


Resonant Photovoltaic Effect in Doped Magnetic Semiconductors

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The rectified nonlinear response of a clean, time-reversal symmetric, undoped semiconductor to an ac electric field includes a well known intrinsic shift current. We show that when Kramers degeneracy is broken, a distinct second order rectified response appears due to Bloch state anomalous velocities in a system with an oscillating Fermi surface. This effect, which we refer to as the resonant photovoltaic effect, produces a resonant galvanic current peak at the interband absorption threshold in doped semiconductors or semimetals with approximate particle-hole symmetry. We evaluate the resonant photovoltaic effect for a model of the surface states of a magnetized topological insulator.

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Introduction.—The interband coherence responses of crystals to dc and ac driving electric fields have both been studied extensively in recent years. The intrinsic anomalous velocity dc response, which is due to interband coherence and related to momentum-space Berry curvature, is essential for the chiral anomaly [1,2] in Weyl semimetals, and that it often dominates the anomalous Hall effect of magnetic materials [3,4]. Separately, a number of conceptually novel nonlinear response effects [5–7] have been identified recently that involve interband coherence. Notably, the nonlinear optical response of a semiconductor at frequencies above the band gap includes an intrinsic dc photocurrent associated with an interband coherence related shift of intracell coordinates. The intrinsic shift current [6–44] has received particular attention because it is closely related to topological band characteristics [45–47], and has been identified experimentally in some noncentrosymmetric ferroelectrics [48–51]. In this Letter, we identify a new nonlinear response effect by showing that the dc galvanic photocurrent in doped semiconductors can contain an anomalous velocity contribution.

The understanding of interband coherence and its relation to disorder in the nonlinear optical response of semiconductors is still in its infancy. Most studies to date have focused on undoped materials, although possible Fermi surface effects in doped systems have started to gain attention [38,52–55] very recently. The resonant photovoltaic effect (RPE) mechanism for rectified response to linearly polarized light [Fig. 1(a)] is due to the combination of Bloch state anomalous velocities and Fermi surface shifts, which both oscillate when driven by an ac field as indicated in Fig. 1(b) and produce a current with a nonzero time average. The RPE involves an interplay between Bloch state wave function topology, disorder, and interband optical excitation. The RPE is active in doped

semiconductors with broken time-reversal symmetry, and strongest in semiconductors with approximate particle-hole symmetry. It is therefore especially strong in magnetized topological materials whose surface states have approximate particle-hole symmetry, reflecting the fundamental connection between nonlinear response and nontrivial band topology [45,56–60], and the importance of the Berry curvature in nonlinear optical response [61]. The RPE is related in part to the nonlinear Hall conductivity, which contains a related intrinsic contribution proportional to the Berry curvature dipole [45,57–59] but may also have extrinsic contributions [38,62–64]. Nonlinear phenomena in topological materials have been discussed previously, e.g., the observation of the nonlinear Hall effect [65,66], the prediction of a nonlinear anomalous Hall effect [67], and valley-driven second harmonic generation [68].

Theory of the resonant photovoltaic effect.—We now outline the transport theory that we use to identify and

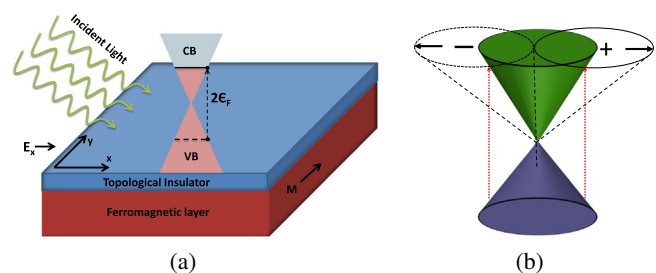


FIG. 1. (a) Resonant photovoltaic effect induced by linearly polarized light incident on the surface of a warped topological insulator on a ferromagnet with an in-plane magnetization. (b) Carriers excited from the valence band to the oscillating Fermi surface.

evaluate the RPE; a detailed derivation is provided in the Supplemental Material [69]. We consider a Hamiltonian of the general form $\hat{H} = \hat{H}_0 + \hat{H}_E + \hat{U}$, where \hat{H}_0 is a crystal Bloch-state Hamiltonian, $\hat{H}_E(t) = e\mathbf{E}(t) \cdot \hat{\mathbf{r}}$ the interaction with a time-dependent external electric field that is assumed spatially uniform, and \hat{U} is the random disorder potential. The impurities are uncorrelated and the average of $|\langle \mathbf{k}m | \hat{U} | \mathbf{k}'m' \rangle|^2$ over impurity configurations is $n_i |\bar{U}_{kk'}^{mm'}|^2 / V$, where n_i is the impurity density, V the crystal volume, and $\bar{U}_{kk'}^{mm'}$ the matrix element of the potential of a single impurity. We consider short-range impurities such that $U(\mathbf{r}) = U_0 \sum_i \delta(\mathbf{r} - \mathbf{r}_i)$, with \mathbf{r}_i labeling impurity sites. We focus on temperatures close to absolute zero, so that phonon scattering is negligible. The system is described by a density operator $\hat{\rho}$, which obeys the quantum Liouville equation [70]. In the Born approximation $\langle \rho \rangle$, the density matrix averaged over impurity configurations obeys

$$\frac{d\langle \rho \rangle}{dt} + \frac{i}{\hbar} [H_0, \langle \rho \rangle] + J(\langle \rho \rangle) = -\frac{i}{\hbar} [H_E, \langle \rho \rangle], \quad (1)$$

$$J(\langle \rho \rangle) = \frac{1}{\hbar^2} \int_0^\infty dt' \langle [U, [e^{-iH_0 t'/\hbar} U e^{iH_0 t'/\hbar}, \langle \rho(t) \rangle]] \rangle. \quad (2)$$

The impurity average restores translational periodicity so that in the crystal momentum representation $\langle \rho \rangle$ remains diagonal in the wave vector \mathbf{k} . We expand the density matrix in powers of the electric field as $\langle \rho \rangle = \langle \rho \rangle^{(0)} + \langle \rho \rangle^{(1)} + \langle \rho \rangle^{(2)} + \dots$ where the superscript (n) refers to order n in the electric field. The equilibrium part $\langle \rho \rangle^{(0)}$ is the solution of Eq. (1) with the right-hand side (RHS) set to zero. It is diagonal in the band index m and has the form $\langle \rho \rangle_{mm'}^{(0)} = f_{mk}^0 \delta_{mm'}$, where $f_{mk}^0 \equiv f_{mk}^0(\varepsilon_{mk})$ is the Fermi-Dirac distribution occupation probability at the energy ε_{mk} of band m . To evaluate $\langle \rho \rangle^{(1)}$ we set $\langle \rho \rangle \rightarrow \langle \rho \rangle^{(1)}$ on the left-hand side of Eq. (1), and $\langle \rho \rangle \rightarrow \langle \rho \rangle^{(0)}$ on the RHS. Finally, $\langle \rho \rangle^{(2)}$ contains the nonlinear response of second order in the electric field, which is of interest to us in this work. To determine it we set $\langle \rho \rangle \rightarrow \langle \rho \rangle^{(2)}$ on the left-hand side of Eq. (1), and $\langle \rho \rangle \rightarrow \langle \rho \rangle^{(1)}$ on the RHS.

The commutator $[H_0, \langle \rho \rangle]$ accounts for interband dynamics. It is convenient to make the decomposition $\langle \rho \rangle_{\mathbf{k}} = f_{d,\mathbf{k}} + f_{od,\mathbf{k}}$ with $f_{d,\mathbf{k}}$ and $f_{od,\mathbf{k}}$, respectively, purely diagonal and purely off-diagonal in the band indices. The diagonal response $f_{d,\mathbf{k}}$ tracks Bloch state repopulation while the off-diagonal part $f_{od,\mathbf{k}}$ accounts for interband coherence. These two responses can be expanded separately in powers of $\mathbf{E}(t)$ as $f_{d,\mathbf{k}} = f_{d,\mathbf{k}}^{(0)} + f_{d,\mathbf{k}}^{(1)} + f_{d,\mathbf{k}}^{(2)} + \dots$ and $f_{od,\mathbf{k}} = f_{od,\mathbf{k}}^{(1)} + f_{od,\mathbf{k}}^{(2)} + \dots$. The zeroth order term in the expansion is the equilibrium term $f_{mk}^0(\varepsilon_{mk})$, which is diagonal in the Bloch eigenstate representation, hence $f_{d,\mathbf{k}}$ starts at zeroth order in $\mathbf{E}(t)$ while $f_{od,\mathbf{k}}$ starts at first order in $\mathbf{E}(t)$. It is useful to separate the quantum kinetic equation

Eq. (1) into coupled equations for $f_{d,\mathbf{k}}$ and $f_{od,\mathbf{k}}$. The scattering term couples the diagonal and off-diagonal response: $J(\langle \rho \rangle) = J_d(f_{d,\mathbf{k}} + f_{od,\mathbf{k}}) + J_{od}(f_{d,\mathbf{k}} + f_{od,\mathbf{k}})$. To determine $J_{od}(f_{d,\mathbf{k}})$, first $f_{d,\mathbf{k}}$ is found, then it is fed into Eq. (2), and the off-diagonal part is selected.

We consider linearly polarized light $\mathbf{E}(t) = E \cos \omega t$ having ω an oscillating frequency. The electric field and scattering terms both connect $f_{d,\mathbf{k}}$ and $f_{od,\mathbf{k}}$. The solution in powers of $\mathbf{E}(t)$ is

$$\frac{df_{d,\mathbf{k}}^{(n)}}{dt} + J_d[f_{d,\mathbf{k}}^{(n)}] = \frac{e\mathbf{E}(t)}{\hbar} \cdot \frac{\partial f_{d,\mathbf{k}}^{(n-1)}}{\partial \mathbf{k}} - J_d[f_{od,\mathbf{k}}^{(n)}], \quad (3)$$

$$\frac{df_{od,\mathbf{k}}^{(n)}}{dt} + \frac{i}{\hbar} [H_{0\mathbf{k}}, f_{od,\mathbf{k}}^{(n)}] + J_{od}[f_{od,\mathbf{k}}^{(n)}] = \frac{e\mathbf{E}(t)}{\hbar} \cdot \frac{Df_{od,\mathbf{k}}^{(n-1)}}{D\mathbf{k}} - J_{od}[f_{d,\mathbf{k}}^{(n)}]. \quad (4)$$

The covariant derivative $Df_{od,\mathbf{k}}/D\mathbf{k} = (\partial f_{od,\mathbf{k}}/\partial \mathbf{k}) - i[\mathcal{R}_{\mathbf{k}}, f_{od,\mathbf{k}}]$ arises from the \mathbf{k} dependence of the basis functions. The Berry connection matrix elements $\mathcal{R}_{\mathbf{k}}^{mm'} = \langle u_{\mathbf{k}}^m | i(\partial u_{\mathbf{k}}^{m'}/\partial \mathbf{k}) \rangle$, with $|u_{\mathbf{k}}^m\rangle$ the lattice-periodic Bloch functions are interband matrix elements of the position operator [The full expression is $\mathbf{r}_{kk'}^{mm'} = i\delta^{mm'} \partial/\partial \mathbf{k} \delta(\mathbf{k} - \mathbf{k}') + \mathcal{R}_{\mathbf{k}}^{mm'} \delta(\mathbf{k} - \mathbf{k}')$. The covariant derivative term is absent in the equation for $f_{d,\mathbf{k}}$ because the commutator has no diagonal terms.], which also appear in the current density operator $\mathbf{j} = -(e/\hbar)DH_{0\mathbf{k}}/D\mathbf{k}$. We evaluate the nonlinear response in the limit $\varepsilon_F \tau/\hbar \gg 1$, where ε_F is the Fermi energy and τ the relaxation time, with $\tau_k^{-1} = \int d^2\mathbf{k}'/4\pi^2 \hbar |U_{kk'}^{\pm\pm}|^2 \delta(\varepsilon_{\mathbf{k}} - \varepsilon_{\mathbf{k}'})$.

The general solution of Eq. (1) up to second order in the electric field is derived in the Supplemental Material [69]. The linear response contains the oscillatory factors $e^{\pm i\omega t}$ as required for time-independent unperturbed Hamiltonians. The second order response has both second-harmonic term $\propto e^{\pm 2i\omega t}$, and the time-independent terms on which we focus in which the $e^{\pm i\omega t}$ factors cancel. In the strong disorder $\omega\tau \ll 1$ limit a clear hierarchy can be established in powers of the impurity density [70] which can be extended to nonlinear response [64]. In the weak disorder limit $\omega\tau \gg 1$, one naively expects scattering to play virtually no role. This is because, first, the cross-scattering terms $J_d(f_{od,\mathbf{k}})$ and $J_{od}(f_{d,\mathbf{k}})$ connecting $f_{d,\mathbf{k}}$ and $f_{od,\mathbf{k}}$ are suppressed by $1/\omega\tau$ and higher powers. Hence, it appears that $f_{d,\mathbf{k}}$ and $f_{od,\mathbf{k}}$ can be treated independently. Second, the leading term in $f_{d,\mathbf{k}}$ simply yields the Drude conductivity, which at high frequencies is $\propto 1/\omega$. We specialize here to frequencies $\omega\tau \gg 1$ and focus on systems in which the second harmonic terms are suppressed by factors $\propto (\omega\tau)^{-1}$ and higher, as is the case in Bi_2Te_3 with an in-plane magnetization [Fig. 3(a)].

Writing the current density as $j_i = \chi_{ijk} E_j E_k$, it is clear that the nonlinear response tensor χ_{ijk} must break both

time-reversal and mirror symmetry. The RPE arises primarily from the second-order off-diagonal response driven by the first-order off-diagonal response— $f_{\text{od},k}^{(2)}$ driven by $f_{\text{od},k}^{(1)}$. In linear response the off-diagonal part of the density matrix oscillates due to interband coupling, and this oscillation has a component that is in phase with the electric field. To second order in \mathbf{E} this produces a term with a nonzero time average, which is responsible for the RPE. One first takes the imaginary part of $f_{\text{od},k}^{(1)}$, breaking time reversal, and the real part of $f_{\text{od},k}^{(2)} \propto \tau$, which again breaks time reversal. Hence for the RPE to be nonzero the system itself needs to break time reversal.

Our theory includes all second-order contributions to the density matrix, and we identify the term that is primarily responsible for the peak in the RPE current, Fig. 3(a). For a two-band system with particle-hole symmetry the band index $m \in \{+, -\}$, as is the case for Bi_2Te_3 in Eq. (7) considered below, and $\varepsilon_{\mathbf{k}}^- = -\varepsilon_{\mathbf{k}}^+$, this yields the first contribution to the RPE current

$$j_{x,\text{od}}^{(2)} = \frac{e^3 E_x^2}{4\hbar} \int \frac{d^2k}{(2\pi)^2} \frac{|\mathcal{R}_{k_x}^{\pm}|^2 (\partial f_{\pm k}^0 / \partial k_x) (\hbar/\tau)}{(2\varepsilon_{\mathbf{k}}^{\pm} - \hbar\omega)^2 + (\hbar/\tau)^2}. \quad (5)$$

As $T \rightarrow 0$ the derivative of the Fermi function tends to $-\delta(\varepsilon_F - \varepsilon_{\mathbf{k}}^{\pm})$, so the RPE current becomes a Lorentzian centered around $\hbar\omega = 2\varepsilon_F$, as expected from Fig. 3(a). If we examine the value at the peak itself, setting $\hbar\omega = 2\varepsilon_F$ in the integrand, it is immediately seen that the integrand is $\propto \tau$, and $(\partial f_{\pm k}^0 / \partial k_x)\tau$ is the displacement of the Fermi surface. Noting that $\partial f_{\pm k}^0 / \partial k_x = (\partial f_{\pm k}^0 / \partial \varepsilon_{\mathbf{k}}) (\partial \varepsilon_{\mathbf{k}} / \partial k_x)$, it is clear that $2(\partial \varepsilon_{\mathbf{k}}^{\pm} / \partial k_x)\tau$ corresponds to the displacement undergone by a particle excited from a state in the valence band with group velocity $-(1/\hbar)(\partial \varepsilon_{\mathbf{k}}^+ / \partial k_x)$ to a state in the conduction band with group velocity $+(1/\hbar)(\partial \varepsilon_{\mathbf{k}}^+ / \partial k_x)$. Evidently, if Kramers degeneracy is present, so that $\varepsilon_{\mathbf{k}}^+ = \varepsilon_{-\mathbf{k}}^+$, the displacements cancel between opposite sides of the Fermi surface. So Kramers degeneracy needs to be broken for the effect to be finite. Formally the RPE peak is indistinguishable from a steady-state shift in the Fermi surface, whose magnitude depends on τ , as in the dc limit.

Importantly, disorder couples the diagonal and off-diagonal sectors of the density matrix, and this coupling enhances the RPE. An additional contribution arises when $f_{\text{od},k}^{(2)}$ is fed into the scattering term, whose diagonal part then acts as a driving term for $f_{d,k}^{(2)}$,

$$\begin{aligned} \frac{df_{d,k}^{(2)}}{dt} + J_d[f_{d,k}^{(2)}] &= -J_d[f_{\text{od},k}^{(2)}] \\ \Rightarrow j_{x,d}^{(2)} &= \frac{e\tau}{\hbar} \int \frac{d^2k}{(2\pi)^2} \frac{\partial \varepsilon_{\mathbf{k}}^+}{\partial k_x} J_d[f_{\text{od},k}^{(2)}]. \end{aligned} \quad (6)$$

This corresponds to interband transitions driven by scattering and demonstrates that, contrary to naive expectation,

scattering plays a crucial role in the dc current, as do the cross-scattering terms.

Resonant photovoltaic effect for warped topological insulator surface states.—Topological insulators (TI) such as Bi_2Te_3 can host strong spin-orbit torques [71–73], and produce strong spin-orbit coupling signatures in optics, transport and magnetism [74–93]. Time-reversal symmetry breaking in these systems Fig. 2 can be accomplished by placing the topological insulator on a ferromagnet, as sketched in Fig. 1(a). A sizable proximity effect can lead surface-state exchange fields parallel to the magnetization of order 10 meV [94,95]. The surface state Hamiltonian $H_0 = H_R + H_M + H_W$, where $H_R = A(\sigma_x k_y - \sigma_y k_x)$ is the Rashba spin-orbit interaction with A a material-specific constant, and the σ_i 's are Pauli matrices. The exchange term $H_M = \boldsymbol{\sigma} \cdot \mathbf{M}$ with magnetization $\mathbf{M} \parallel \hat{y}$. We will consider a nonlinear response to an electric field $\mathbf{E} \parallel \hat{x}$. The warping term $H_W = \lambda \sigma_z (k_x^3 - 3k_x k_y^2)$ having λ a warping constant describes hexagonal warping that causes the Fermi surface to acquire its well-known snowflake shape [96–99]. The quasiparticle energy dispersion is particle-hole symmetric with

$$\varepsilon_{\mathbf{k}}^{\pm} = \pm \sqrt{A^2 k^2 + M^2 + 2AkM \cos \theta + \lambda^2 k^6 \cos^2 3\theta}, \quad (7)$$

where $\theta = \arctan(k_y/k_x)$ is the polar angle of the wave-vector \mathbf{k} . The in-plane magnetization breaks Kramers degeneracy [Fig. 2(a)]. In Fig. 3(a) we have plotted the total RPE current as a function of photon energy $\hbar\omega$ at different warping constants and at $\varepsilon_F = 250$ meV. It has a sharp and tunable peak at $\hbar\omega = 2\varepsilon_F$, an attractive feature for infrared light detection.

Discussion.—The physical explanation of the RPE is as follows. For $\hbar\omega \ll 2\varepsilon_F$ no carriers can be excited into the conduction band. As $\hbar\omega$ approaches $2\varepsilon_F$ electrons can be excited from energy $-\varepsilon_F$ in the valence band to ε_F in the conduction band. The constant energy surface at $-\varepsilon_F$ in the valence band is not oscillating, while the Fermi surface ε_F

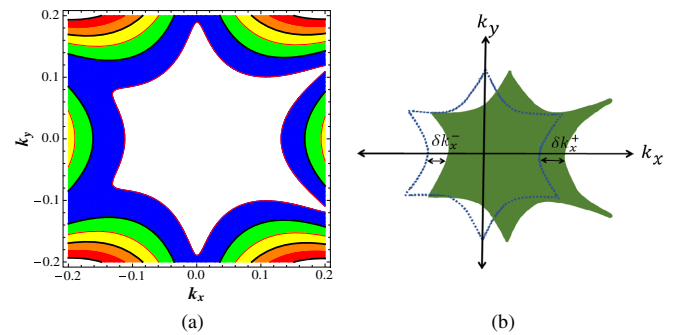


FIG. 2. (a) Constant energy contour showing the breaking of Kramers degeneracy by an in-plane magnetization, with $\lambda = 200$ eV \AA^3 and $M = 0.05$ eV. (b) Schematic picture showing the displacement of the hexagonally distorted Fermi surface.

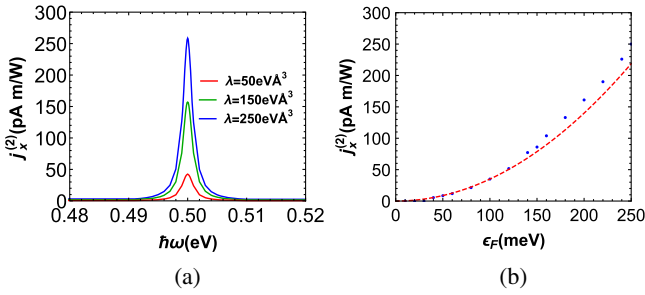


FIG. 3. (a) RPE for magnetized TI surface states with different warping coefficients λ using $\varepsilon_F = 250$ meV, $A = 2.55$ eV \AA , $T = 1$ K, $M = 10$ meV, $\tau = 1$ ps. Blue: experimental value of λ for Bi_2Te_3 . (b) Blue: peak value of RPE for $\lambda = 250$ eV \AA^3 as a function of ε_F in Bi_2Te_3 . Red: quadratic fit.

in the conduction band oscillates under the action of the ac electric field. Importantly, the Fermi surface is inversion asymmetric here due to the breaking of Kramers degeneracy by an in-plane magnetization. Hence, as the Fermi surface oscillates, its displacement along $+k_x$ is not equal to that along $-k_x$ Fig. 2(b), resulting in a net current. This current depends on the anomalous velocity, contained in the Berry connection, and on the momentum relaxation time τ . This effect occurs only for excitation around the Fermi surface, which explains the resonance in the signal. More importantly, if time reversal symmetry is preserved, Kramers degeneracy implies that $\varepsilon_k = \varepsilon_{-k}$, and the effect cancels between the two sides of the Fermi surface as the electric field oscillates along the \hat{x} axis. In the example given the in-plane magnetization breaks Kramers degeneracy, which can be seen clearly in Fig. 2, so that the positive and negative \hat{x} axes are not equivalent, and the effect does not cancel as the electric field oscillates in the positive and negative \hat{x} directions. In our model mirror-symmetry breaking comes about both due to warping and due to the magnetic field. Warping reduces the infinite numbers of mirror planes available in the Dirac Hamiltonian to three, while the in-plane magnetic field breaks mirror symmetry between x and $-x$. Without warping the in-plane magnetic field effect on a TI Dirac cone can be gauged away. The in-plane magnetic field thus fulfills a dual role: it breaks both time reversal and mirror symmetry. A tilt, which breaks time reversal and mirror symmetry, also gives rise to the RPE.

The RPE strengthens with ε_F , as shown in Fig. 3(b), with the degree of warping (λ) and the degree of asymmetry of the Fermi surface (M). The effect is correspondingly $\propto M$, and, at small λ (or small densities), it is $\propto \lambda^2$. Increasing λ distorts the Fermi contour from its original circular shape by a larger amount, increasing the current. Conversely, the effect vanishes as $\lambda \rightarrow 0$: as expected, trivially shifting the origin of the Dirac cone by an in-plane magnetization cannot generate a current without the presence of hexagonal warping. Likewise, since the effect is driven by Kramers

degeneracy breaking, increasing the in-plane magnetization leads to a larger peak. Increasing ε_F and/or the momentum relaxation time results in a larger Fermi surface displacement. The model we consider has particle-hole symmetry, and in this case the size of the peak at $2\varepsilon_F$ is determined by the scattering time τ . In high mobility systems the peak becomes sharper and taller, and can increase by orders of magnitude, which could be achieved by hybridizing TIs with graphene [100–104]. Current samples possess some degree of particle-hole asymmetry, which may be the ultimate factor determining the size of the RPE in experiment. For small particle-hole asymmetry our conclusions hold provided the asymmetry does not exceed \hbar/τ . At higher temperatures scattering must be taken into account. The complicated many-body terms that come in through the Pauli blocking factors will be considered in a future study. Likewise, our present study does not incorporate many-body interactions, which may alter the effect at a quantitative level as in linear response.

The RPE differs qualitatively from known nonlinear optical effects such as the shift current, as calculated in Ref. [31] for the same TI that we consider in this work, yet unmagnetized. The treatment in Ref. [31] is similar in spirit to Ref. [13]. The shift current appears in systems time-reversal symmetry. In Ref. [31] time-reversal symmetry is broken when the infinitesimal imaginary part of the response function is considered. The shift current is strong in an undoped system and, within the approximation scheme of Ref. [31], is independent of the light frequency ω . The shift current is captured in our formalism, and we have included in the Supplemental Material [69] a derivation of it in agreement with Ref. [31]. Importantly, the intrinsic shift current as calculated in Ref. [31] is zero in the configuration considered in this work, in which $\mathbf{E} \parallel \hat{x}$. The RPE is likewise qualitatively different from injection charge and spin currents as considered in Refs. [7] and [6] respectively, in which the dynamics of the Fermi surface does not play a part, while the Zeeman term creates an asymmetry between the electron and hole bands. (The injection currents derived in Refs. [6,7] can also be calculated using the density matrix formalism we present in this Letter.)

For experimental observation the TI layer should be as thin as possible so as to enable a strong proximity effect. Strictly speaking, our model applies to films thicker than 3 nm with no tunneling between the top and bottom surfaces [105,106]. Yet the effect will be very strong even in thinner films, and our model is still approximately applicable since ε_F is much larger than the interlayer tunneling strength. We expect a strong RPE in $\text{Bi}_{2-x}\text{Mn}_x\text{Te}_3$ synthesized recently [107–109]. If, instead of ferromagnetism, an in-plane magnetic field is used to break time reversal symmetry, in a geometry very similar to Ref. [72], the effect will be observable but relatively small due to the inherent smallness of the Bohr magneton.

The RPE can occur in conventional semiconductors, yet due to the large asymmetry between the valence and conduction bands and the smallness of the Fermi energy we expect it to be much weaker than in TIs.

In summary, we have developed the general formalism describing the second order optical response and identified a resonance in the dc photocurrent at $\hbar\omega = 2\varepsilon_F$ with a height and width determined by the relaxation timescale. The theory will be extended to second harmonic generation, circularly polarized light, and other materials such as transition metal dichalcogenides [110,111].

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