $\mathbf{k} \cdot \mathbf{p}$ functionality of the **WannierBerri** code [93]. Fig. 4.3b displays the resulting

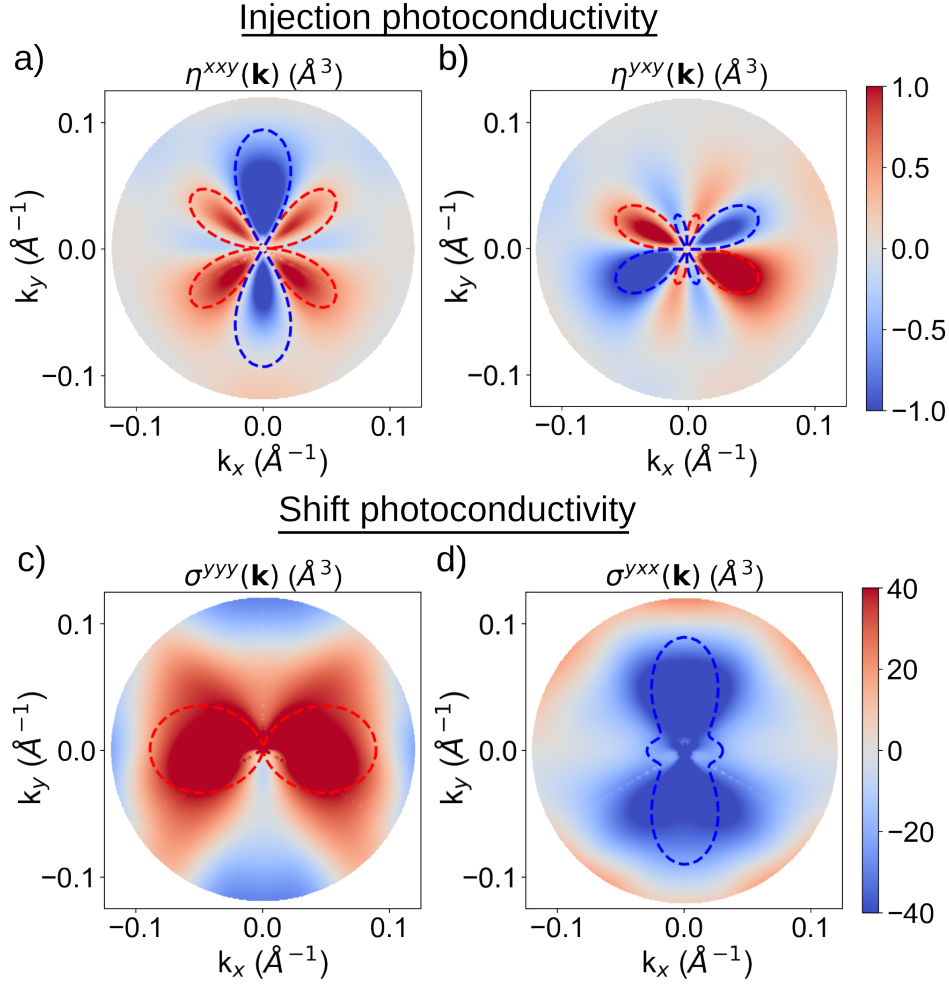


Figure 4.2: Components of $\mathbf{k}$ -resolved transition matrix elements of the injection [(a) and (b)] and shift [(c) and (d)] photoconductivities, showing with a colormap the values calculated by DFT for the Au(111) surface states. The dashed lines represent contour lines of constant values from the analytical calculations based on the Rashba model.

spectra for both the fitted Rashba model and the ab initio Au(111) surface states. The comparison shows reasonable agreement, with both methods yielding results of the same order of magnitude across the studied frequency range.

Overall, despite its limitations in fully capturing the geometric details of the shift current, the Rashba model provides a quantitatively reasonable first-order description of both shift and injection photoconductivities. This supports its utility as an interpretative framework for understanding nonlinear photoresponses in spin-split surface states.

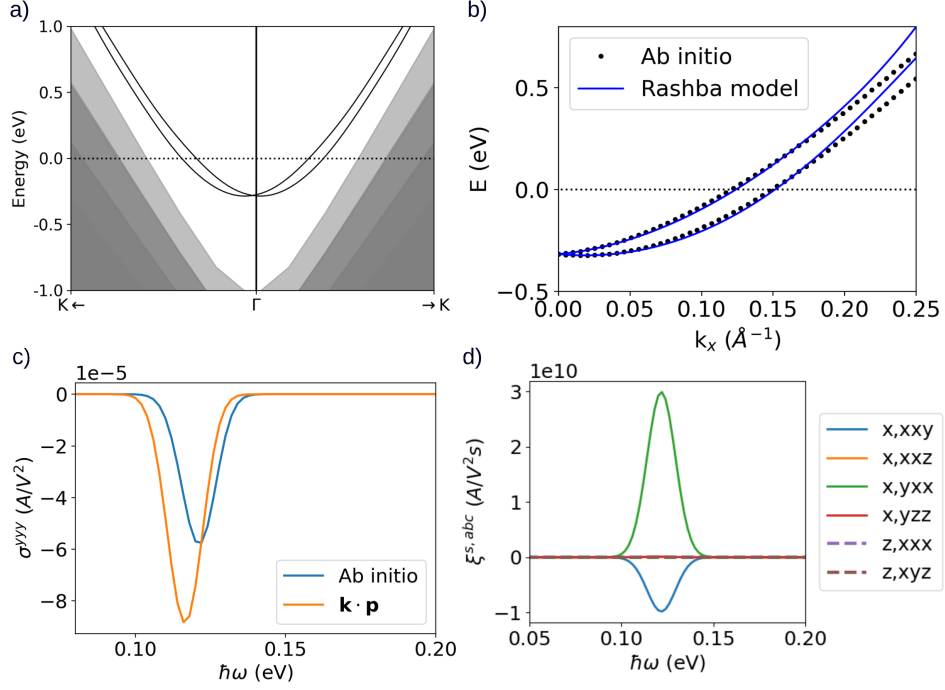


Figure 4.3: (a) Band structure of Au(111) close to Γ . The shaded areas denote the projected bulk bands. (b) Fitted energy dispersion around Γ with parameters $\alpha = 0.54 \text{ eV}\text{\AA}$, $\beta = -3.57 \text{ eV}\text{\AA}^3$, $\gamma = -6.57 \text{ eV}\text{\AA}^3$ and $\hbar^2/2m = 16.0 \text{ eV}\text{\AA}^2$. (c) Calculated shift current spectra of Au(111) by means of ab-initio and $\mathbf{k} \cdot \mathbf{p}$ methods. (d) Spin injection photoconductivity spectra of Au(111).

4.3 Toward a material realization in Tl/Si(111)

Our results for Au(111) highlight the internal structure of the quadratic photoresponse driven by Rashba-like surface states, opening up the possibility of extracting the hexagonal warping constant β through optical measurements of the symmetry-allowed shift conductivity component σ^{yyy} . However, the metallic nature of bulk Au presents a practical challenge for this purpose, as the bulk states might contribute in practice to the low-energy optical response, complicating the isolation of the surface response.

Consequently, we turn to the Tl/Si(111) surface, whose electronic properties are also strongly influenced by spin-orbit interaction and which offers key advantages over Au(111). The band structure, plotted in Fig. 4.4a, reveals several notable features. First, its semiconducting nature ensures that the surface photocurrent is well isolated and clearly distinguishable from any bulk contribution [144, 145]. Second, Tl/Si(111) hosts a pair of unoccupied,

spin-split surface states accessible via inverse photoemission spectroscopy at the $\bar{K}$ and $\bar{K}'$ valleys [146, 147]. Third, these surface states exhibit a large spin-orbit splitting of approximately 0.6 eV, a value well suited for optical applications. Finally, the spin polarization of these states is predominantly out-of-plane at the valleys and mostly in-plane around Γ , contrasting sharply with the standard Rashba model predictions [148, 149].

4.3.1 Methodology

To model the unoccupied surface states of the Tl/Si(111) system, we employed a Wannierization procedure that isolates only those bands, excluding all others. We used a spinor p_z orbital centered on the Tl atom as the initial projection. For the Tl/Si(111) calculations, we proceeded analogously to the Au(111) case. The simulation parameters included a slab thickness of 4 unit cells, a plane-wave energy cutoff of 200 Ry, a k -point grid of $24 \times 24 \times 1$, and initial projections with angular momentum quantum numbers $l = 1, m_r = 1$ targeting the unoccupied states. We plot the resulting bands in Fig. 4.4a, which show a distinct out-of-plane spin polarization at the $\bar{K}$ valleys and an in-plane polarization at $\bar{\Gamma}$.

To estimate the generated photocurrent we employ the methodology described in Sec. 2.2.2.4. In our calculations, we consider a laser spot size of 5 μm , consistent with Ref. [99]. Since n-doped Tl/Si(111) exhibits metallic character, we include the Drude contribution to $\epsilon(\omega)$ following the implementation in Ref. [150]. Figure 4.4d shows the resulting frequency-dependent reflectivity for $\mu = 0.3$ eV. Our calculations indicate that near the surface-state spin-splitting energy of ~ 0.6 eV, approximately 3% of the incident light is absorbed by the surface states (see Fig. 4.4d), in agreement with previous estimates for similar spin-split systems [151].

4.3.2 *Ab-initio* results of nonlinear photocurrents

As Tl/Si(111) belongs to the $3m$ point group, the allowed photoconductivity components are those listed in Table 4.1. We therefore focus on the symmetry-allowed shift component σ^{yyy} associated with optical transitions between the spin-orbit split surface states indicated in Fig. 4.4a, where the lowest band can be populated via electron doping.

The inset in Fig. 4.4b shows that for a moderate doping level of $\mu = 0.3$ eV, the shift photoconductivity peaks around $\omega \simeq 0.6$ eV, reaching a maximum value of $|\sigma^{yyy}| \simeq 2 \mu\text{A}/\text{V}^2$. This surface-state photoconductivity translates into a measurable in-plane photocurrent. The main panel of Fig. 4.4b illustrates how the maximum of the photocurrent-to-power ratio J^y/P behaves as a function of doping. For doping levels ranging from 0 to ~ 0.6 eV, the nonlinear shift photocurrent flowing along the surface plane is substantial, comparable to or even larger than values reported in prototypical

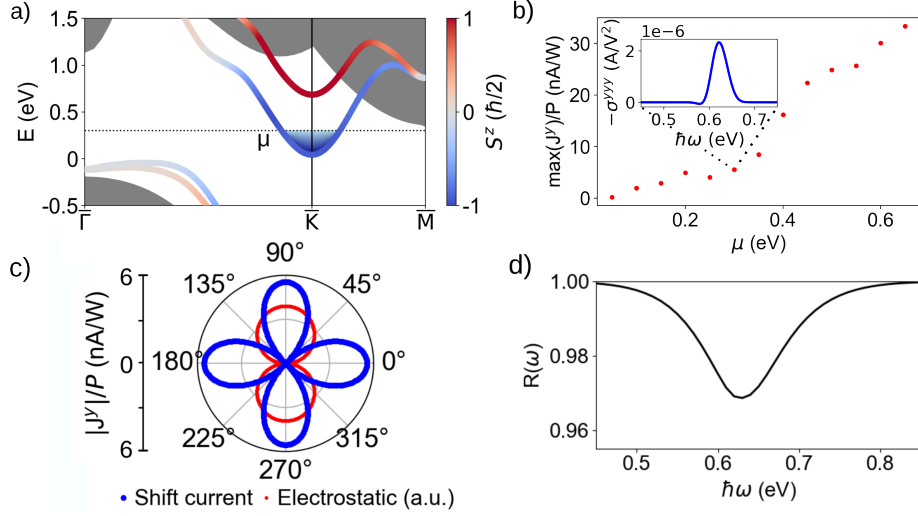


Figure 4.4: (a) Band structure of Tl/Si(111) showing the out-of-plane spin polarization of the surface bands (given by the color code). The dotted line represents the chemical potential, μ , for a n-doped system. (b) Maximum value of the shift current as a function of doping. At each value of μ , the frequency and polarization of the light is chosen to maximize the current. The inset shows the 3D shift photoconductivity spectra for $\mu = 0.3$ eV. (c) In blue, angular distribution of the shift current generated by linearly polarized light with varying polarization angle θ and frequency $\omega = 0.63$ eV for $\mu = 0.3$ eV. In red, the pattern of the possible electrostatic contribution (arbitrary units). (d) Reflectivity of Tl/Si(111) for $\mu = 0.30$ eV.

bulk photovoltaic materials such as BaTiO₃ [72], BiFeO₃ [152], and other semiconductors [1, 58, 153–155]. This prediction is a central result of this chapter, as it incorporates critical factors such as reflection and absorption via the Glass coefficient [73] described previously, which are essential for realistic estimation of nonlinear optical processes [58].

In addition to its magnitude, the angular dependence of the photocurrent provides a clear experimental signature. More specifically, if the electric field polarization is set in the $x - y$ plane as

$$\mathbf{E}(\omega) = E(\omega)(\cos(\theta), \sin(\theta), 0), \quad (4.25)$$

with θ the polarization angle, the resulting current in the y -direction becomes a function of θ :

$$J^y(0) = \sigma^{yxx} \cos(\theta)^2 + \sigma^{yyy} \sin(\theta)^2 + 2\sigma^{xyy} \cos(\theta) \sin(\theta). \quad (4.26)$$

Applying the symmetry restrictions of the $3m$ point group, that is, $\sigma^{yyy} = -\sigma^{yxx}$ and $\sigma^{xyy} = 0$, the current simplifies to

$$J^y(0) = \sigma^{yyy}(\cos(\theta)^2 - \sin(\theta)^2). \quad (4.27)$$

An analogous angular distribution holds when the Glass coefficient is used in place of the photoconductivity.

Figure 4.4c shows the photocurrent as a function of the in-plane polarization angle θ of linearly polarized light. The shift current is maximized along the crystallographic x and y axes, whereas it vanishes at angles $\theta = 45 + n \cdot 90^\circ$ for integer n . This pattern provides a distinct fingerprint for identifying the surface-state nonlinear DC photocurrent. In principle, a separate DC contribution could arise from the conventional photovoltaic effect driven by the surface electrostatic field $E_z(0)$; however, this mechanism exhibits a different angular dependence (see Fig. 4.4c) and is unlikely to generate a significant in-plane current. Nonlinear ballistic currents from electron–phonon scattering could also contribute [127], but in Tl/Si(111) the electron–phonon coupling is particularly weak due to spin-locked intervalley scattering between $\bar{K}$ and $\bar{K}'$ [156]. Consequently, the angular dependence of the DC photocurrent is expected to be dominated by the shift-current pattern shown in Fig. 4.4c.

4.4 Surface spin currents

In the remaining part of this chapter, we extend our study to the spin contribution of the bulk photovoltaic effect. Nonlinear spin photocurrents have received significantly less attention than their charge counterparts, with notable theoretical progress emerging only recently [94, 126, 157]. While most prior studies have focused on bulk spin currents [157–159], the surface states of heavy-element materials provide an ideal setting to explore the interplay between spin-orbit interaction and nonlinear spin responses [126, 128, 129].

In analogy with the charge photocurrent expression in Eq. (4.12), the quadratic spin current density $J^{s,a}$ in a time-reversal invariant material from Eq. (2.81) can be written as

$$J^{s,a}(0) = \tau \cdot \xi^{s,abc} \text{Re}[E^b(\omega)E^c(-\omega)] + \zeta^{s,abc} \text{Im}[E^b(\omega)E^c(-\omega)], \quad (4.28)$$

where s denotes the spin projection, and $\xi^{s,abc}$ and $\zeta^{s,abc}$ are the spin injection and spin shift photoconductivity tensors, respectively. Both of them are described in Chapter I. Table 4.1 lists the symmetry-allowed spin shift and injection tensor components for Au(111) and Tl/Si(111). It is worth noting that, compared to the charge current in Eq. (4.12), the symmetry relations of the shift and injection mechanisms with respect to light polarization are reversed for the spin current. As sketched in Fig. 4.5a, these mechanisms provide a remarkable spin-filtering functionality; they can generate a DC spin current that is spin-polarized along the out-of-plane or in-plane directions depending on the polarization of light. From the standpoint of symmetry alone, both surfaces should exhibit this functionality. In practice, however, our calculations in Fig. 4.3d show that Au(111) generates negligible out-of-plane spin current, which is a direct consequence of the purely in-plane spin

texture of its surface states. Therefore, we focus our subsequent analysis on Tl/Si(111).

4.4.1 Tunable spin currents in Tl/Si(111)

Following the same methodology as for the charge current, we calculate the transition matrix elements of the spin injection photoconductivity. To clearly visualize the correlation between the spin injection response and the underlying spin texture, we construct symmetry-invariant combinations of the $\mathbf{k}$ -resolved spin injection tensor $\xi^{s,abc}(\mathbf{k})$. For a crystal symmetry operation M , the tensor transforms as

$$\xi^{s,abc}(\mathbf{k}) = \sum_{s'a'b'c'} M_{ss'} M_{aa'} M_{bb'} M_{cc'} \xi^{s',a'b'c'}(M^{-1}\mathbf{k}). \quad (4.29)$$

We define a symmetrized quantity from linear combinations of $\xi^{s,abc}(\mathbf{k})$

$$\Xi(\mathbf{k}) = \sum_{s,abc} C^{s,abc} \xi^{s,abc}(\mathbf{k}) \quad (4.30)$$

that satisfies $\Xi(\mathbf{k}) = \Xi(M^{-1}\mathbf{k})$. The reasoning behind this choice is to show how the spin-polarized injection current along the out-of-plane direction (z, abc components) is correlated to the spin texture which is mostly polarized along z around K in a way that it does not depend on the choice of K . By combining Eq. (4.29) and Eq. (4.30), the relations

$$\Xi(\mathbf{k}) = \sum_{s,abc} C^{s,abc} \sum_{s'a'b'c'} M_{ss'} M_{aa'} M_{bb'} M_{cc'} \xi^{s',a'b'c'}(M^{-1}\mathbf{k}) \quad (4.31)$$

$$\Xi(\mathbf{k}) = \Xi(M^{-1}\mathbf{k}) = \sum_{s,abc} C^{s,abc} \xi^{s,abc}(M^{-1}\mathbf{k}) \quad (4.32)$$

form a system of equations which gives as a result the coefficients $C^{s,abc}$, which need not be unique.

For the $3m$ point group relevant to Tl/Si(111), we find the following invariant combinations that isolate out-of-plane and in-plane spin-polarized responses:

$$\Xi^{\text{out}}(\mathbf{k}) \propto -\xi^{z,xxx}(\mathbf{k}) + \xi^{z,xyy}(\mathbf{k}) + 2\xi^{z,yxy}(\mathbf{k}), \quad (4.33)$$

$$\Xi^{\text{in}}(\mathbf{k}) \propto -\xi^{x,yxx}(\mathbf{k}) + \xi^{y,xyy}(\mathbf{k}) - \xi^{x,yyy}(\mathbf{k}) + \xi^{y,xxx}(\mathbf{k}). \quad (4.34)$$

These combinations, plotted in Fig. 4.5b, allow us to map the spin injection activity across the Brillouin zone in a manner that respects crystal symmetry and directly links to the spin texture.

Figure 4.5b reveals that the in-plane and out-of-plane symmetrized responses share a similar order of magnitude but are distributed differently in

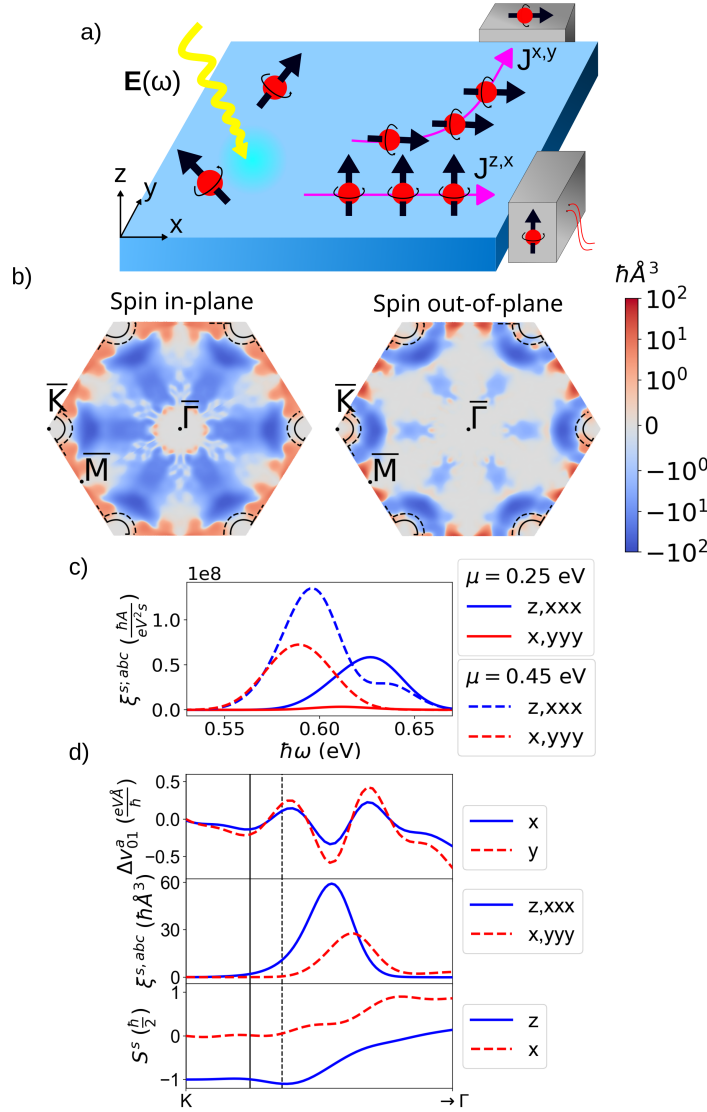


Figure 4.5: (a) Schematic representation of nonlinear spin current generation by surface states. Out-of-plane ($\hat{z}$) or in-plane ($\hat{x}$) spin DC currents can be directed to different field contacts at the surface depending on the polarization of the incident light field. (b) Brillouin zone $\mathbf{k}$ -resolved spin out-of-plane (top) and in-plane (bottom) combinations of the spin injection conductivity tensor components. The continuous and dashed arcs around the valleys denote the projected Fermi surfaces at $\mu = 0.25$ eV and $\mu = 0.45$ eV, respectively. (c) Spectra of $\xi^{z,xxx}$ and $\xi^{x,yyy}$ for $\mu = 0.25$ eV and $\mu = 0.45$ eV. Note that at $\mu = 0.25$ eV only the out-of-plane component contributes significantly. (d) $\mathbf{k}$ -resolved quantities along the $\bar{K} - \bar{\Gamma}$ path, where the vertical solid and dashed lines correspond to the intersection of the path with the Fermi surfaces illustrated in b). Top: variation in the difference of the intraband velocity along $a = x$. Middle: $\xi^{z,xxx}$ and $\xi^{x,yyy}$ components polarized out-of-plane ($\hat{z}$, blue curve) and in-plane ($\hat{x}$, red curve). Bottom: out-of-plane and in-plane spin polarization components.

k-space. The dominant out-of-plane contribution originates from the tensor component $\xi^{z,xxx}$, while the largest in-plane contribution comes from $\xi^{x,yyy}$. Their frequency-dependent spectra are shown in Fig. 4.5c for two representative doping levels, $\mu = 0.25$ eV and $\mu = 0.45$ eV. Notably, at $\mu = 0.25$ eV, the spin injection is dominated by the out-of-plane component, whereas at $\mu = 0.45$ eV the in-plane contribution becomes quantitatively significant. In practice, this means Tl/Si(111) functions as a tunable spin injector or filter: for a doping level near $\mu \sim 0.25$ eV and x -polarized light, it generates a spin-polarized current with a mostly out-of-plane spin component S_z .

To understand the origin of this behavior, Fig. 4.5d plots relevant quantities along the high-symmetry path $\bar{K} - \bar{\Gamma}$. The top panel shows the velocity matrix element differences Δv^x and Δv^y that enter the expressions for $\xi^{z,xxx}$ and $\xi^{x,yyy}$, respectively. Because both surface bands have their minimum at $\bar{K}$ (see Fig. 4.4a), the velocity is small near the valley, leading to a suppression of the spin injection response in its immediate vicinity (middle panel). The key insight comes from comparing the middle and bottom panels: the peak in $\xi^{z,xxx}$ occurs precisely where the out-of-plane spin polarization S_z is large, whereas $\xi^{x,yyy}$ peaks only when S_z becomes small. This demonstrates that the out-of-plane spin polarization—which is absent in conventional Rashba systems like Au(111)—is crucial for generating a nonlinear spin current perpendicular to the surface in Tl/Si(111).

To conclude our analysis, we note that the nonlinear spin accumulation generated by the mechanism described above should be detectable using magneto-optical techniques based on ultrafast laser pulses such as Kerr microscopy [87, 160]. Alternatively, the associated spin transport phenomena could be probed via the inverse spin Hall effect [161, 162]. This is particularly promising, as it would enable an optically controlled, on-demand nonlinear spin filter and injector, without the need for ferroelectric materials [163] or bulk crystals with purely in-plane spin textures [164].

4.5 Conclusion

This chapter has systematically explored the generation of nonlinear charge and spin photocurrents using spin-orbit-split surface states, establishing surfaces as a powerful and generic platform for the BPVE beyond the limitations imposed by bulk crystal symmetry. The work began with an analytical derivation of the quadratic shift and injection photoconductivities within an extended Rashba model that incorporates hexagonal warping—a crucial term for breaking in-plane isotropy and enabling a finite nonlinear response in surfaces with 3m symmetry. These model predictions were quantitatively validated against first-principles density functional theory calculations for the prototypical Rashba system Au(111). While the Rashba model provides a reasonable first-order description for both shift and injection mechanisms,

the comparison highlights the sensitivity of the shift current to quantum-geometric properties of the wavefunction, underscoring the importance of *ab initio* methods for accurate predictions.

Given the experimental challenges posed by metallic substrates like Au(111), the focus shifted to the Tl/Si(111) surface. This system offers distinct advantages: a semiconducting bulk that isolates the surface response, giant spin-orbit splitting (~ 0.6 eV) suitable for optical excitation, and a unique out-of-plane spin polarization at the K valleys. Our calculations demonstrate that the surface-state shift photocurrent in Tl/Si(111) reaches a magnitude comparable to or exceeding that of prominent bulk ferroelectrics like BaTiO₃ and BiFeO₃ when the lowest surface band is populated via moderate electron doping. Furthermore, the photocurrent exhibits a distinct angular signature, vanishing for light polarization at $45^\circ + n \cdot 90^\circ$, which provides a clear experimental fingerprint to distinguish it from other possible DC current contributions.

The study was extended to the nonlinear spin photocurrent, revealing a remarkable spin-filtering functionality inherent to the Tl/Si(111) surface states. We showed that the system can generate pure out-of-plane spin-polarized currents for doping levels near $\mu \sim 0.25$ eV with x-polarized light. This capability stems directly from the strong out-of-plane spin texture near the K valleys, a feature absent in conventional Rashba systems like Au(111). The spin response is highly tunable with doping and light polarization, offering a versatile mechanism for all-optical spin current generation that surpasses the geometric constraints of the linear spin Hall effect.

These results are not limited to the specific materials studied. The underlying principle that any surface provides a noncentrosymmetric environment where spin-split states can drive nonlinear responses is general. It paves the way for discovering similar phenomena in other extensively studied heavy-element surfaces and interfaces. This connection between spin texture and nonlinear behavior enables new approaches for generating spin-polarized currents with spatial and spin selectivity, offering greater flexibility and precision for spintronic device design.

Chapter 5

Spin symmetry predictions of optical properties of magnetic materials

5.1 Introduction

Symmetry principles play a central organizing role across science, providing a unifying framework for understanding structure, dynamics, and classification. For instance, symmetry underlies group theory, which formalizes invariance and serves as a foundational language for modern algebra and geometry. When applied to physics, symmetries dictate fundamental laws through Noether's theorem, linking continuous invariances to conservation laws and shaping theories from classical to quantum mechanics. In the particular case of solid state physics, these diverse symmetry concepts converge in the classification of phases of matter, where symmetry and its breaking determine the possible ordered states and their emergent physical properties, ranging from magnetic ordering to a material's response.

The recent reclassification of magnetic phases highlights the central role of symmetry in condensed matter physics. Magnetic materials have long been classified as either ferromagnets, in which magnetic moments align parallel in real space, or antiferromagnets, characterized by antiparallel alignment. The traditional approach to this categorization is based on the symmetry description of magnetic crystal structures, which considers transformations acting jointly in real space and in the space of magnetic moment vectors, forming magnetic space groups [165]. Because they combine coupled operations in real space with rotations in spin space, these symmetry transformations are intrinsically relativistic, given that the lowest-order term in the Hamiltonian coupling spin with real space is the relativistic spin-orbit interaction.

These ideas have motivated the recent use of *spin-group* symmetries in the

classification of magnetic materials. The notion of altermagnetism, introduced in Refs. [166, 167], provides a symmetry-based framework that captures and categorizes magnetic states through the structure of their spin order. Spin groups extend the concept of conventional magnetic space groups by lifting the constraint that ties spin rotations to real-space symmetry operations. As a result, their symmetry structure is substantially more general: independent rotations may act concurrently in spin space and in real space, with only the latter being subject to crystallographic constraints. Remarkably, this symmetry description offers a natural explanation for the unconventional antiferromagnets that exhibit pronounced, fully compensated spin splittings known from Refs. [166–170].

Beyond altermagnets, another novel class of magnetic materials that has emerged recently is odd-parity magnets or P-wave magnets [171]. These materials are characterized by a particular type of spin ordering that breaks parity ($\mathcal{P}$) while preserving time-reversal symmetry in combination with a fractional translation. Their study similarly benefits from the spin-group perspective, as will be discussed later in Sec. 5.3. A detailed formal introduction of spin groups, altermagnets and odd-parity magnets is deferred to Sections 5.2.1.1, 5.2.2 and 5.3, respectively.

Nonrelativistic spin groups provide a prototypical example of approximate, or so-called hidden, symmetries: their consequences are not strictly exact, since relativistic effects, however weak, are inevitably present in all materials. Their significance stems from their ability to provide meaningful predictions for physical observables that are not dominated by relativistic effects. The central subject of this work is the optical response of magnetic materials, which falls into this category as it is typically governed by strong nonrelativistic electromagnetic crystal fields. Because magnetic space groups constitute only a limited subset of the broader class of spin groups, classifications based solely on magnetic groups can overlook significant predictions of the magnetic optical response.

In this chapter we examine the role of spin symmetries in the optical responses of various magnetic materials. The chapter is organized in two parts. In the first part, we focus on first-order response, addressing both charge and spin currents. We investigate altermagnets, which serve as the perfect example because they are intrinsically related to spin symmetries as they appear in their definition. In the second part, we extend the concept to quadratic optical responses. For that, we consider P-wave magnets, which by definition break $\mathcal{P}$ (parity), making them an ideal platform to study quadratic effects. Within each part, we analyze how spin symmetries constrain the relevant response tensors, drawing on theoretical arguments, model calculations, and *ab initio* material simulations.

5.2 Part I: Linear response in Altermagnets

5.2.1 Magnetic versus spin symmetries

5.2.1.1 Generalities

The symmetry of nonmagnetic crystals is captured by space groups, whose elements are denoted $\{R|\mathbf{t}\}$, where R represents a proper or improper rotation and $\mathbf{t}$ a fractional translation. When magnetic order is present, the symmetry description must be extended to include time reversal $\mathcal{T}$, leading to magnetic space groups (also known as Shubnikov groups). In such groups, symmetry operations may combine spatial transformations with $\mathcal{T}$. Crucially, each operation must preserve both the atomic positions and the orientation of the magnetic moments, which typically results in a reduction of symmetry compared to the nonmagnetic case. The role of spin–orbit coupling (SOC) is central here: it couples orbital and spin degrees of freedom, so any true symmetry operation must act consistently on both spatial coordinates and spin orientations. Consequently, the relevant symmetry group in the presence of SOC is the magnetic space group.

In the nonrelativistic limit where SOC vanishes, the Hamiltonian acquires additional symmetries. Because spin and spatial rotations become independent, the symmetry group expands beyond the magnetic space group. These so-called spin symmetries were first introduced by Brinkman and Elliott [172, 173] and later generalized by Litvin and Opechowski [174]. They have recently attracted renewed attention in condensed matter physics, as they provide a powerful framework for classifying magnetic materials when relativistic effects are weak or when one is interested in phenomena dominated by nonrelativistic physics.

A spin symmetry operation is denoted $g = \{U||\{R|\mathbf{t}\}\}$, where U acts on spin space and $\{R|\mathbf{t}\}$ acts on real space. Its effect on the electronic charge density $\rho(\mathbf{r})$ and the spin magnetization density $\mathbf{S}(\mathbf{r})$ is given by [175]

$$\rho(\mathbf{r}) \xrightarrow{g} \rho(\{R|\mathbf{t}\}^{-1}\mathbf{r}), \quad (5.1)$$

$$\mathbf{S}(\mathbf{r}) \xrightarrow{g} U\mathbf{S}(\{R|\mathbf{t}\}^{-1}\mathbf{r}). \quad (5.2)$$

This decoupling of spin and spatial transformations is the defining feature that distinguishes spin groups from magnetic groups.

5.2.2 Overview of altermagnets

Altermagnets are a recently identified class of collinear compensated magnets that combine the zero net magnetisation of antiferromagnets with the spin-split electronic bands typical of ferromagnets [166, 167, 176]. Unlike conventional antiferromagnets, where bands of opposite spin are degenerate everywhere in the Brillouin zone when SOC is neglected, altermagnets exhibit

a large non-relativistic spin splitting that originates from the crystal and magnetic symmetries alone, without requiring relativistic effects.

The defining symmetry feature of an altermagnet can be understood through spin groups. While the magnetic space group of a collinear antiferromagnet typically contains only operations that either preserve the sublattice identity or combine a spatial transformation with time reversal, an altermagnet possesses an additional spin-group operation that connects the two opposite-spin sublattices via a real-space operation that is not inversion or a pure translation. Formally, there exists a spin-symmetry element $\{C_2 || \{R|\mathbf{t}\}\}$ with C_2 a spin-space rotation that flips the spin quantisation axis and $\{R|\mathbf{t}\}$ a real-space transformation that maps one magnetic sublattice onto the other. This operation leaves the magnetic structure invariant while imposing the characteristic alternating spin polarization in momentum space, that is, the spin polarization is reversed along directions related by the operation R and therefore vanishes when summed over all $\mathbf{k}$ states, preserving the compensated nature of the magnetic order. The momentum dependence of the splitting can take the form of d -wave, g -wave, or higher-order angular harmonics, depending on the underlying lattice symmetry. The resulting spin splitting is protected by the non-relativistic exchange interaction, and its magnitude can be as large as the exchange scale, typically on the order of tenths of an electronvolt, in stark contrast to the meV-scale SOC-induced splittings in non-centrosymmetric antiferromagnets.

Altermagnets are highly relevant for spintronics because they retain the ultrafast dynamics, robustness against external magnetic fields, and absence of stray fields of antiferromagnets, yet they generate spin-polarised currents without the need for a macroscopic magnetisation. This enables a range of phenomena previously thought to be exclusive to ferromagnets, such as the anomalous Hall effect [177], the anomalous Nernst effect, the magneto-optical Kerr effect, and spin Seebeck effects. Consequently, altermagnets offer a new paradigm for designing highly efficient spin-based devices, combining the best of both ferromagnetic and antiferromagnetic worlds. The classification of altermagnets using spin groups has revealed hundreds of candidate materials [178], establishing a vast playground for exploring unconventional transport and optical phenomena rooted in non-relativistic spin splitting.

5.2.3 Transformation properties of response tensors

The difference between magnetic and spin symmetries becomes particularly transparent when examining how they constrain material response tensors. Since translational symmetries do not directly restrict the tensor forms, the relevant symmetries are those of the point group. In the following, we illustrate the distinction using the two central quantities of this part: the linear optical conductivity and the spin conductivity.

Optical conductivity. The linear optical conductivity described in Sec. 2.2.1 is a second-rank tensor, and as such, it can be decomposed into symmetric and antisymmetric parts, $\sigma_S^{ab} = (\sigma^{ab} + \sigma^{ba})/2$ and $\sigma_A^{ab} = (\sigma^{ab} - \sigma^{ba})/2$. Onsager reciprocity imposes well-known constraints: the symmetric part is even under time reversal ($\mathcal{T}$ -even), while the antisymmetric part is $\mathcal{T}$ -odd.¹

Under a magnetic symmetry operation $\{R|\mathbf{t}\}$, which may or may not include time reversal, the conductivity transforms as

$$\sigma_S^{ab} \xrightarrow{\{R|\mathbf{t}\}} R_{aa'} R_{bb'} \sigma_S^{a'b'}, \quad (5.3)$$

$$\sigma_A^{ab} \xrightarrow{\{R|\mathbf{t}\}} \theta R_{aa'} R_{bb'} \sigma_A^{a'b'}, \quad (5.4)$$

where $\theta = +1$ if the operation does not involve time reversal, and $\theta = -1$ if it does.

For a spin symmetry operation $g = \{U || \{R|\mathbf{t}\}\}$, the transformation rules become

$$\sigma_S^{ab} \xrightarrow{g} R_{aa'} R_{bb'} \sigma_S^{a'b'}, \quad (5.5)$$

$$\sigma_A^{ab} \xrightarrow{g} \det(U) R_{aa'} R_{bb'} \sigma_A^{a'b'}. \quad (5.6)$$

At first glance, the two descriptions appear similar, because the optical conductivity does not carry an explicit spin index. However, a crucial difference lies in the spatial rotations R : in the spin-symmetry case, R is decoupled from the magnetic moments and is not required to preserve the spin orientation. Consequently, a spin group can contain spatial rotations that would not be valid symmetry operations in the magnetic group. The result is that purely charge response tensors, such as σ^{ab} , transform under the effective point group formed by the spatial parts of the spin symmetry operations, which is generally larger than the point group of the magnetic space group. This enlargement can impose additional constraints on the tensor components, leading to distinct predictions for the optical response.

The above notion is illustrated in the two-dimensional toy examples in Fig. 5.1, which shows two square lattices with compensated magnetic moments. In Fig. 5.1a, C_4 symmetry is preserved in the magnetic symmetry sense. Consequently, the x and y directions are equivalent, which imposes constraints on physical properties such as $\sigma^{xx} = \sigma^{yy}$. In Fig. 5.1b, C_4 magnetic symmetry is broken by the magnetic moments. Here, no magnetic operation connects the x and y components, so σ^{xx} and σ^{yy} are independent. Conversely, the spin symmetry $\{C_2 || C_4\}$ leaves the system unchanged. Because the optical

¹For a general response tensor $\chi_{ab}(\omega)$ connecting a current j_a to a field F_b , the Onsager relations state $\chi_{ab}(\omega; \mathbf{B}) = \pm \chi_{ba}(\omega; -\mathbf{B})$, where the sign depends on the parity of the quantities under time reversal. For the conductivity, j_a is odd under $\mathcal{T}$ and E_b is even, leading to $\sigma_{ab}(\omega; \mathbf{B}) = \sigma_{ba}(\omega; -\mathbf{B})$. In zero magnetic field, this implies σ_S is $\mathcal{T}$ -even and σ_A is $\mathcal{T}$ -odd.

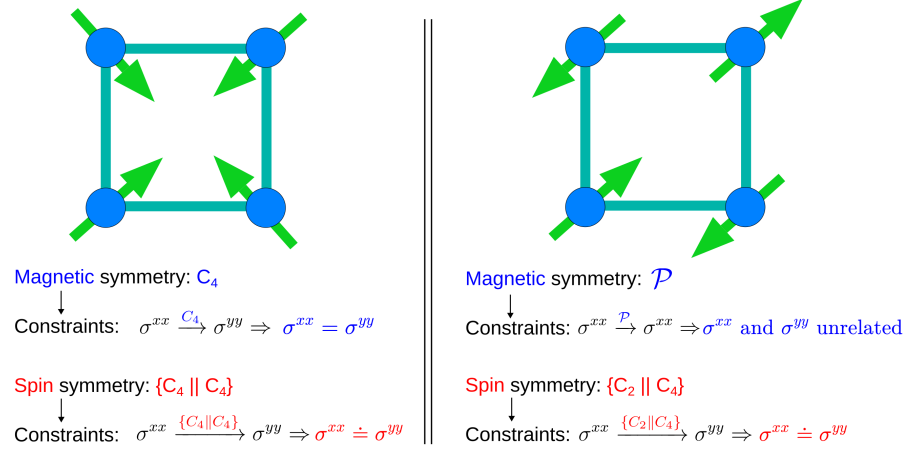


Figure 5.1: Two square lattices with different orientations of the magnetic moments. In both cases, the corresponding magnetic and spin symmetries as well as their constraints on the diagonal optical coefficients are denoted. For the magnetic group, the structure on the left imposes the exact relation $\sigma^{xx} = \sigma^{yy}$, whereas for the structure on the right the two coefficients are unrelated. For the spin group, both structures impose the “non-relativistic” constraint $\sigma^{xx} \doteq \sigma^{yy}$.

conductivity tensor is unaffected by the spin part of the spin symmetry, the real-space operation C_4 enforces $\sigma^{xx} \doteq \sigma^{yy}$, where we use the symbol $\doteq$ to denote equalities predicted by spin symmetries.

Spin conductivity. The spin conductivity $\eta^{s,ab}(\omega)$ described in Sec. 2.2.3.1 differs from the previous case in that it explicitly includes a spin index s , and the tensor transforms as a third-rank object. Onsager relations now dictate that the antisymmetric part in the spatial indices, $\eta_A^{s,ab} = (\eta^{s,ab} - \eta^{s,ba})/2$, is $\mathcal{T}$ -even, while the symmetric part $\eta_S^{s,ab} = (\eta^{s,ab} + \eta^{s,ba})/2$ is $\mathcal{T}$ -odd.

Under a magnetic symmetry operation $\{R|\mathbf{t}\}$, the spin conductivity transforms as

$$\eta_A^{s,ab} \xrightarrow{\{R|\mathbf{t}\}} R_{ss'} R_{aa'} R_{bb'} \eta_A^{s',a'b'}, \quad (5.7)$$

$$\eta_S^{s,ab} \xrightarrow{\{R|\mathbf{t}\}} \theta R_{ss'} R_{aa'} R_{bb'} \eta_S^{s',a'b'}. \quad (5.8)$$

For a spin symmetry operation $g = \{U \parallel \{R|\mathbf{t}\}\}$, the transformation reads

$$\eta_A^{s,ab} \xrightarrow{g} U_{ss'} R_{aa'} R_{bb'} \eta_A^{s',a'b'}, \quad (5.9)$$

$$\eta_S^{s,ab} \xrightarrow{g} \det(U) U_{ss'} R_{aa'} R_{bb'} \eta_S^{s',a'b'}. \quad (5.10)$$

Here the explicit appearance of the spin rotation U , which acts directly on the spin index s , reveals a fundamental distinction between magnetic and

spin symmetries. In collinear magnetic materials, U is often determined by the symmetry of the spin distribution [175], and the constraints imposed by spin groups can be significantly more restrictive than those of magnetic groups.

5.2.4 Lieb lattice model

We begin our analysis by considering a two-dimensional Lieb lattice model, which offers a transparent framework for describing altermagnetic spin-split states. Our main goal is to identify how the optical response evolves under controlled variations of spin-orbit coupling (SOC) within the model. We restrict ourselves to the optical conductivity; the spin Hall conductivity is strongly suppressed by the collinear nature of the altermagnetic order and is not pursued here.

5.2.4.1 Setup and ground state properties

We adopt the altermagnetic Lieb lattice tight-binding model introduced in Refs. [179, 180] with some extensions. The lattice structure is shown in Fig. 5.2. It consists of a square lattice with atomic sites at $(0,0)$, $(0.5,0)$, and $(0,0.5)$. The central site at $(0,0)$ is nonmagnetic, while the sites at $(0.5,0)$ and $(0,0.5)$ carry compensated magnetic moments. In contrast to Refs. [179, 180], we include three p orbitals (p_x , p_y , p_z) on every atomic site. This choice allows us to explicitly incorporate the intra-atomic contribution to SOC among the p states.

The Hamiltonian reads

$$\begin{aligned}
 H = & \sum_{\langle i,j \rangle, \alpha} t_{1ij} \left(\hat{c}_{i\alpha}^\dagger \hat{c}_{j\alpha} + \text{H.c.} \right) + \sum_{\langle\langle i,j \rangle\rangle, \alpha} t_{2ij} \left(\hat{c}_{i\alpha}^\dagger \hat{c}_{j\alpha} + \text{H.c.} \right) \\
 & + J \sum_{i, \alpha, \beta} \mathbf{m}_i \cdot \hat{c}_{i\alpha}^\dagger \mathbf{S}_{\alpha\beta} \hat{c}_{i\beta} + \sum_{i, j, \alpha, \beta} \left(\lambda_{i\alpha; j\beta} \hat{c}_{i\alpha}^\dagger \hat{c}_{j\beta} + \text{H.c.} \right), \quad (5.11)
 \end{aligned}$$

where i and j label orbitals situated exclusively on the magnetic atoms, and α , β denote spin indices. The first two sums describe nearest-neighbor (t_{1ij}) and next-nearest-neighbor (t_{2ij}) hopping. Because we work with three p orbitals per site, we introduce the minimal distance d_{ij} between any two orbitals and weight the hopping strengths as $t_{ij} = t_1/d_{ij}$; orbitals that are closer thus acquire larger hopping amplitudes. For next-nearest-neighbor hopping we distinguish two cases: $t_{2ij} = t_{2a}/d_{ij}$ when the hopping path crosses the nonmagnetic site, and $t_{2ij} = t_{2b}/d_{ij}$ otherwise. The third term encodes the non-relativistic exchange interaction typical of altermagnets [181], coupling the local magnetic moment $\mathbf{m}_i$ to the electron spin with $\mathbf{S}$ the vector of Pauli matrices.

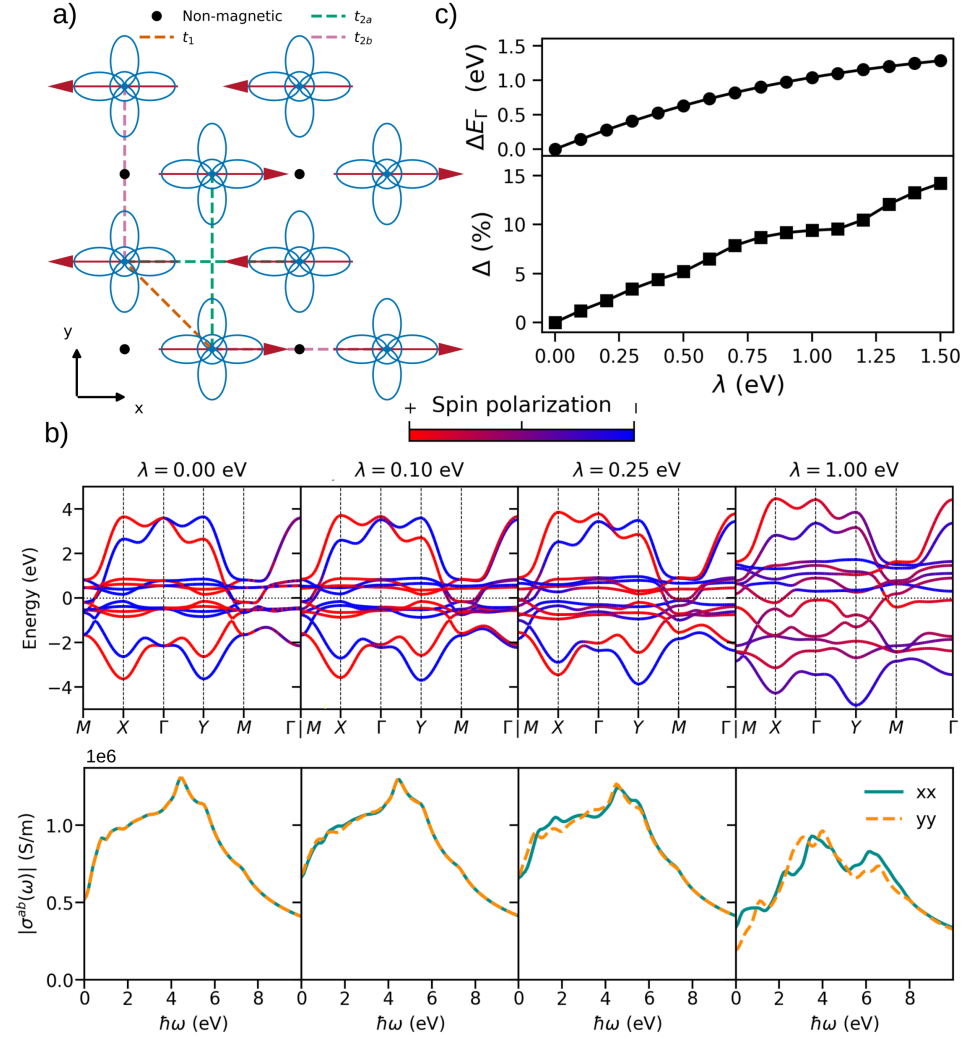


Figure 5.2: a) Lieb lattice with magnetic moments and tunnelings highlighted. b) Band structure and optical conductivity for different values of the spin-orbit coupling λ . c) Evolution of the spin splitting ΔE_T and the linear dichroism metric Δ for increasing values of λ .

The last term in Eq. (5.11) represents the intra-atomic SOC, whose matrix elements among p orbitals are given by

$$\lambda_{i\alpha j\beta} = \langle i\alpha | \mathbf{L} \cdot \mathbf{S} | j\beta \rangle. \quad (5.12)$$

The non-zero elements are [182]:

$$\begin{aligned}
\lambda_{i\alpha j\beta} &= -i\lambda \quad (i\alpha = p_x^\uparrow, j\beta = p_y^\uparrow), \\
\lambda_{i\alpha j\beta} &= i\lambda \quad (i\alpha = p_x^\downarrow, j\beta = p_y^\downarrow), \\
\lambda_{i\alpha j\beta} &= \lambda \quad (i\alpha = p_x^\uparrow, j\beta = p_z^\downarrow), \\
\lambda_{i\alpha j\beta} &= i\lambda \quad (i\alpha = p_y^\uparrow, j\beta = p_z^\downarrow).
\end{aligned} \tag{5.13}$$

The numerical parameters used in the calculations are: $a = 5 \text{ \AA}$, $J = t_1$, $t_{2a} = 2.5t_1$, $t_{2b} = -1.5t_1$, with $t_1 = 0.5 \text{ eV}$. A finite size of $0.3a$ is assigned to the p orbitals, which determines the minimal distances d_{ij} .

The band structures for SOC parameters $\lambda = 0, 0.1, 0.25$, and 1 eV are shown in Fig. 5.2b. At $\lambda = 0$ the non-relativistic spin splitting is typically of order 1 eV , while the bands remain spin degenerate along the Γ -M line, consistent with Refs. [179, 180]. When λ becomes finite, a relativistic spin splitting appears along Γ -M. For $\lambda = 0.25 \text{ eV}$ the splitting at Γ is roughly 0.3 eV , whereas for $\lambda = 1 \text{ eV}$ it reaches about 1 eV , comparable to the non-relativistic scale. Therefore, $\lambda < 0.25 \text{ eV}$ corresponds to a weak relativistic regime, while $\lambda = 1 \text{ eV}$ marks the onset of a strong relativistic regime.

5.2.4.2 Optical conductivity

We now examine the optical response of the model. We first derive the constraints imposed by both magnetic and spin symmetries on the tensor components of Eq. (2.53), and then present numerical results.

Symmetry predictions The two-dimensional magnetic point group of the model in Fig. 5.2 is $mm.1'$, containing the identity $\mathcal{I}$, the two-fold rotation C_{2z} , the mirrors M_x and M_y , and their combinations with time reversal $\mathcal{T}$. Spin-symmetry analysis reveals additional operations, namely $\{\mathcal{I}|\mathcal{I}\}$, $\{\mathcal{I}|C_{2z}\}$, $\{\mathcal{I}|M_y\}$, $\{\mathcal{I}|M_x\}$, and $\{C_{2z}|C_{4z}\}$. The spatial parts of these spin symmetries alone generate the point group $4mm$.

We now derive the constraints on the symmetric part of the optical conductivity tensor, $\sigma_S^{ab}(\omega)$. Magnetic symmetries do not relate the x and y axes, as is evident from the magnetic moment pattern in Fig. 5.2, which makes the two directions inequivalent. Hence the components σ^{xx} and σ^{yy} are independent. Spin symmetries, on the other hand, relate them. From Eq. (5.6):

$$\sigma^{xx} \xrightarrow{\{C_2|C_{4z}\}} \sigma^{yy}. \tag{5.14}$$

By Neumann's principle, which demands that response tensors be invariant under all symmetries of the crystal, we obtain

$$\sigma^{xx} \doteq \sigma^{yy}. \tag{5.15}$$

Numerical results The Lieb lattice tight-binding model was built using the `PythTB` package [183]. The calculation of the response properties was subsequently carried out with the `WannierBerri` code [93], employing a grid of 100×100 and a fixed smearing parameter of 0.2 eV. The matrix elements of the position operator, $\hat{\mathbf{r}}$, were evaluated within the tight-binding approximation, in which the position operator is assumed to be diagonal in the Wannier basis and nonzero only for Wannier functions located at the same lattice site, *i.e.* $\langle n\mathbf{0} | \hat{\mathbf{r}} | m\mathbf{R} \rangle = \tau_n \delta_{\mathbf{0R}} \delta_{nm}$. This approximation is consistent with the localized nature of the Wannier functions and is commonly employed in tight-binding implementations of linear and nonlinear response theories.

Figure 5.2b shows the band structures and the corresponding optical conductivity components $\sigma^{xx}(\omega)$ and $\sigma^{yy}(\omega)$ (lower panels) for $\lambda = 0, 0.1, 0.25$, and 1 eV. Before analysing the optical response, we emphasise a key consequence of the spin symmetry $\{C_2 \| C_{4z}\}$: it enforces an altermagnetic compensation of the spin polarization along the k_x and k_y directions. The symmetry operation connects opposite-spin sublattices, so that the net spin polarization cancels when averaged over the two in-plane directions, despite the presence of local spin splittings. Turning to the optical conductivity, we observe that for $\lambda = 0$ (Fig. 5.2b.i) the spin-symmetry prediction of Eq. (5.15) is exactly satisfied, while for finite λ deviations appear across the spectrum. For $\lambda = 0.25$ eV only small differences are visible, whereas for $\lambda = 1$ eV the differences become pronounced, especially at low frequencies and in the peak structure near $\omega \sim 4$ eV. Nevertheless, the overall trends of $\sigma^{xx}(\omega)$ and $\sigma^{yy}(\omega)$ remain remarkably similar even in the strong SOC limit of $\lambda = 1$ eV, although no magnetic symmetry relates the two quantities.

To quantify this behaviour, we introduce the metric Δ , defined as the normalised L_2 (Euclidean) norm of the difference between $\sigma^{xx}(\omega)$ and $\sigma^{yy}(\omega)$:

$$\Delta = \frac{\sqrt{\int d\omega [\sigma^{xx}(\omega) - \sigma^{yy}(\omega)]^2}}{\sqrt{\int d\omega [\sigma^{xx}(\omega) + \sigma^{yy}(\omega)]^2}}. \quad (5.16)$$

This quantity measures the overall anisotropy of the diagonal optical conductivity and is directly related to linear dichroism, $\sigma^{xx}(\omega) - \sigma^{yy}(\omega)$. Specifically, $\Delta \simeq 0$ indicates the isotropic behaviour predicted by spin symmetries (negligible linear dichroism), while $\Delta \simeq 1$ corresponds to a maximal possible difference, *i.e.* a high degree of linear dichroism and complete departure from the spin-symmetry predictions.

The metric is plotted in the bottom panel of Fig. 5.2c as a function of SOC strength λ . We also display a proxy quantity $\Delta E_\Gamma(\lambda)$, defined as the energy difference between the two highest bands at Γ , which roughly captures the effect of SOC on the eigenvalues. The evolution of Δ shows that in the weak SOC regime ($\lambda < 0.25$ eV) the anisotropy remains below approximately

Table 5.1: Symmetry constraints on the optical (and spin) conductivity for the materials studied in this work. The magnetic point group and its effect on the relevant tensor components are compared with the constraints imposed by spin symmetries.

	Magnetic symmetries		Spin symmetries	
	Point group	Effect on σ^{ab} or η_s^{ab}	Relevant symmetry op.	Effect on σ^{ab} or η_s^{ab}
Lieb lattice	$mm.1'$	σ^{xx} and σ^{yy} unrelated	$\{C_{2z} C_{4z}\}$	$\sigma^{xx} = \sigma^{yy}$
RbMnF ₄	-1.1	Unrestricted	$\{C_2 M_y\}$	$\sigma^{xy} = \sigma^{yz} = 0$
UCr ₂ Si ₂ C	$m'm'm$	σ^{xx} and σ^{yy} allowed	$\{C_{2z} C_{4z}\}$	$\sigma^{xx} = \sigma^{yy}$
ScMnO ₃	$6m'm'$	$\eta^{x,y,z}$ allowed	$\{M_z Z\}$	$\eta^{x,y,z} = 0$

5%. Even for strong SOC, approaching $\lambda = 1$ eV, the anisotropy stays below 15%. These model results therefore demonstrate that, although the band structure is substantially modified (Fig. 5.2), the two optical conductivity components related solely by spin symmetries remain remarkably similar deep into the strong SOC regime. This highlights the intrinsic non-relativistic nature of the optical response, which is well captured by spin symmetries even when SOC is large.

5.2.5 Ab-initio results

Having established the behaviour of a simple tight-binding model with intra-atomic SOC in the previous section, we now turn to more realistic DFT calculations for several magnetic materials. In all cases SOC is explicitly included, allowing us to assess the predictive power of spin symmetries beyond model Hamiltonians.

5.2.5.1 Lieb lattice realization in UCr₂Si₂C; large SOC limit

Structure and symmetry properties The first material we consider is UCr₂Si₂C, which has attracted significant interest within the actinide community following experimental reports of long-range antiferromagnetic order. Very recently, this compound has been identified as a *d*-wave altermagnet in a high-throughput materials study [184]. In fact, its crystal structure realizes the Lieb lattice model discussed in Sec. 5.2.4.1, making it an ideal material platform to test the large-SOC regime analyzed there owing to the heavy uranium atoms.

UCr₂Si₂C crystallizes in the tetragonal structure shown in Fig. 5.3a. Its parent nonmagnetic point group is $4/mmm$, but it hosts an unusual magnetic ground state: the Cr sublattice orders antiferromagnetically at high temperature ($T_N > 300$ K), whereas the uranium moments remain magnetically disordered down to at least 2 K. The magnetic ordering lowers the magnetic point group symmetry to $m'm'm$. However, when spin

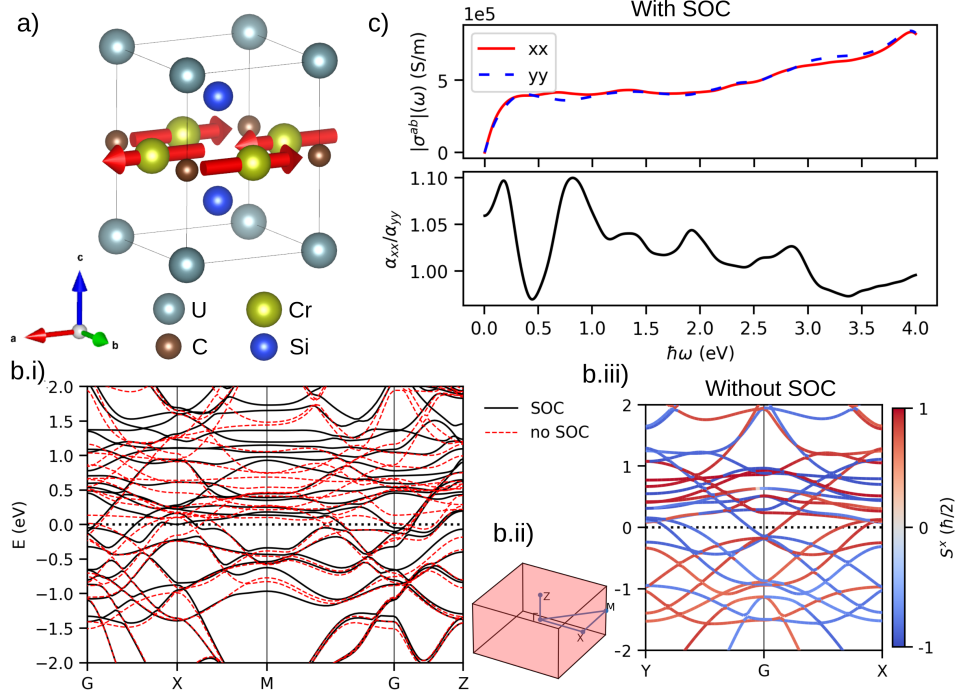


Figure 5.3: (a) Crystal structure of $\text{UCr}_2\text{Si}_2\text{C}$ with the magnetic moments indicated by arrows. (b) Electronic band structure: (b.i) band structure along a high-symmetry path; (b.ii) Brillouin zone showing the k-path; (b.iii) Altermagnetic spin-split bands along $Y-\Gamma-X$. The color scale encodes the spin polarization S^x . (c) Top panel: Absolute value of the diagonal components of optical conductivity $\sigma^{xx}(\omega)$ and $\sigma^{yy}(\omega)$. Bottom panel: dichroic ratio $\alpha_{xx}(\omega)/\alpha_{yy}(\omega)$, where $\alpha_{aa}(\omega)$ is the absorption coefficient.

symmetries are taken into account, additional symmetry operations appear, most notably $\{C_2||C_{4z}\}$. Consequently, the effective real-space point group restored by these spin symmetries is again $4/mmm$, corresponding to the full nonmagnetic point group.

Computational details The DFT calculations were performed using the VASP code [185–187], with the projector augmented wave (PAW) method [188] and the PBE exchange-correlation functional [36]. The plane-wave cutoff energy was set to 600 eV, and a $12 \times 12 \times 12$ Monkhorst-Pack k-point mesh was used for Brillouin zone sampling. SOC was included self-consistently in all calculations except when explicitly stated otherwise. An on-site Hubbard U correction of 3.5 eV was applied to the Cr d states to account for strong electron correlations following Dudarev’s approach [184, 189]. The magnetic configuration was initialized with the experimental values reported in Ref. [190,

191] of $\sim 0.66 \mu_B$ for the Cr atoms, but our calculations yielded around $2.5 \mu_B$; although this value is much larger, it does not change the symmetries, which is what matters for our case.

Electronic structure and linear dichroism Figure 5.3b.i shows the metallic band structure of $\text{UCr}_2\text{Si}_2\text{C}$. A comparison between calculations performed with and without SOC reveals its pronounced influence across several regions of the Brillouin zone (Fig. 5.3b.ii). In particular, near the Γ and M points it induces band splittings of nearly 0.5 eV. In addition, clear signatures of d-wave altermagnetism are visible in Fig. 5.3b.iii for band calculations without SOC, where we have superimposed the spin-polarization

$$\mathbf{S}_n(\mathbf{k}) = \int \Psi_{\mathbf{k}n}^*(\mathbf{r}) \hat{\boldsymbol{\sigma}} \Psi_{\mathbf{k}n}(\mathbf{r}) d^3r, \quad (5.17)$$

with $\hat{\boldsymbol{\sigma}}$ the Pauli spin operator and $\Psi_{\mathbf{k}n}(\mathbf{r})$ the Kohn–Sham spinor state associated with band n . The spin symmetry operation $\{C_2 \| C_{4z}\}$ relates opposite-spin sublattices, giving rise to the compensated altermagnetic spin polarization along the Y– Γ –X path. We now turn to the optical absorption properties of $\text{UCr}_2\text{Si}_2\text{C}$. In close analogy with the model discussed in Sec. 3.2.1, the spin symmetry $\{C_2 \| C_{4z}\}$ enforces the relation $\sigma^{xx}(\omega) \doteq \sigma^{yy}(\omega)$ between the diagonal components of the optical conductivity tensor, even though these components are not connected by the magnetic symmetries alone (see Table 5.1). As shown in the top subplot of Fig. 5.3c, the calculated $\sigma^{xx}(\omega)$ and $\sigma^{yy}(\omega)$ in the presence of SOC are nearly identical across the entire frequency range; the two components therefore exhibit negligible anisotropy.

The small remaining anisotropy can be quantified by the ratio of absorption coefficients, often referred to as the dichroic ratio [192] $\alpha_{xx}(\omega)/\alpha_{yy}(\omega)$, where $\alpha_{aa}(\omega)$ is the absorption coefficient, related to the dielectric tensor via $\alpha_{aa}(\omega) = \frac{\omega}{c} \text{Im} \sqrt{\varepsilon_{aa}(\omega)}$. In contrast with the metric employed for the model calculations in Eq. (5.16), the dichroic ratio is a spectral magnitude. Using the dielectric tensor $\varepsilon_{ab}(\omega) = i\sigma_{ab}(\omega)/\omega\varepsilon_0 + \delta_{ab}$, we evaluate the dichroic ratio and display it in the bottom subplot of Fig. 5.3c. Despite the strong spin–orbit coupling associated with the uranium atoms, $\alpha_{xx}(\omega)/\alpha_{yy}(\omega)$ reaches a peak of approximately 1.1 at low energy and remains below 1.05 for energies above 1 eV, confirming that the two diagonal components are nearly equal across most of the spectrum. Our results thus demonstrate that, even in systems containing heavy elements with strong SOC, spin symmetries can still impose meaningful constraints on response tensors, provided the response is not dominated by strongly spin-dependent effects such as the diagonal components considered here.

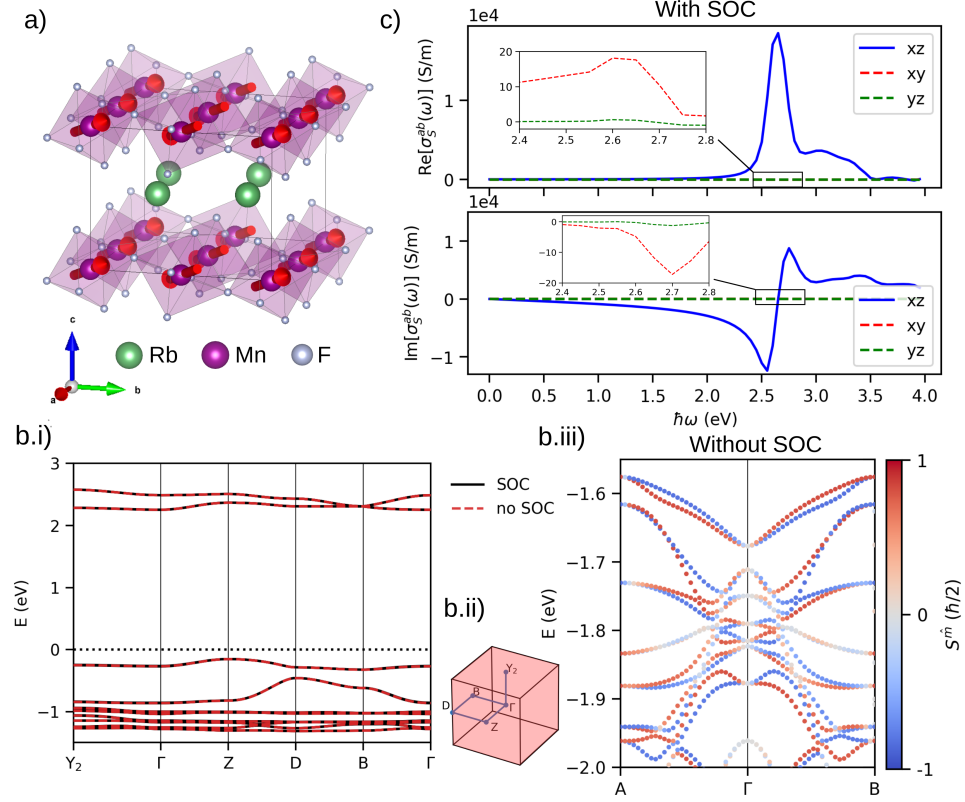


Figure 5.4: (a) Crystal structure of RbMnF₄ with the magnetic moments indicated by arrows. (b) Electronic band structure: (b.i) band structure along the full high-symmetry path; (b.ii) Brillouin zone showing the k-path; (b.iii) zoom into the alternating spin-split bands along A-Γ-B. The color scale encodes the spin polarization along the magnetization direction $S^{\hat{m}}$. (c) Optical conductivity: top – real part $\sigma_1(\omega)$ (main panel: off-diagonal components; inset: magnified σ_{xy} and σ_{yz} in the 2.4–2.8 eV range); bottom – imaginary part $\sigma_2(\omega)$ with the same layout.

5.2.5.2 Birefringence in altermagnetic RbMnF₄

Structure and symmetry properties RbMnF₄ is an altermagnet, with the unit cell displayed in Fig. 5.4a. The heaviest constituent element is Rb (atomic number $Z = 37$), implying that spin-orbit coupling is non-negligible, though not dominant. The nonmagnetic point group of RbMnF₄ is $2/m$ (arising from the space group $P2_1/a$). Because the magnetic moments align along a direction that is not parallel to any lattice vector, the magnetic point group is greatly reduced to -1 , containing only the identity and spatial inversion.

When spin symmetries are taken into account, additional operations

emerge. The spin point group consists of the operations $\{\mathcal{I}|\mathcal{I}\}$, $\{\mathcal{I}|\mathcal{P}\}$, and crucially $\{C_2|\mathcal{M}_y\}$. The latter is the spin operation that links opposite-spin sublattices, providing the fingerprint of altermagnetism. As a result, the effective real-space point group recovered from these spin symmetries is again $2/m$, which additionally comprises M_y beyond the purely magnetic symmetries.

Computational details The electronic structure of RbMnF_4 was obtained following the same methodology as $\text{UCr}_2\text{Si}_2\text{C}$. We also used a plane-wave energy cutoff of 500 eV, a $\mathbf{k}$ -point grid of $8 \times 8 \times 8$. A value of $U = 3$ eV was applied to the Mn d states [189]. A Wannier Hamiltonian was subsequently constructed using Wannier90 [41, 117] by projecting onto Mn d and F p orbitals to create a model comprising 136 Wannier functions. The inner and outer energy windows were both set to $(-8.35, 3.65)$ eV to isolate the relevant group of bands. To preserve the symmetries of the underlying DFT calculations, the localization procedure was performed with zero minimization iterations. Despite the absence of maximal localization, the resulting Wannier functions remain well localized, with a maximum individual spread of 0.75 Å and a total spread of 87.3 Å across all 136 functions.

Electronic structure and birefringence Figure 5.4b shows the calculated band structure of RbMnF_4 , which is a semiconductor with a gap of roughly 2.3 eV. The figure also displays the $\mathbf{k}$ -space spin polarization. Because the magnetic moments are collinear, any spin rotation about the $\hat{m}$ axis is a spin symmetry of the system (with $\hat{m} = (\pm 1.97, \pm 1.97, \pm 1.03)$ [190, 191] denoting the magnetization direction). Consequently, the spin operation $\{C_{2\hat{m}}|\mathcal{I}\}$ relates the spin-up and spin-down projections along the directions normal to the magnetization direction at the same $\mathbf{k}$ point. This symmetry forbids spin polarization along these directions, so we only plot $S^{\hat{m}}$ in Fig. 5.4b. Small residual components remain due to the presence of SOC in the calculations.

Importantly, the zoomed region along A– Γ –B in Fig. 5.4b.iii, with A = (0, 0.5, 0.5) and B = (0, -0.5, 0.5), reveals altermagnetic compensation: the spin operation $\{C_{2\hat{m}}|\mathcal{M}_y\}$ maps points (0, $\mathbf{k}$, $\mathbf{k}$) onto (0, $-\mathbf{k}$, $\mathbf{k}$), thereby reversing the spin polarization. The same behavior occurs along the path C– Γ –D shown in the full band structure of panel (b.i), where C = (0.5, -0.5, 0) and D = (0.5, 0.5, 0). These momentum-space patterns are the hallmark of d-wave altermagnetism.

Coming next to the dielectric tensor, magnetic symmetries impose no constraint on $\sigma^{ab}(\omega)$, which means that all components are allowed and independent. When one considers spin symmetries, on the other hand, the mirror operation M_y of the effective real-space point group requires that any off-diagonal tensor component with one y index must vanish:

$$\sigma^{xy} \doteq \sigma^{yz} \doteq 0. \quad (5.18)$$

The calculated optical conductivity is displayed in Fig. 5.4c. The top panel shows the real part and the bottom panel the imaginary part of the optical conductivity $\sigma^{ab}(\omega)$. In the energy range 2.4–2.8 eV, σ_{xz} reaches values on the order of 10^4 S/cm, whereas σ_{xy} and σ_{yz} remain at the 10^1 S/cm scale. This strong suppression of the off-diagonal components with a y index is fully consistent with the spin-symmetry constraints [Eq. (5.18)]. The residual xy and yz signals originate from the weak spin-orbit coupling.

The presence of off-diagonal responses implies that the principal axes of the dielectric tensor are rotated away from the crystallographic axes, giving rise to birefringence. For each plane (ab), the extinction angle ϕ^{ab} , which measures the orientation of the principal dielectric axes relative to the crystallographic axis normal to the ab plane, can be defined separately for the real and imaginary parts of the dielectric tensor [193]:

$$\tan(2\phi_{\text{Re}}^{ab}) = \frac{2\text{Re}(\varepsilon_{ab})}{\text{Re}(\varepsilon_{aa}) - \text{Re}(\varepsilon_{bb})}, \quad (5.19)$$

$$\tan(2\phi_{\text{Im}}^{ab}) = \frac{2\text{Im}(\varepsilon_{ab})}{\text{Im}(\varepsilon_{aa}) - \text{Im}(\varepsilon_{bb})}. \quad (5.20)$$

The magnetic point group -1.1 leaves all components of $\varepsilon_{ab}(\omega) = \delta_{ab} + i\sigma_{ab}(\omega)/(\varepsilon_0\omega)$ independent, so birefringence and finite extinction angles would in principle be allowed in every plane. The monoclinic effective point group from spin-symmetry considerations restricts a non-zero extinction angle to the xz plane. Using the dielectric function obtained from the calculated conductivity, we find that in the 2.4–2.8 eV range the real-part angle ϕ_{Re}^{xz} exceeds 10° , while ϕ_{Re}^{xy} and ϕ_{Re}^{yz} stay around 0.5° . For the imaginary part, ϕ_{Im}^{xz} reaches about 6° , with the other two angles near 0.3° . This confirms that the birefringence is overwhelmingly dominated by the xz plane, as required by the spin-symmetry-enforced effective monoclinic point group.

5.2.5.3 ScMnO₃: spin photoconductivity

Structure and symmetry properties We use the final example to examine the spin contribution to the optical response, with particular emphasis on the spin Hall conductivity and the manner in which spin-group symmetries constrain this response channel in practical calculations. Given their strong constraint on the spin Hall effect in collinear systems, we turn to a material belonging to the extended altermagnetic class introduced in Refs. [194, 195], which generalizes the class to include non-collinear systems. As an illustrative example, we consider ScMnO₃, a coplanar magnet whose crystal structure is shown in Fig. 5.5a.

The magnetic point group is $6m'm'$, generated by the identity $\mathcal{I}$, a three-fold rotation C_{3z} , a two-fold rotation C_{2z} , and the combined operation $M_x\mathcal{T}$. The spin point group is minimal in this case: it consists of the magnetic symmetries (now applied simultaneously to both real and spin

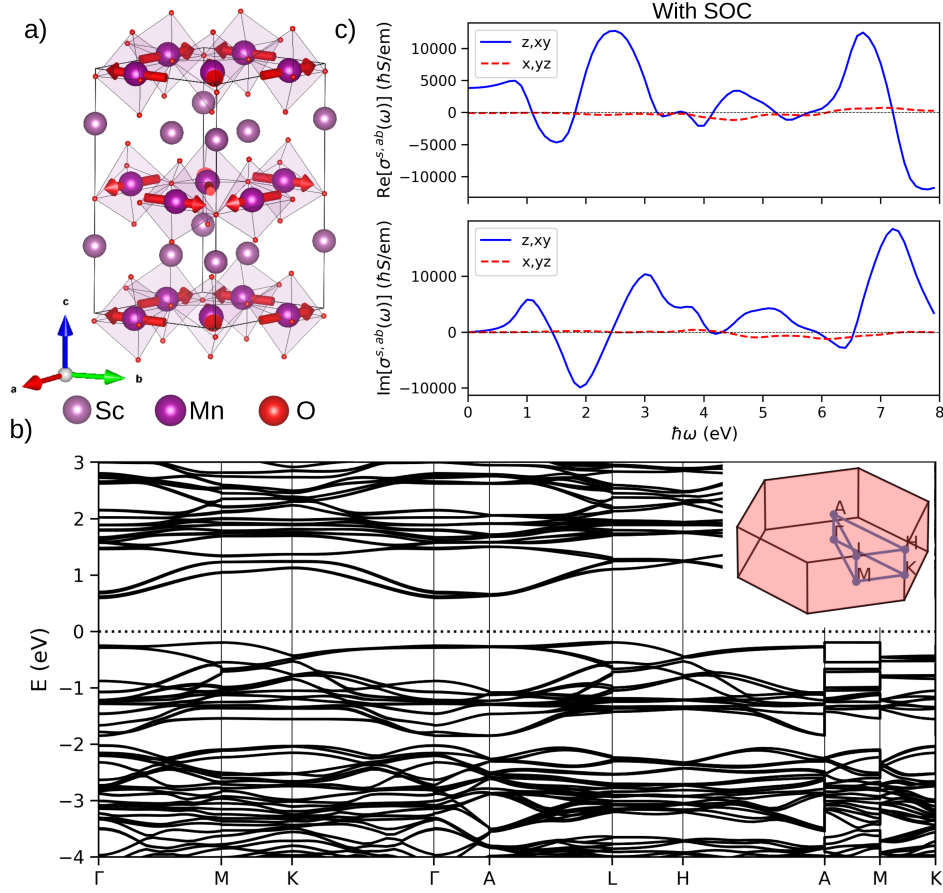


Figure 5.5: (a) Crystal structure of ScMnO₃ with the magnetic moments indicated by arrows. (b) Electronic band structure along a high-symmetry path, displayed in the Brillouin zone shown in the inset. (c) Spin Hall conductivity $\eta_A^{s,ab}(\omega)$: top – real part; bottom – imaginary part. The dominant component is $\eta_A^{z,xy}(\omega)$, as required by the spin symmetries.

space) supplemented by a single spin-only operation. The latter, $\{M_z \parallel \mathcal{I}\}$, arises from the coplanarity of the magnetic structure and reflects the spin degrees of freedom while leaving the real-space lattice invariant.

Computational details For ScMnO₃, fully relativistic DFT calculations were also carried out as in the previous cases, with a plane-wave cutoff energy of 500 eV and an $8 \times 8 \times 8$ $\mathbf{k}$ -point grid. The Wannier representation was generated using Wannier90 [41, 117] using projections from Mn d and Sc p and s orbitals, resulting in a total of 204 Wannier functions. The energy windows were chosen such that all bands were included at the lower-energy end, while the upper bounds of the inner and outer windows were set to 7 eV

and 8 eV, respectively. As in the case of RbMnF_4 , the number of localization iterations was set to zero to retain the crystal symmetries inherited from the DFT calculations. The Wannier functions exhibit good localization properties, with a maximum spread of 1.3 Å and a cumulative spread of 228.6 Å for the full set of 204 functions.

Electronic structure and spin Hall conductivity As a concrete observable sensitive to these spin symmetries, we consider the antisymmetric part of the spin Hall conductivity, $\eta_A^{s,ab}$, which describes the intrinsic spin Hall effect. The magnetic symmetries of $6m'm'$ restrict $\eta_A^{s,ab}$ so that the only non-zero components are $\eta^{x,yz} = \eta^{y,xz}$ and $\eta^{z,xy}$ (plus permutations of the last two indices). The spin-only operation $\{M_z|\mathcal{I}\}$ imposes additional constraints. Applying Eq. (5.9) yields

$$\eta^{x,ab} \doteq \eta^{y,ab} \doteq 0, \quad (5.21)$$

so that the sole surviving component is $\eta^{z,xy}$. Physically, this means that the spin current can carry only a spin polarization perpendicular to the plane of the coplanar magnetic moments, i.e. along the z direction. Our numerical results, shown in Fig. 5.5, confirm this prediction: the z -polarised component is approximately twenty times larger than the in-plane ones.

5.3 Part II: Quadratic optical responses in P-wave magnets

In this part we extend our analysis to quadratic optical responses, focusing on a recently identified class of magnetic materials known as *p-wave magnets* (or odd-parity magnets) [171]. These materials are characterized by a non-collinear magnetic order that breaks spatial inversion $\mathcal{P}$ while preserving the combination of time reversal $\mathcal{T}$ with a fractional translation $\boldsymbol{\tau}$. This leads to a $\mathcal{P}$ -odd compensated Fermi surface with a large spin-splitting of ~ 0.5 eV originating from non-relativistic sources.

Two distinct classes of p-wave magnets have been identified. Class-I systems exhibit a coplanar magnetic configuration, where all magnetic moments lie within a single plane. In these materials, the combined symmetry $\{C_{2\perp}|\mathcal{T}||E|\mathbf{0}\}$ leaves the spin arrangement invariant: a half-rotation $C_{2\perp}$ of the in-plane spin components followed by time reversal brings the spin configuration back to itself. Class-II systems, in contrast, feature a noncoplanar magnetic structure. Here, the absence of a common plane can lead to a large spin splitting even in compounds containing only light elements, driven by noncollinear exchange contributions [171].

In magnetic materials, studies of quadratic optical responses have largely concentrated on $\mathcal{PT}$ -symmetric systems, where both $\mathcal{P}$ and $\mathcal{T}$ are individually

broken but their product is preserved. In those cases, it is the magnetic version of the shift and injection currents which can arise (See Sec. 2.2.2.3). P-wave magnets, by contrast, possess $\mathcal{T}$. Consequently, their quadratic responses are of the conventional shift and injection (non-magnetic type), yet they occur in a magnetically ordered system. This offers a unique opportunity to investigate how the magnitude and configuration of the magnetic moments control these otherwise “non-magnetic” photocurrents. We illustrate the underlying principles with a minimal model, and then apply the analysis to Mn_5Si_3 , a candidate p-wave magnet whose noncollinear spin structure below 60 K remains actively debated [196, 197].

5.3.1 Minimal model

To illustrate how a noncollinear spin configuration and its symmetries influence the quadratic shift photoconductivity σ^{abc} (where a, b, c denote spatial indices), we consider a double-exchange model [198, 199]:

$$H = \sum_{\langle i,j \rangle, \alpha} t_1 (c_{i\alpha}^\dagger c_{j\alpha} + \text{h.c.}) + \sum_{\langle\langle i,j \rangle\rangle, \alpha} t_2 (c_{i\alpha}^\dagger c_{j\alpha} + \text{h.c.}) + J \sum_{i, \alpha, \alpha'} \mathbf{m}^i \cdot c_{i\alpha}^\dagger \mathbf{S}_{\alpha\alpha'} c_{i\alpha'}. \quad (5.22)$$

The Hamiltonian is similar to the one employed in Sec. 5.2.4.1 besides the fact that the magnetic moments $\mathbf{m}$ are noncollinear and α, α' label spin projections along a global axis. Additionally, the SOC term is not included, as the focus will be on the magnetic exchange term. As a concrete example, we take a two-dimensional square lattice with evenly spaced sites and a $\mathcal{P}$ -breaking noncollinear magnetic structure, shown schematically in Fig. 5.6a. The parameters are chosen to be typical for a 3d electron system: lattice constant $a = 2 \text{ \AA}$, hopping amplitudes $t_1 = 1 \text{ eV}$ and $t_2 = 0.25 \text{ eV}$, and exchange constant $J = 0.4 \text{ eV}/\mu_B^2$ [200].

5.3.1.1 Spin symmetry predictions

The lattice belongs to magnetic point group $1.1'$, which contains only the symmetry $\mathcal{T}\boldsymbol{\tau}_m$ with $\boldsymbol{\tau}_m = (a, 2a)$ a fractional translation, constituting a P-wave magnet. Because of this low symmetry, all components of the shift photoconductivity tensor are allowed by magnetic symmetry. We now turn to spin-group symmetries. For the model of Fig. 5.6a, the relevant spin symmetries are $\{\mathcal{T}|\mathcal{I}|\boldsymbol{\tau}_m\}$ and $\{\mathcal{I}|M_x|\mathbf{0}\}$ —the latter involves a real-space mirror M_x combined with the identity in spin space. Similar to the transformation properties of the symmetric part of the optical conductivity, under a spin group operation g , the shift current transforms as

$$\sigma^{abc} \xrightarrow{g} R_{aa'} R_{bb'} R_{cc'} \sigma^{a'b'c'}, \quad (5.23)$$

only affected by the spatial parts of the operation. The spatial parts of the spin symmetry operations generate the point group m , which restricts the independent components of the shift current to σ^{yyy} , σ^{yxx} , and σ^{xxy} [201].

Our numerical calculations confirm that the components allowed by spin symmetries are indeed several orders of magnitude larger than those that are forbidden. Figure 5.6c illustrates this for the allowed component σ^{yxx} and the forbidden component σ^{xxx} .

5.3.1.2 Dependence on the magnetization

In this model, it is the noncollinear spin configuration that reduces the symmetry of the lattice and enables the BPVE. That allows us to examine the dependence of the shift photoconductivity on the magnitude of the magnetic moment. The corresponding band structures are shown in Fig. 5.6b for different values of $|\mathbf{m}|$. In the nonmagnetic limit ($|\mathbf{m}| = 0$), the bands are Kramers degenerate due to $\mathcal{PT}$ symmetry. For $|\mathbf{m}| \neq 0$, this degeneracy is lifted, giving rise to noncollinearly spin-split bands that satisfy $E_{\mathbf{k}\uparrow} = E_{-\mathbf{k}\downarrow}$. The spin splitting grows with increasing $|\mathbf{m}|$, and the system remains metallic for all values considered.

The spectrum of the allowed component σ^{yxx} is shown in Fig. 5.6c for $|\mathbf{m}| = 0.13$ and $0.75 \mu_B$. It exhibits clear peaks at photon energies $\omega_1 \approx 1.4$ eV and $\omega_2 \approx 1.9$ eV. For $|\mathbf{m}| < 0.33 \mu_B$, the ω_1 peak dominates; for $|\mathbf{m}| > 0.38 \mu_B$, the ω_2 peak becomes dominant. Figure 5.6d tracks the magnitude of these two peaks as a function of $|\mathbf{m}|$ in their respective dominance regimes. The shift photoconductivity increases steadily with $|\mathbf{m}|$ and vanishes in the $|\mathbf{m}| \rightarrow 0$ limit. Values above $|\mathbf{m}| \simeq 1 \mu_B$ yield a substantial response, comparable to prototypical ferroelectrics such as BaTiO₃ [84]. For $|\mathbf{m}| \simeq 1.5 \mu_B$, the photoconductivity reaches nearly 10^{-4} A/V², a notable magnitude on par with the highest reported values in the Weyl semimetal TaAs [12]. Thus, noncollinear magnets can not only support but also generate significant quadratic photocurrents, with the magnitude highly sensitive to the magnetic moment size.

5.3.1.3 Spin currents

Finally, we briefly discuss spin photocurrents. As a representative example, the focus will be on the spin shift contribution $\zeta^{s,abc}$ (Eq. (2.82)), which is activated from circularly polarized light in $\mathcal{T}$ -symmetric systems. The symmetry constraints on this third-rank tensor generally involve both spatial and spin operations. In the present model, the spin-group symmetry $\{E||M_x|\mathbf{0}\}$ includes the identity in spin space, so the effective constraint is again the real-space mirror M_x . The transformation of $\zeta^{s,abc}$ under a spin symmetry operation g is similar to the spin Hall conductivity $\eta^{s,abc}$ given in Sec. 5.2.3:

$$\zeta^{s,abc} \xrightarrow{g} \det(U) U_{ss'} R_{aa'} R_{bb'} R_{cc'} \zeta^{s',a'b'c'}, \quad (5.24)$$

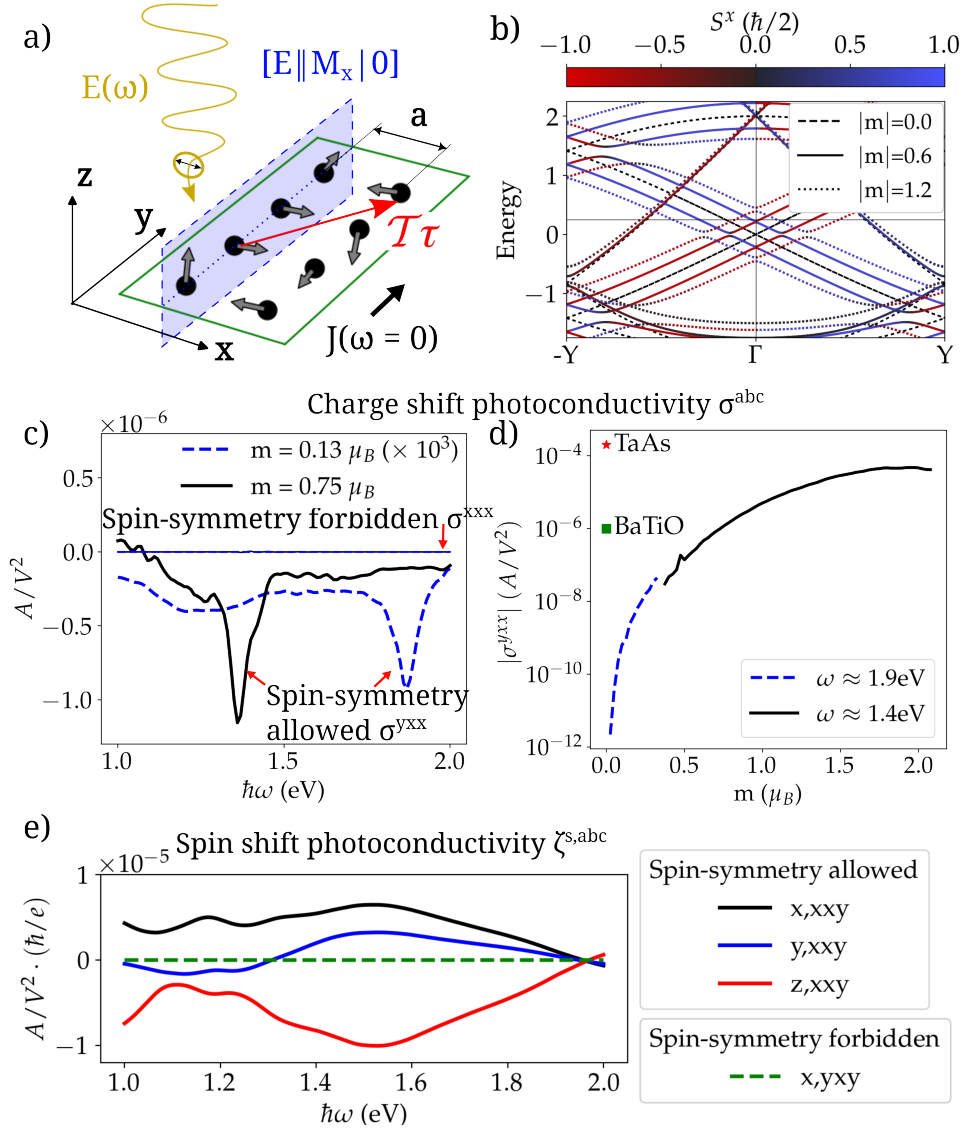


Figure 5.6: a) Schematic illustration of DC photocurrent generated on a rectangular lattice with noncollinear spin arrangement respecting $\mathcal{T}\tau_m$ symmetry with $\tau_m = (a, 2a)$. The spin symmetry $\{E||M_x|\mathbf{0}\}$ has been highlighted (see text). b) Spin polarized bands of the model for different values of $|\mathbf{m}|$ displaying $\mathcal{T}$ -symmetry. c) Charge shift photoconductivity spectra for different values of $|\mathbf{m}|$. A $\times 10^3$ factor has been applied to the $|\mathbf{m}| = 0.13\mu_B$ curve for visibility purposes. d) Evolution of the value of σ^{yxx} for the peaks at $\omega \approx 1.4$ eV and $\omega \approx 1.9$ eV as a function of $|\mathbf{m}|$. For reference, we have included maximum shift photoconductivity of TaAs and BaTiO₃ from Refs. [12] and [84]. e) Spin shift photoconductivity spectra for $m = 0.75\mu_B$, clearly fulfilling the predictions of spin symmetries.

Consequently, the only components allowed by spin symmetries are $\zeta^{x,xy}$, $\zeta^{y,xy}$, $\zeta^{z,xy}$, and the corresponding components with the two spatial indices symmetrized ($b \leftrightarrow c$). This differs from the magnetic-group description, which would permit all components. As exemplified in Fig. 5.6e, the spin-symmetry predictions are also validated for the spin shift contribution, extending the applicability of the spin-group approach to quadratic spin photocurrents.

5.3.2 Material realization: Mn_5Si_3

We continue with a material realization in the magnetic compound Mn_5Si_3 , which has attracted considerable attention in recent years owing to its unconventional transport properties, including a large anomalous Hall effect [202], a topological Hall effect [203], and an inverse magnetocaloric effect [204]. These features make it a promising platform for spintronics. The material exhibits zero net magnetization across all temperatures and displays three distinct magnetic phases: a paramagnetic phase above 100 K [205]; a collinear antiferromagnetic phase between 60 K and 100 K (referred to as AFM2 in the literature) [206–209]; and a noncollinear phase below 60 K, known as AFM1 [210–213].

Our focus is on the low-temperature noncollinear phase, which has recently been classified as a *p-wave magnet* [171]. As introduced in the previous section, p-wave magnets fall into two classes—coplanar (class-I) and noncoplanar (class-II)—distinguished by the presence or absence of a $\{C_{2\perp}\mathcal{T}\|E|\mathbf{0}\}$ symmetry. The ongoing debate regarding the low-temperature structure of Mn_5Si_3 can be naturally framed in terms of these two classes. Early neutron polarimetry experiments [211] proposed the spin arrangement shown in Fig. 5.7a. This structure belongs to magnetic space group $P_51 = \{E, \mathcal{T}\tau_{xy}\}$ with $\tau_{xy} = (1/2, 1/2, 0)$ and features noncoplanar magnetic moments, placing it in class-II. More recently, density functional theory calculations combined with spin dynamics simulations predicted an alternative configuration [197], shown in Fig. 5.7e. This structure is more symmetric, belonging to magnetic space group $P_{C222_1} = \{E, C_{2y}, C_{2x}\tau_z, C_{2y}\tau_z\} \otimes \{E, \mathcal{T}\tau_{xy}\}$ with $\tau_{xy} = (1/2, 1/2, 0)$ and $\tau_z = (0, 0, 1/2)$. Here, all magnetic moments lie in the yz plane, and the spin symmetry $\{C_{2x}\mathcal{T}\|E|\mathbf{0}\}$ holds, consistent with class-I. The debate over the actual magnetic configuration remains active, with new experimental studies continuing to appear [214].

5.3.2.1 P-wave characteristics

Computational details To investigate the electronic properties of the two candidate structures, we performed full-relativistic DFT following the methodology of the previous cases. An energy cutoff of 440 eV, a smearing of 0.05 eV, and a gamma-centered k-point mesh of $9 \times 5 \times 11$ were used. The desired magnetic configurations were stabilized using the constrained local

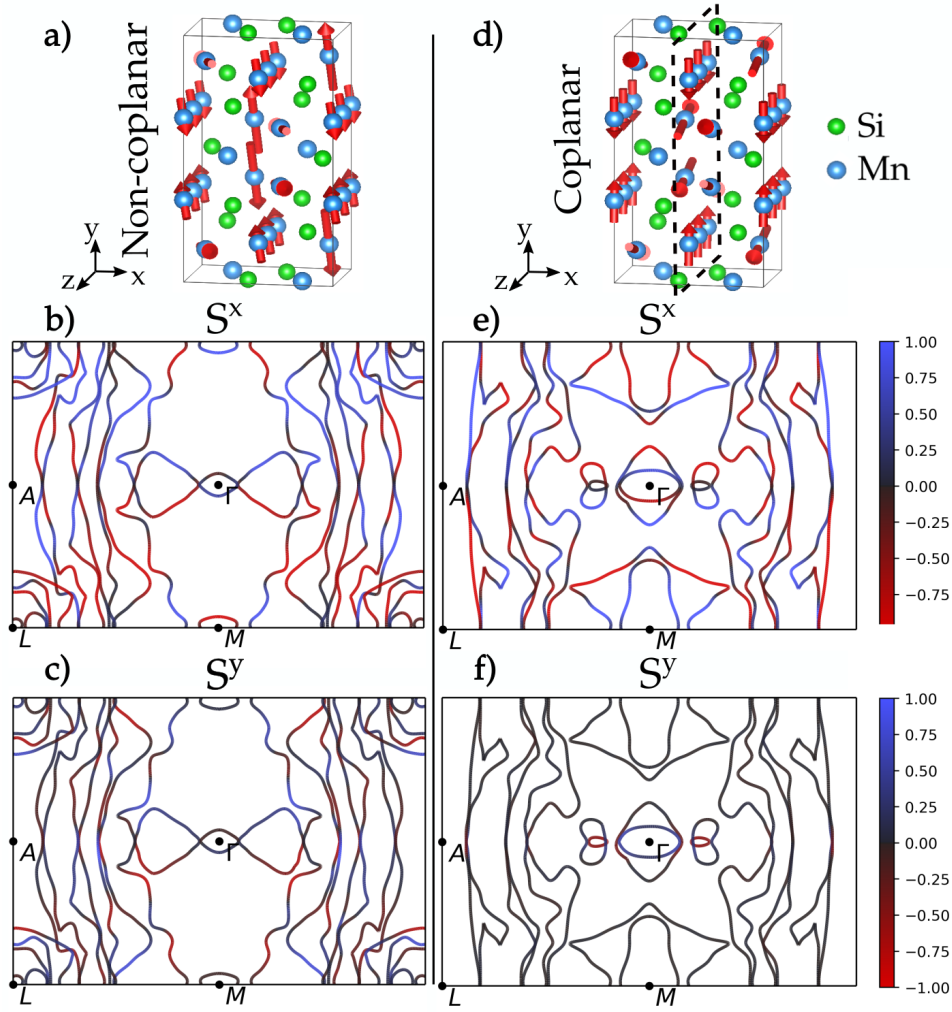


Figure 5.7: Left panel: Lattice (a) and Fermi surface at $k_y = 0$ (b, c) of the non-coplanar structure for spin projections S_x and S_y . Right panel: same as left panel but for coplanar structure. In d), the plane of magnetization in yz is displayed. Spin projection S_z not shown in either panel; it is finite for the non-coplanar structure and virtually zero (like S_y) in the coplanar one.

moments approach [198], yielding local magnetic moments of up to $2.6 \mu_B$, in good agreement with experimental estimates [211].

Electronic structure and spin polarization Figure 5.7 displays the spin-projected Fermi surfaces [215] for the two configurations. Both are metallic and exhibit spin-split bands with opposite spin polarizations across the Γ point, a direct consequence of the $\mathcal{T}\tau$ symmetry. However, the spin polarization patterns differ markedly. In the noncoplanar (class-II) structure,

finite spin polarization is observed in all directions (Fig. 5.7b–c). By contrast, the coplanar (class-I) structure shows negligible S^y and S^z components away from the immediate vicinity of the Γ point (Fig. 5.7f illustrates S^y), meaning that the $\mathbf{k}$ -space spin polarization is effectively perpendicular to the plane of real-space magnetization.

This behavior can be understood from symmetry considerations [171]. In the coplanar structure, the combined operation $\{C_{2x}\mathcal{T}\|E|\mathbf{0}\} \circ \{\mathcal{T}\|E|\boldsymbol{\tau}\}$ shares common eigenstates with the Hamiltonian. Using $\mathcal{T}^2 = -1$ and $\boldsymbol{\tau}\mathbf{S}\boldsymbol{\tau}^{-1} = \mathbf{S}$, the parallel spin-polarization components vanish:

$$S_n^{y,z}(\mathbf{k}) = \langle \psi_{\mathbf{k}n} | C_{2x} S_n^{y,z} C_{2x}^{-1} | \psi_{\mathbf{k}n} \rangle = -S_n^{y,z}(\mathbf{k}), \quad (5.25)$$

while the x component is unaffected. This result, which holds as a reliable approximation in the weak spin–orbit coupling regime, together with the electronic structure shown in Fig. 5.7, confirms the unconventional p-wave nature of both noncollinear spin configurations in Mn_5Si_3 .

5.3.2.2 Nonlinear optical fingerprint

Spectra We now turn to the quadratic shift current in Mn_5Si_3 . In this case, we have found it more convenient to work directly with the Bloch eigenstates rather than constructing Wannier functions. The reason is that the standard minimization procedure to obtain maximally localized Wannier functions does not enforce crystal symmetries. In materials with a non-trivial band structure where the minimization procedure is challenging, like in Mn_5Si_3 , this procedure can produce an effect on symmetry-forbidden tensor components whereby they become numerically finite [216]. Given the importance of symmetry considerations in this analysis, we have chosen to proceed by considering the alternative velocity gauge expression for the shift photoconductivity [217]

$$\begin{aligned} \sigma^{abc}(\omega) = & \frac{\pi|e|^3}{2\hbar^2V} \sum_{\mathbf{k} \in \text{BZ}} \sum_{m,n} \frac{f_{m,n}}{\omega_{m,n}^2} \text{Im} \left[v_{m,n}^b \sum_{l \neq m,n} \left(\frac{v_{n,l}^a v_{l,m}^c}{\omega_{n,l}} - \frac{v_{n,l}^c v_{l,m}^a}{\omega_{lm}} \right) \right. \\ & \left. + (b \leftrightarrow c) \right] \delta(\omega_{m,n} - \omega), \end{aligned} \quad (5.26)$$

where we have calculated all quantities involved directly from Bloch eigenstates, without employing Wannier functions. Eq. (5.26) avoids the troublesome $\mathbf{k}$ -space derivatives involved in the dipole term at the cost of introducing a truncation error in the band summations. We have employed a basis of 300 bands to converge the calculation of the shift current in the two structures of Mn_5Si_3 analyzed in the main text. The considered $\mathbf{k}$ -mesh has been $19 \times 15 \times 21$, which is a modest number compared to usual values obtainable using Wannier interpolation [46]. In return, this way of proceeding makes sure that

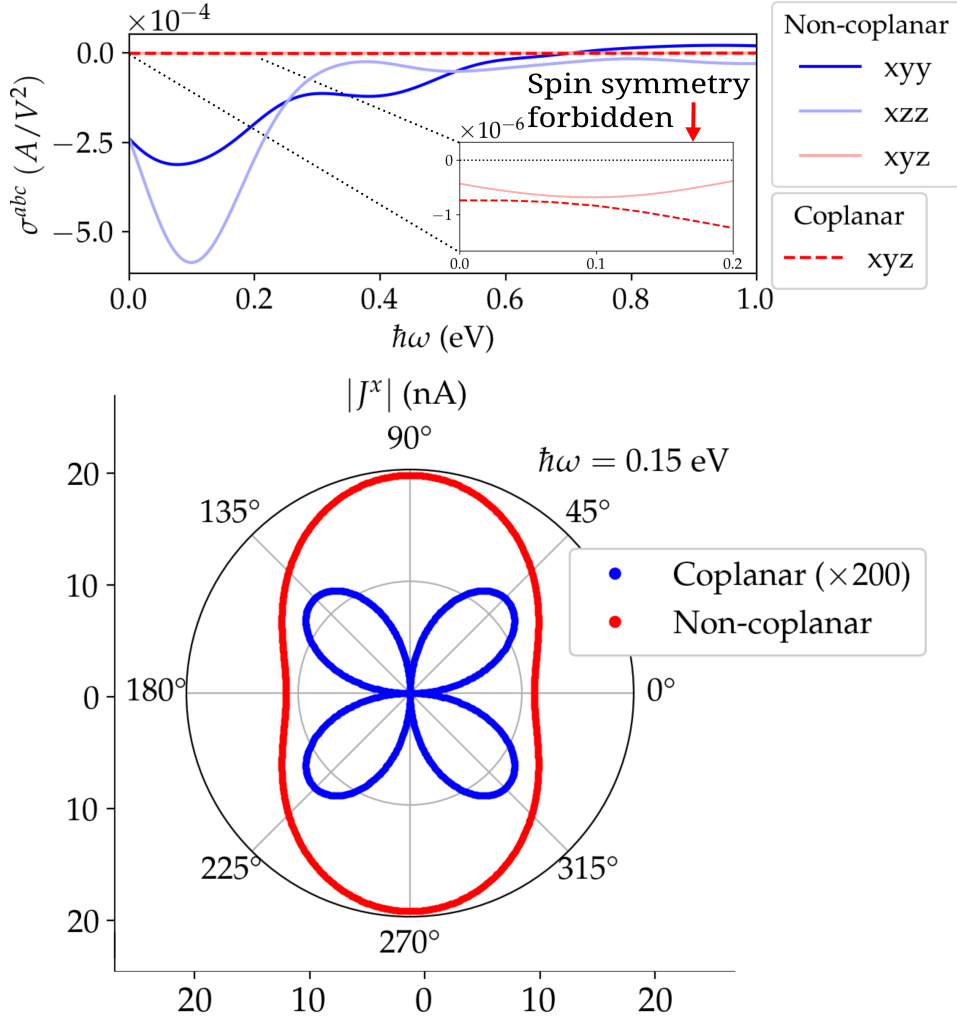


Figure 5.8: (a) Top and bottom: shift photoconductivity of the non-coplanar and coplanar structures of Mn_5Si_3 , respectively. (b) DC photocurrent J^x at $\hbar\omega = 0.15$ eV as a function of polarization angle in the two structures.

the symmetry of the Bloch functions inherited from crystal symmetries is correctly translated into the photoconductivity components.

Symmetry-wise, from the perspective of the magnetic point group, the shift current is symmetry-allowed in both structures: the coplanar configuration permits three independent components (σ^{xyz} , σ^{yzx} , σ^{zxy}), while the noncoplanar configuration allows all 18 tensor components. Spin-group considerations, however, impose much stricter constraints. The effective point group of the noncoplanar structure formed by the spatial part of the spin symmetries is $2mm$, which forces σ^{abc} to vanish whenever the number of z or y is odd. For the coplanar structure, the effective point group is mmm ,

which restores spatial inversion $\mathcal{P}$ and thereby suppresses all nonrelativistic contributions to the quadratic photoresponse.

The numerical evaluation of the shift photoconductivity up to a photon frequency of 1 eV is illustrated in Fig. 5.8a for the non-coplanar and coplanar structures. For clarity, we focus on the photocurrent generated along x under linearly polarized light in the yz plane; the relevant tensor components are σ^{xyy} , σ^{xzz} , and σ^{xyz} . The component σ^{xyz} is particularly instructive: it is allowed by the magnetic group but forbidden by the spin group in both configurations. The results in Fig. 5.8a demonstrate that the spin-symmetry predictions are largely fulfilled. For both structures, σ^{xyz} is two orders of magnitude smaller than the finite components of the noncoplanar structure. The magnitude of the shift photoconductivity in the noncoplanar configuration reaches $\sim 10^{-4}$ A/V², an order of magnitude larger than in prototypical semiconductors such as GaAs [218] or BC₂N [112, 154], and comparable to the highest values reported in Weyl semimetals like TaAs and TaIrTe₄ [12, 99, 101, 219].

Angular distribution of the photocurrent The pronounced difference in the shift-current magnitude between the coplanar and noncoplanar structures can serve as an experimental probe to distinguish the two candidate spin configurations. In an experiment, the directly measured quantity is the photocurrent. The standard expression for the Glass coefficient (see Sec. 2.2.2.4) applies to diagonal components σ^{abb} , while here we are interested in off-diagonal components σ^{abc} . We therefore provide below the relationship between the shift current and the Glass coefficient for the relevant experimental geometry. For simplicity, in this case we neglect the reflectivity of the material ($R(\omega) = 0$).

We consider the situation described above, namely a current generated along J^x under a linearly polarized electric field $\mathbf{E} = E_0(0, \cos \theta, \sin \theta)$. We perform a change of coordinates $\mathbf{r}' = \underline{R}(-\theta) \cdot \mathbf{r}$ such that the electric field is polarized purely along the y' direction:

$$\begin{pmatrix} 0 \\ E_0 \\ 0 \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & \cos(-\theta) & -\sin(-\theta) \\ 0 & \sin(-\theta) & \cos(-\theta) \end{pmatrix} \cdot \begin{pmatrix} 0 \\ E_0 \cos \theta \\ E_0 \sin \theta \end{pmatrix}. \quad (5.27)$$

In this reference frame, since the intensity $I_{y'}$ is only along y' and $x' = x$, from Eq. 2.73 we have

$$J_{\text{shift}}^{x'} = G^{x'y'y'}(\omega) \cdot (1 - R(\omega))(1 - e^{-\alpha_{y'y'} \cdot d}) \cdot w \cdot I_{y'} = J_{\text{shift}}^x, \quad (5.28)$$

so the expression for G^{abb} from the literature can be used, provided it is evaluated in the rotated frame [21, 84]:

$$G^{xy'y'} = 2\sigma^{x'y'y'}(\omega)/c\epsilon_0\sqrt{\epsilon_r} \cdot \alpha_{y'y'}(\omega). \quad (5.29)$$

The rotated components are related to the original ones by $\sigma^{a'b'c'} = R^{a'a} R^{b'b} R^{c'c} \sigma^{abc}$ and $\epsilon^{b'b'} = R^{b'a} R^{b'b} \epsilon^{ab}$. For the present geometry,

$$\epsilon^{y'y'} = \cos^2 \theta \epsilon^{yy} + \sin^2 \theta \epsilon^{zz} + \sin 2\theta \epsilon^{yz}, \quad (5.30)$$

$$\sigma^{xy'y'} = \cos^2 \theta \sigma^{xyy} + \sin^2 \theta \sigma^{xzz} + \sin 2\theta \sigma^{xyz}, \quad (5.31)$$

leading to

$$G^{xy'y'} = 2 \frac{\cos^2 \theta \sigma^{xyy} + \sin^2 \theta \sigma^{xzz} + \sin 2\theta \sigma^{xyz}}{c \epsilon_0 \sqrt{\epsilon_r} \cdot \alpha_{y'y'}(\omega)}, \quad (5.32)$$

with

$$\alpha^{y'y'} = \sqrt{2} \frac{\omega}{c} \left(|\cos^2 \theta \epsilon^{yy} + \sin^2 \theta \epsilon^{zz} + \sin 2\theta \epsilon^{yz}| - \text{Re}(\cos^2 \theta \epsilon^{yy} + \sin^2 \theta \epsilon^{zz} + \sin 2\theta \epsilon^{yz}) \right)^{1/2}. \quad (5.33)$$

We propose measuring the DC photocurrent as a function of the incident polarization angle $\mathbf{E}(\omega) = E_0(\omega)(0, \cos \theta, \sin \theta)$, as illustrated in Fig. 5.8b. For this estimate, we choose a photon energy of 0.15 eV and an intensity of 480 nW distributed over a spot size of 5 μm , parameters well within experimentally accessible ranges [19, 99]. The noncoplanar structure generates a photocurrent of approximately 20 nA, readily measurable, while the coplanar structure yields a current two orders of magnitude smaller—consistent with the photoconductivity components shown in Fig. 5.8a. Moreover, because of the dominant tensor components dictated by symmetries, the angular dependence differs markedly: the noncoplanar structure follows $\sigma^{xyy} \cos^2 \theta + \sigma^{xzz} \sin^2 \theta$, whereas the coplanar structure exhibits a $\sigma^{xyz} \sin 2\theta$ pattern. This combined difference in magnitude and angular form provides a clear fingerprint for identifying the actual spin configuration via photogalvanic measurements. Alternative nonlinear techniques, such as second-harmonic generation [220–223], could similarly be used to probe the material's symmetry.

5.4 Conclusions

Overall, in this chapter we have examined how spin symmetries constrain the optical response of magnetic materials, focusing on both charge and spin currents. Our analysis demonstrates that spin symmetries serve as a powerful approximate tool for understanding optical spectra, especially in systems where relativistic effects are not the dominant physical mechanism.

In Part I, we addressed linear response. Altermagnets emerge as ideal platforms for this purpose: their defining spin splitting is intrinsically non-relativistic, and the most salient features of their electronic structure and optical response are captured already at the spin-symmetry level. We first

illustrated the concept within a Lieb-lattice tight-binding model that includes intra-atomic spin-orbit coupling (SOC). By progressively increasing the SOC strength, we showed that the spin-symmetry relation $\sigma^{xx} \doteq \sigma^{yy}$ remains accurate to within a few percent even when the SOC energy scale approaches the exchange splitting. A quantitative metric Δ confirmed that the linear dichroism stays below 15% in the strong SOC regime.

This behaviour carries over to the real material $\text{UCr}_2\text{Si}_2\text{C}$, which realizes the Lieb-lattice geometry and contains heavy uranium atoms. Despite pronounced SOC-induced band splittings, the diagonal optical conductivity is nearly isotropic, with the dichroic ratio remaining below 1.05 across most of the spectrum. The same spin-symmetry reasoning applied to the altermagnet RbMnF_4 predicts a strong suppression of σ^{xy} and σ^{yz} , a prediction that is quantitatively supported by our *ab initio* calculations and leads to a birefringence pattern dominated by the xz plane. Finally, for the non-collinear altermagnet ScMnO_3 we extended the analysis to spin currents, showing that the main response is an out-of-plane spin polarized current generated by in-plane polarized light, consistent with the spin-symmetry constraints.

In Part II we turned to quadratic photocurrents and the recently identified class of p-wave magnets. These materials preserve $\mathcal{T}$ but break $\mathcal{P}$, enabling conventional shift and injection currents in a magnetically ordered environment. A minimal double-exchange model showed that the shift photoconductivity grows with the magnetic moment and could reach magnitudes comparable to the highest known values in Weyl semimetals. Spin symmetries again dictate the tensor structure: for the model system, only components consistent with an effective mirror symmetry are sizable. The material Mn_5Si_3 served as a case study of two competing non-collinear structures—coplanar (class-I) and non-coplanar (class-II). Spin-symmetry considerations predict dramatically different nonlinear optical fingerprints: the non-coplanar phase permits large shift currents, while the coplanar phase restores an effective inversion symmetry that suppresses the non-relativistic quadratic response. The corresponding DC photocurrent under linearly polarized light exhibits distinct angular dependences, providing a clear optical signature to distinguish the two candidate spin structures.

Beyond the specific materials studied here, the implications of spin symmetries extend to any light-element magnet where these hidden symmetries provide additional constraints beyond those of the magnetic point group. Their influence spans responses at all orders of the electric field, including linear contributions such as the anomalous Hall effect, which is a signature of altermagnets [177]. Moreover, the consequences of spin-symmetry predictions for the dominant light-absorption coefficients are likely to propagate into the behavior of collective excitations such as plasmons and magnons, thereby affecting properties like reflectance and spin transport, e.g., spin Seebeck and spin Nernst effects. Finally, our analysis of spin currents in both linear and quadratic regimes lays the groundwork for a comprehensive classification of

spin photoresponses, with immediate implications for timely topics such as the generation of pure bulk spin photocurrents [157].

Chapter 6

Final conclusions

This thesis has primarily focused on the charge BPVE, while also giving attention to linear optical responses and spin currents, as a sensitive probe of electronic structure, topology, magnetic texture and symmetry. Three distinct classes of systems were studied: topological models, surfaces exhibiting spin-split surface states, and unconventional magnets. By combining model Hamiltonians with first-principles electronic-structure calculations, the work uncovers the peculiar fingerprints that each platform imprints on photocurrents, connecting them to the broader field of the BPVE as a quantum-geometric spectroscopy tool.

In the topological realm, the Haldane model served as a minimal setting where band topology directly shapes the shift photoconductivity. A low-energy analysis revealed that the sign of the band-edge response is dictated by the Dirac mass, giving rise to a robust sign reversal whenever the system crosses a topological phase transition. Exact numerical simulations confirmed that this reversal endures even when off-diagonal position-operator matrix elements—often neglected in tight-binding schemes—become significant, whereas a secondary, valley-driven sign change inside the topological phase proves fragile. The robustness of the transition-induced sign flip establishes the shift current as a clear optical signature of band inversion, complementing the quantized circular photogalvanic effect observed in Weyl semimetals [10] and reinforcing the paradigm of using nonlinear photocurrents to diagnose topological phases.

Shifting to surfaces, the work demonstrated that spin-split surface states could provide a generic route to bypass the inversion symmetry constraint of the BPVE. An extended Rashba model including hexagonal warping captured the essential physics of Au(111), and its predictions were quantitatively benchmarked against density-functional calculations. The focus then moved to Tl/Si(111), where a semiconducting bulk, a giant spin-orbit splitting, and an unusual out-of-plane spin texture at the K valleys give rise to a shift photocurrent comparable in magnitude to that of prominent ferroelectrics

when the surface band is moderately doped. Moreover, the same surface states enable a highly tunable nonlinear spin photocurrent: depending on doping and light polarization, one can generate pure out-of-plane or in-plane spin-polarized currents by accessing different regions of the spin texture. This capability highlights surfaces as versatile platforms for all-optical spintronics, where the interplay of spin texture and nonlinear response offers spatial and spin selectivity beyond the linear spin Hall effect.

In magnetic materials, the concept of spin symmetries was employed as a powerful approximate tool to constrain optical responses. Altermagnets, where spin splitting is nonrelativistic in origin, provided an ideal platform: the spin-symmetry prediction of vanishing linear dichroism was shown to hold when spin-orbit coupling competes with the exchange splitting, as confirmed for the heavy-element compound $\text{UCr}_2\text{Si}_2\text{C}$, and analogous spin-symmetry constraints dictate the birefringence pattern in RbMnF_4 . These constraints also governed the linear spin-current response in the non-collinear altermagnet ScMnO_3 . The analysis was extended to quadratic photocurrents in odd-parity magnets. In those systems, using a double-exchange model revealed that the shift photoconductivity grows with the magnetic moment, while spin symmetries dictate the tensor structure. In the candidate material Mn_5Si_3 , competing non-collinear magnetic configurations leave dramatically different angular fingerprints in the DC photocurrent, offering a clear optical means to distinguish spin structures. These findings underscore that spin symmetries are useful to simplify the interpretation of optical spectra.

Collectively, the results illustrate that both linear and nonlinear photocurrents encode detailed information about band topology, spin texture, and symmetry. The results mentioned above point to the BPVE as a versatile, if specialized, probe. While direct energy-harvesting applications remain challenging, the unique sensitivity of these currents to electronic and spin degrees of freedom positions them as valuable tools for fundamental spectroscopy in future optoelectronic and spintronic devices.

Publications

Part of the work presented here has been published in the following references:

1. Javier Sivianes, Julen Ibañez-Azpiroz, *Shift photoconductivity in the Haldane model*, Phys. Rev. B **108**, 155419 (2023).
2. Javier Sivianes, Flaviano José dos Santos, Julen Ibañez-Azpiroz, *Optical signatures of spin symmetries in unconventional magnets*, Phys. Rev. Lett. **134**, 196907 (2025).
3. Javier Sivianes, Peiro García-Goiricelaya, Daniel Hernangómez-Pérez, Julen Ibañez-Azpiroz, *Surface-state engineering for nonlinear charge and spin photocurrent generation*, Phys. Rev. Lett. **135**, 256201 (2025).
4. Javier Sivianes, Enrique Boquete-Someso, Daniel Hernangómez-Pérez, Julen Ibañez-Azpiroz, *Spin-group symmetry as a guide to optical response: applications to altermagnets*, To be submitted.

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