

Quantum kinetics of the magnetophotogalvanic effect

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Using the Keldysh technique, we derive a set of quasiclassical equations for Bloch electrons in noncentrosymmetric crystals upon excitation with quasimonochromatic radiation in the presence of external electrical and magnetic fields. These equations are the analog to the semiconductor-Bloch equations for the dynamics of electrons including the photogalvanic effect (PGE), in particular the shift mechanism. The shift PGE was recently identified as showing promise for the development of new photovoltaic materials. In addition, our theory may be useful to investigate the interplay between breaking time-reversal symmetry and topological properties as well as the analysis of recent local excitation experiments in nanophotonics. Explicit results for the photogalvanic tensors are presented for linear and circular polarized light and a magnetic field. In addition, we disprove existing statements that the shift-photogalvanic effect does not contribute to the photo-Hall current.

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I. INTRODUCTION

In noncentrosymmetric crystals a direct current can be induced upon the absorption of light under homogeneous conditions. This phenomenon was discovered more than 50 years ago, and it was termed the bulk photovoltaic effect (BPVE) or the photogalvanic effect (PGE; cf. Sturman and Fridkin [1]). As a result of two major discoveries the PGE recently gained an unprecedented boost: the discovery of ferroelectric perovskite materials [2] in 2009 as potentially relevant solar cell materials and the discovery of Weyl semimetals in 2015 with topologically protected states [3]. The underlying physics is intimately connected with the so-called shift mechanism (as described later). The aim of this paper is to work out a semiclassical theory for the PGE which is suited for numerical investigations including external electrical and magnetic fields.

The PGE depends on the properties of the material, applied fields, and the properties of the absorbed light. At first order in the light intensity and in an external magnetic field with induction \mathbf{B} , symmetry requires the following representation for the radiation-induced direct current (no static electrical field, neglecting photon momentum):

$$j_\alpha = I [P_{\alpha\mu\nu}^S(\omega) + R_{\alpha\beta\mu\nu}^S(\omega)B_\beta] \text{Re}(e_\mu^* e_\nu) + I [P_{\alpha\mu\nu}^A(\omega) + R_{\alpha\beta\mu\nu}^A(\omega)B_\beta] \text{Im}(e_\mu^* e_\nu), \quad (1)$$

where I is (local) intensity, ω is frequency, and e_μ is the (Cartesian) components of the (complex) unit polarization vector \mathbf{e} of the light. Indices $\alpha, \beta, \mu, \nu \in \{x, y, z\}$ indicate Cartesian components; an asterisk indicates complex conjugation. \mathbf{P}^S and \mathbf{P}^A denote polar tensors of rank 3, whereas \mathbf{R}^S and \mathbf{R}^A are of rank 4, with axial symmetry. Superscripts S and

A specify symmetry and antisymmetry with respect to polarization indices μ, ν , and their contributions are usually termed “linear” and “circular,” respectively [4]. \mathbf{P}^S is analogous to the piezotensor, whereas \mathbf{P}^A is equivalent to the (rank-2 axial) gyrotensor in gyrotropic media, and \mathbf{R}^A is equivalent to a polar tensor of rank 3 (see Birss [5]).

In the spirit of nonlinear optics [6], the photogalvanic (PG) current results from a quadratic term in the current-field relation. Standard second-order quantum mechanical response theory [7] revealed two different origins of the PGE: a “ballistic” (kinetic) mechanism and a “shift” mechanism. The ballistic PGE results from asymmetric optical transitions in cooperation with impurities or phonon scattering, which is described by the diagonal matrix elements of the density operator (with respect to a Bloch basis). The shift PGE, on the other hand, is a band structure property and results from the nondiagonal elements. It is intimately related to the Bloch representation of the position operator [8], which leads to a shift of Bloch wave packets in real space upon optical transitions [9–11]. The circular PGE (\mathbf{P}^A term) is invariant under time reversal, as opposed to the linear PGE (\mathbf{P}^S term), in which an external magnetic field breaks time reversal explicitly.

For linear polarized light, the shift-current contribution can be represented as (\mathbf{P}^S term, a reformulation of Eq. (19) of Ref. [9])

$$\begin{aligned} \mathbf{j}_{\text{PG}} &= \frac{I}{\hbar\omega} \frac{e^3}{4\pi^2 \omega m_0^2 \epsilon_0 c \eta} \int (f_{v,0} - f_{c,0}) \\ &\quad \times |\langle c, \mathbf{k} | \mathbf{e} \cdot \mathbf{p} | v, \mathbf{k} \rangle|^2 \mathbf{s}_{cv}(\mathbf{e}, \mathbf{k}) \\ &\quad \times \delta(E_c(\mathbf{k}) - E_v(\mathbf{k}) - \hbar\omega) d^3k, \end{aligned} \quad (2)$$

$$\mathbf{s}_{cv}(\mathbf{e}, \mathbf{k}) = \mathbf{X}_{vv}(\mathbf{k}) - \mathbf{X}_{cc}(\mathbf{k}) + \nabla_{\mathbf{k}} \Phi_{cv}(\mathbf{e}, \mathbf{k}), \quad (3)$$

$$\mathbf{X}_{mn}(\mathbf{k}) = \int i u_{m\mathbf{k}}^*(\mathbf{r}) \nabla_{\mathbf{k}} u_{n\mathbf{k}}(\mathbf{r}) d^3r, \quad (4)$$

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where $\Phi_{cv}(\mathbf{e}, \mathbf{k})$ is defined via the expression

$$\langle c, \mathbf{k} | \mathbf{e} \cdot \mathbf{p} | v, \mathbf{k} \rangle = i |\langle c, \mathbf{k} | \mathbf{e} \cdot \mathbf{p} | v, \mathbf{k} \rangle| e^{i \Phi_{cv}(\mathbf{e}, \mathbf{k})}. \quad (5)$$

$|n, \mathbf{k}\rangle$ denotes the Bloch states of (conduction and valence) bands [12] $n = c, v$ at wave vector \mathbf{k} , $E_n(\mathbf{k})$ is the band energy, and $u_{n\mathbf{k}}(\mathbf{r}) = \langle \mathbf{r} | n, \mathbf{k} \rangle$ is the lattice-periodic part of the Bloch function $\langle \mathbf{r} | n, \mathbf{k} \rangle$. $f_{n,0}(\mathbf{k})$ is the equilibrium Fermi function, m_0 is the free-electron mass, and e is the elementary charge. \mathbf{e} (real) denotes the polarization vector, and I is the local intensity of the radiation at frequency ω . η is the refractive index of the material, and integrals over r and k extend over the crystal unit cell and the Brillouin zone, respectively. Note that the shift current does not depend on the carrier mobility.

By construction, the shift vector $\mathbf{s}_{cv}(\mathbf{e}, \mathbf{k})$ is invariant with respect to phase transformations of the Bloch states; however, it depends on the polarization of the light, and therefore, it is not a genuine property of the material (in contrast to \mathbf{P}^S). Second-order quantum response theory was fully exploited by Sipe and collaborators [13], who developed a nowadays widely used approach to study nonlinear optical phenomena on a microscopic level, such as second-order-harmonic generation and the shift PGE. Results (3)–(5) are valid for only linear polarization, and they are implicitly contained in Ref. [13] [Eq. (58) and below, linear polarization of arbitrary direction]. The shift distance is comparable to the crystal unit cell [14,15] and may be even larger (e.g., CdSe: 0.4 nm, GaP: 0.9 nm).

Up to 2006 (to the best of our knowledge) there was only one band structure evaluation [14] of Eq. (2) which was performed for n -doped GaP. This material has been used as a fast and robust IR monitor [16]. First-principles band structure calculations were performed by Nastos and Sipe [15,17] for GaAs and GaP below and above the band gap and for CdSe and CdS. Young and Rappe [18] confirmed the shift mechanism as given by Eqs. (2)–(4) for some “old materials” like BaTiO₃ and KNbO₃ and claimed its key role in the high efficiency of the new ferroelectrics in solar energy conversion of up to 23% (see, e.g., Refs. [19–25]). Recent numerical studies have discovered new groups of promising materials with large shift contributions up to 20 times higher than previously known [26], e.g., the quasi-two-dimensional systems GeS [27] and MoS₂ [28], chiral materials [29], and materials using strain engineering [30].

It became obvious that the shift vector equation (3) is a Berry connection which provides a sensitive tool to analyze the topological nature of quantum states in the recently discovered Weyl semimetals (see, e.g., Refs. [31–34]). A recent revisit of the second-order optical response by Holder *et al.* [35] identified three different mechanisms to generate a dc current: the Berry curvature, a term closely related to the quantum metric, and the diabatic motion. Berry connections have also been recognized as relevant ingredients for the quasiclassical dynamics of Bloch electrons [36] and the anomalous Hall effect [37]. Other interesting phenomena and applications with relation to the shift mechanism are, e.g., (i) far infrared detectors in the form of semiconductor heterostructures [38], (ii) the shift vector as the geometrical origin of beam shifts [39], (iii) nanotubes [40], and (iv) twisted graphene bilayers [41].

By using the Keldysh technique we derive a set of quasiclassical equations for the PGE (Sec. II) upon (inhomogeneous) excitation and including external electrical and magnetic fields. Our theory relies on the following assumptions: (i) electron Bloch states are a relevant basis, (ii) scattering and recombination are treated on a phenomenological level, and (iii) electron-hole Coulomb interaction is neglected. Explicit results for the PG tensors are worked out in Sec. III. Section IV gives a summary and discussion, whereas Appendixes A–C contain technical details and an application to GaP.

II. QUANTUM KINETICS

The quantum kinetic theory of the PGE is based on a Hermitian matrix function \mathbf{f} with elements $f_{mn}(\mathbf{k}, \mathbf{R}, T)$ which describes the single-particle states of the crystal; m and n denote band indices. The arguments of \mathbf{f} are, besides the wave vector \mathbf{k} , the position vector \mathbf{R} and the time T . This theory is a generalization of the classical Boltzmann description; it includes, however, diagonal (local electron concentrations) as well as nondiagonal (nondissipative, coherent) contributions of the density operator.

The basic equations for \mathbf{f} are derived by using the Keldysh technique as formulated by Rammer and Smith [42]. This technique provides a consistent way to construct a quasiclassical description at finite temperatures; it uses solely gauge invariant quantities. External fields can easily be included, and applications are much simpler to work out than a full quantum mechanical treatment as in Eqs. (2)–(4).

A. Keldysh formulation

It is algebraically favorable to use a representation in which all Keldysh matrices have the Jordan normal form (Ref. [42], Sec. II B). For example the Green’s function $\hat{\mathbf{G}}$ reads

$$\hat{\mathbf{G}} = \begin{bmatrix} G^R & G^K \\ 0 & G^A \end{bmatrix}.$$

G^R and G^A denote the usual retarded and advanced Green’s functions, and G^K is the Keldysh function, which plays a crucial role in this formulation,

$$\begin{aligned} G^R(\mathbf{R}, T; \mathbf{r}, t) &= +\theta(t) \{G^>(\mathbf{R}, T; \mathbf{r}, t) - G^<(\mathbf{R}, T; \mathbf{r}, t)\}, \\ G^A(\mathbf{R}, T; \mathbf{r}, t) &= -\theta(-t) \{G^>(\mathbf{R}, T; \mathbf{r}, t) - G^<(\mathbf{R}, T; \mathbf{r}, t)\}, \\ G^K(\mathbf{R}, T; \mathbf{r}, t) &= G^>(\mathbf{R}, T; \mathbf{r}, t) + G^<(\mathbf{R}, T; \mathbf{r}, t). \end{aligned}$$

All these functions are special combinations of the Kadanoff-Baym functions $G^<$ and $G^>$ (Ref. [42], Secs. II A and II B, and [43]),

$$G^<(\mathbf{R}, T; \mathbf{r}, t) = +i \langle \langle \psi^+(\mathbf{r}_2, t_2) \psi(\mathbf{r}_1, t_1) \rangle \rangle, \quad (6)$$

$$G^>(\mathbf{R}, T; \mathbf{r}, t) = -i \langle \langle \psi(\mathbf{r}_1, t_1) \psi^+(\mathbf{r}_2, t_2) \rangle \rangle. \quad (7)$$

$\psi(\mathbf{r}_1, t_1)$ and $\psi^+(\mathbf{r}_2, t_2)$ are the electron field operators in the Heisenberg picture. $\mathbf{R} = (\mathbf{r}_1 + \mathbf{r}_2)/2$ and $T = (t_1 + t_2)/2$ denote a “center-of-mass” coordinate and a “mean” time, respectively. In addition relative variables $\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2$ and $t = t_1 - t_2$ will be needed. $\langle \langle \dots \rangle \rangle$ corresponds to the grand-canonical ensemble average (at finite temperatures).

Our starting point is—as laid out by Sipe and Shkreptii [13]—an independent particle description with the Hamiltonian

$$H(\mathbf{r}, \mathbf{p}, t) = \frac{(\mathbf{p} - q\mathbf{A})^2}{2m_0} + V(\mathbf{r}) + q\Phi. \quad (8)$$

\mathbf{p} denotes the canonical momentum, $V(\mathbf{r})$ is the periodic crystal potential, and m_0 and q are the mass and charge ($q = -e$) of the electrons. $\mathbf{A} = \mathbf{A}(\mathbf{r}, t)$ and $\Phi = \Phi(\mathbf{r}, t)$ are the vector and scalar potentials of the radiation and external (classical) electromagnetic field, $\mathbf{A} = \mathbf{A}_{\text{rad}} + \mathbf{A}_{\text{cl}}$, $\text{div}\mathbf{A} = 0$. In the following, we assume that the energies $E_n(\mathbf{k})$ and Bloch states $|n, \mathbf{k}\rangle$ of the electrons are known from a band structure calculation ($\mathbf{A} = \Phi = 0$).

The photogalvanic effect is independent of photon momentum [see Eq. (1)]. Therefore, the magnetic field of the radiation can be neglected; that is, $\mathbf{A}_{\text{rad}}(\mathbf{r}, t)$ can be approximated by a position-independent field (equivalent to the electrical dipole approximation), $\mathbf{A}_{\text{rad}}(t)$, $\Phi_{\text{rad}} = 0$. Regrouping the remaining terms in Eq. (8), we obtain

$$H(\mathbf{r}, \mathbf{p}, t) = H_{\text{cl}}(\mathbf{r}, \mathbf{p}, t) + H_{\text{int}}(\mathbf{r}, \mathbf{p}, t), \quad (9)$$

$$H_{\text{cl}}(\mathbf{r}, \mathbf{p}, t) = \frac{(\mathbf{p} - q\mathbf{A}_{\text{cl}})^2}{2m_0} + V(\mathbf{r}) + q\Phi_{\text{cl}}, \quad (10)$$

$$H_{\text{int}}(\mathbf{r}, \mathbf{p}, t) = -\frac{q}{m_0}[\mathbf{p} - q\mathbf{A}_{\text{cl}}(\mathbf{r}, t)]\mathbf{A}_{\text{rad}}(t). \quad (11)$$

Radiation will be treated in terms of a photon propagator; additionally, \mathbf{A}_{cl} enters as a vertex operator.

In thermal equilibrium ($\mathbf{A} = \Phi = 0$) the Green's functions (6) and (7) can be represented in terms of Bloch functions of Eq. (8) ($\mathbf{A} = \Phi = 0$),

$$\hat{\mathbf{G}}_0(\mathbf{R}; \mathbf{r}, t) = \sum_{n, \mathbf{k}} \left\langle \mathbf{R} + \frac{\mathbf{r}}{2} \middle| n, \mathbf{k} \right\rangle \hat{\mathbf{g}}_{n,0}(\mathbf{k}, t) \left\langle n, \mathbf{k} \middle| \mathbf{R} - \frac{\mathbf{r}}{2} \right\rangle, \quad (12)$$

where

$$\hat{\mathbf{g}}_{n,0} = \begin{bmatrix} -i\theta(t) e^{-iE_n t} & -i[1 - 2f_{n,0}(\mathbf{k})] e^{-iE_n t} \\ 0 & i\theta(-t) e^{-iE_n t} \end{bmatrix}. \quad (13)$$

$f_{n,0}(\mathbf{k})$ denotes the Fermi function. Here and in the following, units are used where $\hbar = 1$.

The radiation field will be treated as an external quasichlassical field with no internal dynamics; that is, there exists only a contribution to the Keldysh component of the photon Green's function $\hat{\mathbf{D}}$,

$$D_{\mu\nu}^K(t) = -i \frac{I}{\omega^2 \epsilon_0 c \eta} (e_\mu e_\nu^* e^{-i\omega t} + \text{c.c.}). \quad (14)$$

For a derivation, see Appendix A.

The equation of motion for $\hat{\mathbf{G}}$ is identical to the Dyson equation,

$$\hat{\mathbf{G}}_{\text{cl}}^{-1} \otimes \hat{\mathbf{G}} = \delta(\mathbf{r})\delta(t)\hat{\mathbf{1}} + \hat{\Sigma} \otimes \hat{\mathbf{G}}, \quad (15)$$

$$\hat{\mathbf{G}}_{\text{cl}}^{-1} = [i\partial_{t_1} - H_{\text{cl}}(\mathbf{r}_1, \mathbf{p}_1, t_1)] \hat{\mathbf{1}}. \quad (16)$$

\otimes means matrix multiplication, H_{cl} stands for Eq. (10), and $\hat{\Sigma}$ denotes the electron-photon self-energy, which is calculated using $\hat{\mathbf{D}}$ from Eq. (14), with $-\frac{q}{m_0}(\mathbf{p} - q\mathbf{A}_{\text{cl}})$ being the vertex operator (Ref. [42], Sec. II C).

B. Kinetic equations

In order to set up a quasiclassical description the following (standard) approximation for the Green's function with inclusion of the external electromagnetic field is made [44]:

$$\begin{aligned} \hat{\mathbf{G}}(\mathbf{R}, T; \mathbf{r}, t) &= \sum_{n, n', \mathbf{k}} \left\langle \mathbf{R} + \frac{\mathbf{r}}{2} \middle| n, \mathbf{k} \right\rangle \hat{\mathbf{g}}_{nn'}(\mathbf{R}, T; \mathbf{k}, t) \\ &\times \left\langle n', \mathbf{k} \middle| \mathbf{R} - \frac{\mathbf{r}}{2} \right\rangle e^{iq[\mathbf{r}\mathbf{A}_{\text{cl}}(\mathbf{R}, T) - t\Phi_{\text{cl}}(\mathbf{R}, T)]}, \end{aligned} \quad (17)$$

where

$$\hat{\mathbf{g}}_{nn'}(\mathbf{R}, T; \mathbf{k}, t) = \begin{bmatrix} g_{nn'}^R & g_{nn'}^K \\ 0 & g_{nn'}^A \end{bmatrix}.$$

Here, $I(\mathbf{R}, T)$, $\mathbf{A}_{\text{cl}}(\mathbf{R}, T)$ [$\mathbf{B} = \nabla \times \mathbf{A}_{\text{cl}}(\mathbf{R}, T)$] and $\Phi_{\text{cl}}(\mathbf{R}, T)$ [$\mathbf{E} = -\partial_T \mathbf{A}_{\text{cl}}(\mathbf{R}, T) - \nabla \Phi_{\text{cl}}(\mathbf{R}, T)$] denote classical macroscopic fields which are assumed to be constant on atomic scales so that Bloch functions are still a suitable basis and will be noticeable only in $\hat{\mathbf{g}}_{nn'}$. The phase factor $e^{iq\mathbf{r}\mathbf{A}_{\text{cl}}(\mathbf{R}, T)}$ takes into account the phase shift induced by a vector potential \mathbf{A}_{cl} along the direct path of the particle from \mathbf{r}_2 to \mathbf{r}_1 and reduces the contribution of the diamagnetic part $q\mathbf{A}_{\text{cl}}$ in the vertex operator $-\frac{q}{m_0}(\mathbf{p} - q\mathbf{A}_{\text{cl}})$. Likewise, $e^{-iqt\Phi_{\text{cl}}(\mathbf{R}, T)}$ collects the local shifts of the energy levels due to an electrical potential $\Phi_{\text{cl}}(\mathbf{R}, T)$.

Observable quantities such as the charge current density \mathbf{j}_q are calculated with the aid of the Keldysh component ($G^K(\mathbf{R}, t; \mathbf{r}, t)$), averaged over the volume of an elementary cell, of Eq. (17):

$$\mathbf{j}_q(\mathbf{R}, T) = -i \frac{q}{m_0} \left(\frac{1}{i} \nabla_{\mathbf{r}} - q\mathbf{A}_{\text{cl}} \right) \langle G^K(\mathbf{R}, T; \mathbf{r}, t) \rangle_{|\mathbf{r}=0, t=0},$$

where the spin factor of 2 is already included here. Using the definition $f_{nn'}(\mathbf{R}, T; \mathbf{k}) = \frac{1}{2i} g_{nn'}^K(\mathbf{R}, T; \mathbf{k}, t=0)$, the charge current density becomes, in terms of \mathbf{f} ,

$$\mathbf{j}_q(\mathbf{R}, T) = \frac{2q}{m_0 V} \sum_{n, n', \mathbf{k}} f_{nn'}(\mathbf{R}, T, \mathbf{k}) \langle n', \mathbf{k} | \mathbf{p} | n, \mathbf{k} \rangle. \quad (18)$$

V is the volume of the crystal.

We are looking for the current contribution which is linear in the intensity (quadratic in the electric field); therefore, only the ‘‘turtle’’ photon self-energy diagram [45] is needed. For the Feynman rules see Ref. [42] [Eqs. (2.39)–(2.43)]. Moreover, only the anti-Hermitian parts of the self-energies $\hat{\Sigma}$ (photons and phonons) will be taken into account because these describe irreversible processes that occur as a consequence of the absorption processes. Hermitian parts of $\hat{\Sigma}$, on the contrary, describe band-renormalization effects which can be safely neglected [46].

The basic equations for $f_{nn'}$ are obtained from the Dyson equation by subtracting its adjoint, [$\dots = \dots$], and performing the integral transformation (Ref. [42], Sec. II E):

$$\begin{aligned} &-\frac{1}{2} \int d^3 R \int d^3 r \left\langle n, \mathbf{k} \middle| \mathbf{R} + \frac{\mathbf{r}}{2} \right\rangle \left\langle \mathbf{R} - \frac{\mathbf{r}}{2} \middle| n', \mathbf{k} \right\rangle \\ &\times e^{-iq[\mathbf{r}\mathbf{A}_{\text{cl}}(\mathbf{R}, T) - t\Phi_{\text{cl}}(\mathbf{R}, T)]} [\dots = \dots]. \end{aligned}$$

\mathbf{R} and \mathbf{r} integrations extend over a unit cell and the whole crystal, respectively. Eventually, the relative time t is set equal to zero. As the result, we obtain diagonal elements $f_n = f_{nn}$:

$$(\partial_T + q\mathbf{E} \cdot \nabla_{\mathbf{k}})f_n(\mathbf{R}, T; \mathbf{k}) + \nabla_{\mathbf{R}} \cdot \mathbf{j}_n(\mathbf{R}, T; \mathbf{k}) + q\mathbf{B} \cdot [\nabla_{\mathbf{k}} \times \mathbf{j}_n(\mathbf{R}, T; \mathbf{k})] = G_n^{(0)}(\mathbf{R}, T; \mathbf{k}) + \delta G_n^{(\mathbf{B})}(\mathbf{R}, T; \mathbf{k}) + I_{n,pn} + I_{n,r}. \quad (19)$$

This is a modified Boltzmann equation for the distribution function f_n of band n . The total particle current density $\mathbf{j}_n(\mathbf{R}, T; \mathbf{k})$ in the drift and acceleration terms acts as the driving term,

$$\mathbf{j}_n(\mathbf{R}, T; \mathbf{k}) = \frac{1}{2m_0} \sum_{n'} [\langle n, \mathbf{k} | \mathbf{p} | n', \mathbf{k} \rangle f_{n'n}(\mathbf{R}, T; \mathbf{k}) + \text{H.c.}] = \mathbf{v}_n(\mathbf{k}) f_n(\mathbf{R}, T; \mathbf{k}) + \mathbf{j}_n^{\text{ND}}(\mathbf{R}, T; \mathbf{k}). \quad (20)$$

$G_n^{(0)}$, $\delta G_n^{(\mathbf{B})}$, $I_{n,pn}$, and $I_{n,r}$ will be defined below.

In Eq. (20), the particle current density is decomposed in terms of a kinetic and a “nondiagonal” contribution \mathbf{j}_n^{ND} [see Eq. (26) below]. The latter corresponds to the particle shift–current density of the state \mathbf{k} in the band n and is only different from zero if absorption of radiation causes an interband transition.

We also obtain nondiagonal elements $f_{nn'}$ ($n \neq n'$):

$$i[E_n(\mathbf{k}) - E_{n'}(\mathbf{k})] f_{nn'}(\mathbf{R}, T; \mathbf{k}) = G_{nn'}^{(0)}(\mathbf{R}, T; \mathbf{k}) + \delta G_{nn'}^{(\mathbf{B})}(\mathbf{R}, T; \mathbf{k}) + \delta G_{nn'}^{(\mathbf{E})}(\mathbf{R}, T; \mathbf{k}). \quad (21)$$

These elements are determined by a comparatively simple equation because there is a dominant term $[i(E_n - E_{n'}) f_{nn'}]$ on the left side of this equation, in light of which all others ($\partial_T f_{nn'}$, $q\mathbf{E} \cdot \nabla_{\mathbf{k}} f_{nn'}$, etc.) can safely be neglected. In order to get a closed set of equations, the particle current density \mathbf{j}_n and the generation matrix $G_{nn'}$ have still to be specified.

The generation matrix $G_{nn'}(\mathbf{R}, T; \mathbf{k})$ consists of the exclusively intensity dependent part $G_{nn'}^{(0)}$ with diagonal elements $G_n^{(0)} = G_{nn}^{(0)}$ and the parts $\delta G_{nn'}^{(\mathbf{B})}$ and $\delta G_{nn'}^{(\mathbf{E})}$ which depend linearly on \mathbf{B} and \mathbf{E} , respectively. The latter parts stem from the phase factor in Eq. (17), and their diagonal elements $\delta G_n^{(\mathbf{B})}$ and $\delta G_n^{(\mathbf{E})}$ are all equal to zero [dependence on $(\mathbf{R}, T; \mathbf{k})$ is suppressed]. In addition, there is a contribution $\delta G_n^{(\mathbf{B}, dia)}$ from the diamagnetic part of the vertex operator to Eq. (19) which is exploited in Appendix B.

$I_{n,pn}$ describes the momentum relaxation (e.g., by phonon collisions), and $I_{n,r}$ describes thermalization and recombination. As $G_{nn'}$ is a Hermitian matrix, it is conveniently written in the form

$$G_{nn'}(\mathbf{k}) = \bar{G}_{nn'}(\mathbf{k}) + \text{H.c.} \quad (22)$$

There are three contributions to the generation rate $G_{nn'}$:

$$\begin{aligned} \bar{G}_{nn'}^{(0)}(\mathbf{R}, T; \mathbf{k}) &= I(\mathbf{R}, T) \frac{\pi q^2}{2\omega^2 m_0^2 \epsilon_0 c \eta} \sum_{\substack{n_1 \\ \Omega = \pm\omega}} [f_{n_1,4,0}(\mathbf{k}) - f_{n',0}(\mathbf{k})] \delta[E_{n_1}(\mathbf{k}) - E_{n'}(\mathbf{k}) - \Omega] \\ &\times \langle n, \mathbf{k} | p_\mu | n_1, \mathbf{k} \rangle \langle n_1, \mathbf{k} | p_\nu | n', \mathbf{k} \rangle e_{\mu,\Omega}^* e_{\nu,\Omega}, \end{aligned} \quad (23)$$

$$\begin{aligned} \delta \bar{G}_{nn'}^{(\mathbf{B})}(\mathbf{R}, T; \mathbf{k}) &= I(\mathbf{R}, T) \frac{\pi q^3}{4\omega^2 m_0^2 \epsilon_0 c \eta} \sum_{\substack{n_1, n_2 \\ \Omega = \pm\omega}} ([\nabla_{\mathbf{Q}_1} \times \nabla_{\mathbf{Q}_2}]_\beta \{ [f_{n_2,0}(\mathbf{k} + \mathbf{Q}_2) - f_{n_1,0}(\mathbf{k} + \mathbf{Q}_1)] \delta[E_{n_2}(\mathbf{k} + \mathbf{Q}_2) - E_{n_1}(\mathbf{k} + \mathbf{Q}_1) - \Omega] \\ &\times \langle n, \mathbf{k} | p_\mu + k_\mu | n_1, \mathbf{k} + \mathbf{Q}_1 \rangle \langle n_1, \mathbf{k} + \mathbf{Q}_1 | p_\nu + k_\nu | n_2, \mathbf{k} + \mathbf{Q}_2 \rangle \langle n_2, \mathbf{k} + \mathbf{Q}_2 | n', \mathbf{k} \rangle (1 - \delta_{n,n'}) \}) B_\beta \frac{1}{i} e_{\mu,\Omega}^* e_{\nu,\Omega}, \end{aligned} \quad (24)$$

$$\begin{aligned} \delta \bar{G}_{nn'}^{(\mathbf{E})}(\mathbf{R}, T; \mathbf{k}) &= I(\mathbf{R}, T) \frac{\pi q^3}{4\omega^2 m_0^2 \epsilon_0 c \eta} \sum_{\substack{n_1 \\ \Omega = \pm\omega}} (\nabla_{\mathbf{Q},\alpha} \{ [f_{n',0}(\mathbf{k} + \mathbf{Q}) - f_{n_1,0}(\mathbf{k} + \mathbf{Q})] \partial_\Omega \delta[E_{n_1}(\mathbf{k} + \mathbf{Q}) - E_{n'}(\mathbf{k} + \mathbf{Q}) + \Omega] \\ &\times \langle n, \mathbf{k} | p_\mu + k_\mu | n_1, \mathbf{k} + \mathbf{Q} \rangle \langle n_1, \mathbf{k} + \mathbf{Q} | p_\nu + k_\nu | n', \mathbf{k} \rangle \}) E_\alpha \frac{1}{i} e_{\mu,\Omega}^* e_{\nu,\Omega}. \end{aligned} \quad (25)$$

After differentiation, the vectors \mathbf{Q} , \mathbf{Q}_1 , and \mathbf{Q}_2 have to be set to zero. The expressions $\langle n_1, \mathbf{k}_1 | \dots | n_2, \mathbf{k}_2 \rangle$ are matrix elements, which are calculated with respect to the lattice-periodic parts of the Bloch functions, and $e_{\mu,\omega} = e_\mu$ and $e_{\mu,-\omega} = e_\mu^*$ are the components of the complex-valued polarization vector.

\mathbf{j}_n^{ND} is obtained from Eq. (20) with $\bar{G}_{nn'}^{(0)}$ from Eq. (23):

$$\mathbf{j}_{n,\alpha}^{\text{ND}}(\mathbf{R}, T; \mathbf{k}) = \frac{1}{m_0} \sum_{m \neq n} \text{Im} \left(\frac{\langle n, \mathbf{k} | p_\alpha | m, \mathbf{k} \rangle \bar{G}_{mn}^{(0)}(\mathbf{R}, T; \mathbf{k}) + \bar{G}_{nm}^{(0)*}(\mathbf{R}, T; \mathbf{k}) \langle m, \mathbf{k} | p_\alpha | n, \mathbf{k} \rangle}{E_m - E_n} \right) \quad (26)$$

$$= I(\mathbf{R}, T) \frac{\pi e^2}{2\omega^2 m_0^3 \epsilon_0 c \eta} \sum_{\substack{m \neq n, n_1 \\ \Omega = \pm\omega}} [(f_{n_1,0} - f_{n,0}) \delta(E_{n_1} - E_n - \Omega) + (f_{n_1,0} - f_{m,0}) \delta(E_{n_1} - E_m - \Omega)] \quad (27)$$

$$\times \left[\operatorname{Im} \left(\frac{\langle n, \mathbf{k} | p_\alpha | m, \mathbf{k} \rangle \langle m, \mathbf{k} | p_\mu | n_1, \mathbf{k} \rangle \langle n_1, \mathbf{k} | p_\nu | n, \mathbf{k} \rangle}{E_m - E_n} \right) \operatorname{Re}(e_{\mu, \Omega}^* e_{\nu, \Omega}) \right] \quad (28)$$

$$+ \operatorname{Re} \left(\frac{\langle n, \mathbf{k} | p_\alpha | m, \mathbf{k} \rangle \langle m, \mathbf{k} | p_\mu | n_1, \mathbf{k} \rangle \langle n_1, \mathbf{k} | p_\nu | n, \mathbf{k} \rangle}{E_m - E_n} \right) \operatorname{Im}(e_{\mu, \Omega}^* e_{\nu, \Omega}) \Big]. \quad (29)$$

The term (28) is an even function of \mathbf{k} that contributes to \mathbf{P}^S , Eq. (32), whereas the odd term (29) does not.

III. DERIVATION OF THE PG TENSORS

As an application of the kinetic theory we verify the result (2) for \mathbf{P}^S and give the representations of the other PG tensors \mathbf{P}^A , \mathbf{R}^S , and \mathbf{R}^A as defined by Eq. (1). The following assumptions are made: (i) there is no external electrical field, (ii) there is external magnetic field \mathbf{B} , and the (monochromatic) radiation intensity I is constant in space and time so that $f_{nn'}$ does not depend on (\mathbf{R}, T) . Under these assumptions the kinetic equations (19)–(21) become

$$n = n': q\mathbf{B} \cdot [\nabla_{\mathbf{k}} \times \mathbf{j}_n(\mathbf{k})] = G_n^{(0)}(\mathbf{k}) - \frac{f_n(\mathbf{k}) - \langle f_n(\mathbf{k}) \rangle_E}{\tau_n} + I_{n,r}, \quad (30)$$

$$n \neq n': i[E_n(\mathbf{k}) - E_{n'}(\mathbf{k})] f_{nn'}(\mathbf{k}) = G_{nn'}^{(0)}(\mathbf{k}) + \delta G_{nn'}^{(B)}(\mathbf{k}). \quad (31)$$

In addition, Eqs. (20) and (26)–(29) will be needed. To simplify matters, the collision operator $I_{n,pm}$ was replaced within a relaxation time approximation. $\langle f_n(\mathbf{k}) \rangle_E$ denotes the average of the distribution function over a surface of constant energy, and τ_n is the relaxation time for each band n ; numerical values are taken from experiment. The operator $I_{n,r}$

which ensures thermalization and recombination is assumed to be only energy dependent. Obviously, the PG current solely stems from $f_{nn'}(\mathbf{k})$ terms which are asymmetric with respect to \mathbf{k} , $\delta f_{nn'}(\mathbf{k}) = -\delta f_{nn'}^*(-\mathbf{k})$, which in turn originate from generation terms with $\delta G_n(\mathbf{k}) = -\delta G_n(-\mathbf{k})$ and $\delta G_{nn'}(\mathbf{k}) = \delta G_{nn'}^*(-\mathbf{k})$. Therefore, only such terms will be considered when deriving representations for the tensors.

A. Tensor \mathbf{P}^S

Linearly polarized light and $\mathbf{B} = 0$ are implied in Eqs. (30) and (31). The relevant contributions of the state function are

$$n = n': \delta f_n = 0, \\ n \neq n': \delta f_{nn'} = \frac{G_{nn'}^{(0)}(\mathbf{k})}{i[E_n(\mathbf{k}) - E_{n'}(\mathbf{k})]}.$$

The corresponding PG-current density \mathbf{j}_{PG} is determined from Eq. (26) by summation over all states (including the spin factor of 2),

$$\mathbf{j}_{PG} = \frac{2q}{V} \sum_{n,\mathbf{k}} \mathbf{j}_n^{\text{ND}}(\mathbf{k}),$$

which is performed along the route described in Refs. [9,11]. As a result, we obtain [12]

$$P_{\alpha\mu\nu}^S = \frac{e^3}{4\pi^2 \omega^2 m_0^2 \epsilon_0 c \eta} \int_{1.BZ} d^3k (f_{v,0} - f_{c,0}) \delta[E_c(\mathbf{k}) - E_v(\mathbf{k}) - \omega] \\ \times \left\{ \frac{1}{2} \operatorname{Im}[(\nabla_{\mathbf{k},\alpha} \langle c, \mathbf{k} | p_\nu | v, \mathbf{k} \rangle) \langle v, \mathbf{k} | p_\mu | c, \mathbf{k} \rangle - \langle c, \mathbf{k} | p_\nu | v, \mathbf{k} \rangle (\nabla_{\mathbf{k},\alpha} \langle v, \mathbf{k} | p_\mu | c, \mathbf{k} \rangle)] \right. \\ \left. + \operatorname{Re}[\langle c, \mathbf{k} | p_\nu | v, \mathbf{k} \rangle \langle v, \mathbf{k} | p_\mu | c, \mathbf{k} \rangle] [X_{vv,\alpha} - X_{cc,\alpha}] \right\}. \quad (32)$$

Equation (32) is identical to Eq. (2), as can be checked by decomposing $\mathbf{e} \cdot \mathbf{p}$ into components.

B. Tensor \mathbf{P}^A

Circularly polarized light and $\mathbf{B} = 0$ are implied in Eqs. (30) and (31). The relevant contribution of the state function to determine \mathbf{P}^A is

$$n = n': \delta f_n = \tau_n \delta G_n^{(0)}(\mathbf{k}), \quad (33)$$

$$n \neq n': \delta f_{nn'} = 0. \quad (34)$$

$\delta G_n^{(0)}(\mathbf{k})$ is the part of the generation rate $G_n^{(0)}(\mathbf{k})$ given by Eqs. (22) and (23),

$$\delta G_n^{(0)}(\mathbf{k}) = I \frac{\pi q^2}{\omega^2 m_0^2 \epsilon_0 c \eta} \sum_{\substack{n' \\ \Omega = \pm \omega}} [f_{n,0}(\mathbf{k}) - f_{n',0}(\mathbf{k})] \delta[E_{n'}(\mathbf{k}) - E_n(\mathbf{k}) - \Omega] \\ \times \operatorname{Im}(\langle n, \mathbf{k} | p_\mu | n', \mathbf{k} \rangle \langle n', \mathbf{k} | p_\nu | n, \mathbf{k} \rangle) \operatorname{Im}(e_{\mu, \Omega}^* e_{\nu, \Omega}). \quad (35)$$

Insertion of Eqs. (33) and (35) into Eq. (18) leads to

$$j_{\alpha}^{\text{circ}} = \frac{2q}{V} \sum_{\substack{n=v,c \\ \mathbf{k}}} v_{n,\alpha}(\mathbf{k}) \delta f_n(\mathbf{k}), \quad (36)$$

and the tensor element $P_{\alpha\mu\nu}^A$ reads

$$P_{\alpha\mu\nu}^A = \frac{e^3}{4\pi^2 \omega^2 m_0^2 \epsilon_0 c \eta} \sum_{\substack{n',n \\ \Omega=\pm\omega}} \int_{1.BZ} d^3k [f_{n',0}(\mathbf{k}) - f_{n,0}(\mathbf{k})] \delta[E_{n'}(\mathbf{k}) - E_n(\mathbf{k}) - \Omega] \\ \times \tau_n v_{n,\alpha}(\mathbf{k}) (\delta_{v,n} + \delta_{c,n}) \text{Im}(\langle n, \mathbf{k} | p_{\mu} | n', \mathbf{k} \rangle \langle n', \mathbf{k} | p_{\nu} | n, \mathbf{k} \rangle) \text{sgn}(\Omega). \quad (37)$$

Performing the sums over Ω , n and n' , we obtain [12]

$$P_{\alpha\mu\nu}^A = \frac{e^3}{4\pi^2 \omega^2 m_0^2 \epsilon_0 c \eta} \int_{1.BZ} d^3k [f_{v,0}(\mathbf{k}) - f_{c,0}(\mathbf{k})] \delta[E_c(\mathbf{k}) - E_v(\mathbf{k}) - \omega] \\ \times [\tau_c v_{c,\alpha}(\mathbf{k}) - \tau_v v_{v,\alpha}(\mathbf{k})] \text{Im}(\langle v, \mathbf{k} | p_{\mu} | c, \mathbf{k} \rangle \langle c, \mathbf{k} | p_{\nu} | v, \mathbf{k} \rangle). \quad (38)$$

In contrast to the linear PGE (\mathbf{P}^S term) the circular PGE is ballistic as only diagonal elements of the state function contribute and it depends on the scattering times of the (hot) photogenerated carriers.

C. Tensor \mathbf{R}^S

Linearly polarized light and $\mathbf{B} \neq 0$ are implied in Eqs. (30) and (31). The relevant contributions of the state function are

$$n = n': \quad \delta f_n = -q \tau_n \mathbf{B} \cdot [\nabla_{\mathbf{k}} \times \mathbf{j}_n(\mathbf{k})], \quad (39)$$

$$n \neq n': \quad \delta f_{nn'} = \frac{G_{nn'}^{(0)}(\mathbf{k})}{i[E_n(\mathbf{k}) - E_{n'}(\mathbf{k})]}. \quad (40)$$

The first equation describes the portion of the charge current density which is deflected by the magnetic field, analogous to the Hall effect. The current density $\mathbf{j}_n(\mathbf{k})$ is inserted from Eq. (20), and the contribution of Eq. (40) is used therein as the driving term. The resulting charge current density \mathbf{j}^{Hall} reads

$$j_{\alpha}^{\text{Hall}} = \frac{2q}{V} \sum_{\substack{n=v,c \\ \mathbf{k}}} v_{n,\alpha}(\mathbf{k}) \delta f_n(\mathbf{k}) = \frac{-2q^2}{V} B_{\beta} \epsilon_{\beta\gamma\delta} \sum_{\substack{n=v,c \\ \mathbf{k}}} v_{n,\alpha}(\mathbf{k}) \tau_n \nabla_{\mathbf{k},\gamma} j_{n,\delta}^{\text{ND}}(\mathbf{k}), \\ j_{\alpha}^{\text{Hall}} = \frac{2q^2}{V} B_{\beta} \epsilon_{\beta\gamma\delta} \sum_{\substack{n=v,c \\ \mathbf{k}}} \nabla_{\mathbf{k},\gamma} [v_{n,\alpha}(\mathbf{k}) \tau_n] j_{n,\delta}^{\text{ND}}(\mathbf{k}). \quad (41)$$

Inserting Eqs. (27) and (28) into Eq. (41), we get for the tensor element $R_{\alpha\beta\mu\nu}^S$ the expression

$$R_{\alpha\beta\mu\nu}^S = \frac{e^4}{16\pi^2 \omega^2 m_0^3 \epsilon_0 c \eta} \epsilon_{\beta\gamma\delta} \sum_{\substack{m \neq n, n_1 \\ n, \Omega=\pm\omega}} \int_{1.BZ} d^3k [f_{n_1,0}(\mathbf{k}) - f_{n,0}(\mathbf{k})] \delta[E_{n_1}(\mathbf{k}) - E_n(\mathbf{k}) - \Omega] \\ \times \{ \nabla_{\mathbf{k},\gamma} [\tau_n v_{n,\alpha}(\mathbf{k}) (\delta_{v,n} + \delta_{c,n}) + \tau_m v_{m,\alpha}(\mathbf{k}) (\delta_{v,m} + \delta_{c,m})] \} \\ \times \text{Im} \left(\frac{\langle n, \mathbf{k} | p_{\delta} | m, \mathbf{k} \rangle \langle m, \mathbf{k} | p_{\mu} | n_1, \mathbf{k} \rangle \langle n_1, \mathbf{k} | p_{\nu} | n, \mathbf{k} \rangle}{E_m - E_n} + \text{terms with } \mu \text{ and } \nu \text{ interchanged} \right). \quad (42)$$

Performing all sums [12] leads to \mathbf{R}^S :

$$R_{\alpha\beta\mu\nu}^S = \frac{e^4}{16\pi^2 \omega^2 m_0^3 \epsilon_0 c \eta} \epsilon_{\beta\gamma\delta} \int_{1.BZ} d^3k [f_{v,0}(\mathbf{k}) - f_{c,0}(\mathbf{k})] \delta[E_c(\mathbf{k}) - E_v(\mathbf{k}) - \omega] \\ \times \left\{ [\nabla_{\mathbf{k},\gamma} \tau_n v_{c,\alpha}(\mathbf{k})] \left[-\text{Im}(\langle v, \mathbf{k} | p_{\nu} | c, \mathbf{k} \rangle \langle c, \mathbf{k} | \mathcal{R}_{\delta}^{\dagger} p_{\mu} | v, \mathbf{k} \rangle) + \frac{v_{c,\mu}}{\omega} \text{Im}(\langle v, \mathbf{k} | p_{\nu} | c, \mathbf{k} \rangle \langle c, \mathbf{k} | p_{\delta} | v, \mathbf{k} \rangle) \right] \right. \\ \left. + [\nabla_{\mathbf{k},\gamma} \tau_v v_{v,\alpha}(\mathbf{k})] \left[-\text{Im}(\langle v, \mathbf{k} | p_{\nu} | c, \mathbf{k} \rangle \langle c, \mathbf{k} | p_{\mu} \mathcal{R}_{\delta} | v, \mathbf{k} \rangle) - \frac{v_{v,\mu}}{\omega} \text{Im}(\langle v, \mathbf{k} | p_{\nu} | c, \mathbf{k} \rangle \langle c, \mathbf{k} | p_{\delta} | v, \mathbf{k} \rangle) \right] \right. \\ \left. + \text{all terms with } \mu \text{ and } \nu \text{ interchanged} \right\}. \quad (43)$$

\mathcal{R} is the shift operator [9,11]; in position representation,

$$\mathcal{R}_{n,\mathbf{k}}(\mathbf{r}) = \langle \mathbf{r} | \mathcal{R} | n, \mathbf{k} \rangle = e^{i\mathbf{k}\mathbf{r}} \{ \nabla_{\mathbf{k}} + i\mathbf{X}_{nn}(\mathbf{k}) \} u_{n\mathbf{k}}(\mathbf{r}).$$

The shift operator \mathcal{R} is of importance when photogalvanic current densities are described by the nondiagonal elements of the state function \mathbf{f} . In particular, the shift vector (3) can be expressed as

$$\mathbf{s}_{cv}(\mathbf{e}, \mathbf{k}) = \frac{\text{Im}(\langle c, \mathbf{k} | \mathcal{R}^\dagger \mathbf{e} \mathbf{p} + \mathbf{e} \mathbf{p} \mathcal{R} | v, \mathbf{k} \rangle \langle v, \mathbf{k} | \mathbf{e} \mathbf{p} | c, \mathbf{k} \rangle)}{\langle v, \mathbf{k} | \mathbf{e} \mathbf{p} | c, \mathbf{k} \rangle \langle c, \mathbf{k} | \mathbf{e} \mathbf{p} | v, \mathbf{k} \rangle}. \quad (44)$$

The elements of \mathbf{R}^S show almost the same ω dependence as those of \mathbf{P}^S , and as a rule of thumb, $|\mathbf{R}^S| \approx |\mathbf{P}^S| \cdot \mu$ may be expected, where μ is the mobility of the (hot) photocarriers.

Result (43) is completed by the diamagnetic contribution (B3),

$$R_{\alpha\beta\mu\nu}^{S,\text{dia}} = \frac{e}{\omega m_0} \epsilon_{\beta\nu\gamma} P_{\alpha\mu\gamma}^A.$$

D. Tensor \mathbf{R}^A

Circularly polarized light and $\mathbf{B} \neq 0$ are implied in Eqs. (30) and (31). The relevant contributions are

$$n = n': \quad \delta f_n = -q\tau_n \mathbf{B} \cdot [\nabla_{\mathbf{k}} \times (\tau_n \mathbf{v}_n \delta G_n^{(0)})], \quad (45)$$

$$n \neq n': \quad \delta f_{nn'} = \frac{\delta G_{nn'}^{(\mathbf{B})}(\mathbf{k})}{i[E_n(\mathbf{k}) - E_{n'}(\mathbf{k})]}. \quad (46)$$

Equation (45) describes the deflection of the ballistic charge current density Eq. (36) by the magnetic field and is present only—like \mathbf{P}^A —in gyrotropic media, whereas the contribution (46) is directly related to the change in the generation matrix by the external magnetic field \mathbf{B} . Therefore, \mathbf{R}^A consists of two contributions,

$$\mathbf{R}^A = \mathbf{R}^{A,\text{bal}} + \mathbf{R}^{A,\text{shift}}. \quad (47)$$

1. Tensor $\mathbf{R}^{A,\text{bal}}$

Equation (45) is equivalent to Eq. (39). Following the same route as taken by Eqs. (41) and (43) and using Eq. (35), we arrive at [12]

$$R_{\alpha\beta\mu\nu}^{A,\text{bal}} = \frac{e^4}{4\pi^2 \omega^2 m_0^2 \epsilon_0 c \eta} \epsilon_{\beta\gamma\delta} \int_{1.BZ} d^3k [f_{v,0}(\mathbf{k}) - f_{c,0}(\mathbf{k})] \delta[E_c(\mathbf{k}) - E_v(\mathbf{k}) - \omega] \\ \times \{ \tau_v v_{v,\delta}(\mathbf{k}) [\nabla_{\mathbf{k},\gamma} \tau_v v_{v,\alpha}(\mathbf{k})] - \tau_c v_{c,\delta}(\mathbf{k}) [\nabla_{\mathbf{k},\gamma} \tau_c v_{c,\alpha}(\mathbf{k})] \} \text{Im}(\langle v, \mathbf{k} | p_\mu | c, \mathbf{k} \rangle \langle c, \mathbf{k} | p_\nu | v, \mathbf{k} \rangle). \quad (48)$$

2. Tensor $\mathbf{R}^{A,\text{shift}}$

The corresponding current density is

$$j_\alpha^{ND,\mathbf{B}} = \frac{4q}{m_0} \sum_{\substack{n,n' \\ n \neq n'}} \frac{1}{(2\pi)^3} \int_{1.BZ} \text{Im} \left(\frac{\langle n, \mathbf{k} | p_\alpha | n', \mathbf{k} \rangle \delta \bar{G}_{n'n}^{(\mathbf{B})}(\mathbf{k})}{E_{n'} - E_n} \right) d^3k. \quad (49)$$

Inserting $\delta \bar{G}_{n'n}^{(\mathbf{B})}(\mathbf{k})$ from Eq. (24) and regrouping terms, we get

$$j_\alpha^{ND,\mathbf{B}} = I \frac{e^4}{16\pi^2 \omega^2 m_0^3 \epsilon_0 c \eta} \sum_{\substack{n_1, n_2 \\ \Omega = \pm\omega}} \int_{1.BZ} d^3k ([\nabla_{\mathbf{Q}1} \times \nabla_{\mathbf{Q}2}]_\beta \{ [f_{n_2,0}(\mathbf{k} + \mathbf{Q}_2) - f_{n_1,0}(\mathbf{k} + \mathbf{Q}_1)] \\ \times \delta[E_{n_2}(\mathbf{k} + \mathbf{Q}_2) - E_{n_1}(\mathbf{k} + \mathbf{Q}_1) - \Omega] \text{sgn}(\Omega) M_{\alpha\mu\nu}^{n_1 n_2}(\mathbf{k}, \mathbf{Q}_1, \mathbf{Q}_2) \}) B_\beta \text{Im}(e_\mu^* e_\nu), \quad (50)$$

with

$$M_{\alpha\mu\nu}^{n_1 n_2}(\mathbf{k}, \mathbf{Q}_1, \mathbf{Q}_2) = \sum_{\substack{n, n' \\ n \neq n'}} \text{Im} \left\{ (n, \mathbf{k} | n_2, \mathbf{k} + \mathbf{Q}_2) (n_2, \mathbf{k} + \mathbf{Q}_2 | p_\nu + k_\nu | n_1, \mathbf{k} + \mathbf{Q}_1) \right. \\ \left. \times \frac{(n_1, \mathbf{k} + \mathbf{Q}_1 | p_\mu + k_\mu | n', \mathbf{k}) (n', \mathbf{k} | p_\alpha + k_\alpha | n, \mathbf{k})}{E_n - E_{n'}} - \text{all terms with } \mu \text{ and } \nu \text{ interchanged} \right\} \\ = m_0 \sum_n \text{Im} \{ (n, \mathbf{k} | n_2, \mathbf{k} + \mathbf{Q}_2) (n_2, \mathbf{k} + \mathbf{Q}_2 | p_\nu + k_\nu | n_1, \mathbf{k} + \mathbf{Q}_1) (n_1, \mathbf{k} + \mathbf{Q}_1 | (p_\mu + k_\mu) \mathcal{R}_\alpha | n, \mathbf{k}) \\ - \text{all terms with } \mu \text{ and } \nu \text{ interchanged} \}. \quad (51)$$

In expression (51) we have used the representation of the shift operator \mathcal{R} with respect to the lattice-periodic part of the Bloch functions, $\langle \mathbf{r} | \mathcal{R} | n, \mathbf{k} \rangle = [\nabla_{\mathbf{k}} + i\mathbf{X}_{nn}(\mathbf{k})] u_{n\mathbf{k}}(\mathbf{r})$.

As a result, we obtain [12]

$$\begin{aligned} R_{\alpha\beta\mu\nu}^{A,\text{shift}} = & \frac{e^4}{16\pi^2 \omega^2 m_0^3 \epsilon_0 c \eta} \int_{1.BZ} d^3k ([\nabla_{\mathbf{Q}_1} \times \nabla_{\mathbf{Q}_2}]_{\beta} \{ [f_{v,0}(\mathbf{k} + \mathbf{Q}_1) - f_{c,0}(\mathbf{k} + \mathbf{Q}_2)] \\ & \times \delta[E_c(\mathbf{k} + \mathbf{Q}_2) - E_v(\mathbf{k} + \mathbf{Q}_1) - \omega] [M_{\alpha\mu\nu}^{cv}(\mathbf{k}, \mathbf{Q}_2, \mathbf{Q}_1) - M_{\alpha\mu\nu}^{vc}(\mathbf{k}, \mathbf{Q}_1, \mathbf{Q}_2)] \}). \end{aligned} \quad (52)$$

After differentiation, the vectors \mathbf{Q}_1 and \mathbf{Q}_2 have to be set to zero. Due to the differentiations with respect to \mathbf{Q}_1 and \mathbf{Q}_2 , even an approximate evaluation of the tensor elements of \mathbf{R}^A requires details of the band structure [$E_n(\mathbf{k})$ and momentum matrix elements], at least at a symmetry point \mathbf{k}_0 where the optical transition occurs. If the bands are isotropic near \mathbf{k}_0 , the cross-product operation $(\nabla_{\mathbf{Q}_1} \times \nabla_{\mathbf{Q}_2})$, whose terms are exclusively dependent on \mathbf{Q}_i via the energy $E(\mathbf{k} + \mathbf{Q}_i)$, does not contribute. We therefore expect warped energy bands as a favorite ingredient for the circular shift magneto-PGE.

IV. SUMMARY AND DISCUSSION

We have developed a systematic semiclassical description of the PGE within the Kadanoff-Baym-Keldysh technique which ensures gauge invariance as well as particle conservation from the beginning. In addition, band-renormalization terms (Hermitian parts of the self-energies $\hat{\Sigma}$) are identified, and external (slowly varying) electric and magnetic fields are included. This approach is based on a Boltzmann-type equation for the diagonal elements of the state operator and captures nondiagonal contributions by simple algebraic equations, similar to the well-known semiconductor-Bloch equations [47] (but without Coulomb interaction).

In our approach, the PGE is a band structure property of the noncentrosymmetric crystal, and the photogalvanic current is caused by the absorption of light in combination with (symmetric) scattering by phonons and impurities. Sections III A–III D gave explicit results for the tensors \mathbf{P}^S , \mathbf{P}^A , \mathbf{R}^S , and \mathbf{R}^A . Here, only the case of an external magnetic field was considered because the influence of an electrical field on the PGE was studied recently in detail by Fregoso [48]. Not included are (i) asymmetric scattering terms, (ii) the magnetic field dependence of scattering, and (iii) transitions from bound impurity states. Result (32) for \mathbf{P}^S is identical to the known result of Eq. (2) and serves as a check, and we also gave results for \mathbf{P}^A , \mathbf{R}^S , and \mathbf{R}^A . Here, \mathbf{P}^A , Eq. (38), is equivalent to Eq. (29) of Holder *et al.* [35,49]. Implementation of the p -matrix elements within density functional theory (DFT) calculations is described in Ref. [50]. Appendix C provides a numerical application to GaP.

For linear polarization there are several examples which clearly demonstrate that the magnitude and spectral structure are dominated by the shift mechanism: (i) n -GaP [14] (pseudopotential theory) and (ii) BaTiO₃ [18,51] (DFT includes the calculated phonon spectrum and electron-phonon couplings). In both cases, there is almost perfect agreement with experiment [16,52]; nevertheless, asymmetric phonon contributions cannot be excluded in general. For GaAs a purely ballistic theory gave a good overall description, but the predicted spectrum differed from that observed [53]. For a critique of the

shift mechanism as a main source of the PGE see Sturman [54].

Nonlocal aspects of the PGE are usually neglected but have shown up in connection with the analysis of volume-phase holograms in ferroelectrics [55]. Such phenomena are captured by the semiclassical description, Eqs. (19)–(21), and may become relevant for optical nanodevices, as recently studied by local photoexcitation [56], and are under discussion in connection with spatiotemporal quantum pumping by femtosecond light pulses [57].

Quantum kinetic descriptions for the PGE were implicitly used in several previous publications, e.g., [10]; Deyo *et al.* [58] worked out a semiclassical theory of nonlinear transport and the PGE but only the influence of electric and magnetic fields on the scattering probabilities were considered, and recently, Kral [59] presented a quasiclassical description of the PGE for the problem of electron pumping in semiconductors. Barik and Sau [60] showed that the PGE/BPVE can be attributed to the dipole moment of the photogenerated excitons, which resembles the difference [$X_{vv,\alpha} - X_{cc,\alpha}$] in Eq. (32). An attempt for a systematic theory in terms of the Kadanoff-Baym-Keldysh technique was undertaken by one of the present authors in Ref. [61].

There are several numerical studies of the shift vector $\mathbf{s}_{cv}(\mathbf{e}, \mathbf{k})$ as well as an analytic estimate to find optimal parameters (concerning band structure and polarization directions) for the PG response [18,62]. These investigations, however, are based on a simplified version of the shift vector (3) with restricted combinations of the current and light-polarization components (see discussion around Eq. (58) in Ref. [13]). To overcome such restrictions, we have worked out the general coordinate-free form of the shift vector given by Eqs. (2)–(4).

In an external magnetic field \mathbf{B} , the currents described by \mathbf{P}^S and \mathbf{P}^A are deflected like Hall currents, which result in ballistic contributions described by \mathbf{R}^S (proportional to the mobility) and $\mathbf{R}^{A,\text{bal}}$ [proportional to the square of the mobility; see Eqs. (40) and (45)]. In addition, \mathbf{R}^A includes a shift contribution $\mathbf{R}^{A,\text{shift}}$, which is related to the influence of magnetic field \mathbf{B} on the generation matrix $G_{mn}(\mathbf{k})$. Concerning the experimental situation, we refer to the work of Fridkin and his group [1,63]. For tellurium theoretical and experimental studies were carried out by Ivchenko *et al.* [64,65]. However, application of their theoretical results in first-principles calculations does not seem to be straightforward.

The Hall property of the linear PGE in a magnetic field (described by \mathbf{R}^S) has been used to determine the mobility of photogenerated charge carriers [53,63,66]. Very large mobilities have been reported: $0.5 \times 10^6 \text{ cm}^2/\text{V s}$ (4.2 K) for GaAs, approximately $6000 \text{ cm}^2/\text{V s}$ for piezoelectric Bi₁₂GeO₂₀ (point group 23), and up to $1900 \text{ cm}^2/\text{V s}$ (room temperature) for ferroelectric BaTiO₃ (point group $4mm$). The analysis of

the measurements is based on the standard Hall formula,

$$\mathbf{j}^{\text{Hall}} = \mu \mathbf{j}^{(0)} \times \mathbf{B}, \quad (53)$$

which stems from a Drude-type description and holds under isotropic conditions. For $\text{Bi}_{12}\text{GeO}_{20}$ the PG current without magnetic field $\mathbf{j}^{(0)}$ is strongest just below the gap (3.2 eV) and is believed to originate from impurity transitions into the conduction band; that is, it is of the ballistic type. Hence, Eq. (53) is a suitable basis for the experimental analysis. For BaTiO_3 , however, the PGE is mainly due to interband transitions [18,51,52], so that Eq. (53) is not appropriate, even if $\mu_c \gg \mu_v$ [compare Eq. (32) with (43)].

The idea to separate shift and ballistic contributions of the PG current by using a magnetic field in combination with linearly and circularly polarized light has been pursued by Fridkin and collaborators (see, e.g., Ref. [63]) and, more recently, by Burger *et al.* [67,68] for $\text{Bi}_{12}\text{GeO}_{20}$ and $\text{Bi}_{12}\text{SiO}_{20}$. Their analysis, however, is based on the assumption that the shift mechanism does not contribute to the photo Hall current (“ j_{sh} describes coherence between wave packets rather than a transport process” [68]), which is at odds with our results given by Eqs. (41) and (49). It also contradicts a previous result of Ref. [65] [their formula (13)]. Moreover, in these studies the PG current is due to (ballistic) impurity transitions and does not originate from interband transitions, which are the origin of the shift mechanism [69].

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APPENDIX A: PHOTON GREEN'S FUNCTION

The Keldysh Green's function $\mathbf{D}_{\mu\nu}$ for photons has the usual Jordan normal form, and each matrix element is a polar tensor of rank 2. We start from (Ref. [42], Sec. II A)

$$D_{\mu\nu}^<(\mathbf{r}_1, t_1; \mathbf{r}_2, t_2) = -i \langle\langle A_\nu(\mathbf{r}_2, t_2) A_\mu(\mathbf{r}_1, t_1) \rangle\rangle. \quad (\text{A1})$$

$A_\mu(\mathbf{r}_j, t_j)$ ($j = 1, 2$) denotes the (Hermitian) vector potential (field operator) of the radiation, and μ and ν refer to the polarization of the photons. $D_{\mu\nu}^>(\mathbf{r}_1, t_1; \mathbf{r}_2, t_2) = D_{\nu\mu}^<(\mathbf{r}_2, t_2; \mathbf{r}_1, t_1)$;

the other photon-correlation functions are defined in the same way as for the electrons.

As thermal radiation at ambient temperature plays no role, radiation is described as a classical external field of a single mode. Its quantum analog is a coherent state $|\alpha\rangle$, $a|\alpha\rangle = \alpha|\alpha\rangle$, $\langle\langle \dots \rangle\rangle \rightarrow \langle\alpha| \dots |\alpha\rangle$. a and a^\dagger denote destruction and creation operators of the mode, $aa^\dagger - a^\dagger a = 1$. $\alpha = |\alpha| \exp(i\phi)$ is a complex number, where $|\alpha|^2$ is the mean photon number of the mode which is proportional to the light intensity.

The vector potential operator reads

$$A_\mu(\mathbf{r}_j, t_j) = \sqrt{\frac{1}{2\epsilon\epsilon_0 V}} \frac{1}{\omega} (e_\mu a e^{i(\mathbf{q}\mathbf{r}_j - \omega t_j)} + \text{H.c.}),$$

where \mathbf{q} , $\omega = \omega(\mathbf{q})$, and \mathbf{e} denote the wave vector, frequency, and polarization vector of the mode. $\epsilon = \eta^2$ is the dielectric constant of the medium, and V is the volume of the cavity (periodic boundary conditions are implied; see, e.g., Louisell [70], Sec. 4.3). To simplify notation mode indices have been suppressed.

The phase ϕ of the radiation is a statistical quantity; hence, terms in (A1) containing $\alpha^2 = \langle\alpha|a^2|\alpha\rangle$ vanish upon averaging on ϕ [the same thing happens for $(\alpha^*)^2$, equally distributed phases on $0, \dots, 2\pi$]. Apart from a very small difference of $|\alpha|^2$ and $|\alpha|^2 + 1$, $D_{\mu\nu}^<(\mathbf{r}, t)$ and $D_{\mu\nu}^>(\mathbf{r}, t)$ become equal and depend only on $\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2$, $t = t_1 - t_2$. As a result, the retarded and advanced D vanish, and the Keldysh component becomes

$$D_{\mu\nu}^K(\mathbf{r}, t) = -i \frac{I}{\omega^2 \epsilon_0 c \eta} (e_\mu e_\nu^* e^{i(\mathbf{q}\mathbf{r} - \omega t)} + \text{c.c.}). \quad (\text{A2})$$

As the light wavelength is much larger than the crystal unit cell, we may approximate $e^{\pm i\mathbf{q}\mathbf{r}} \rightarrow 1$ (the dipole approximation, neglecting the photon-drag effect). This is result (14).

APPENDIX B: DIAMAGNETIC CONTRIBUTION TO THE TENSOR \mathbf{R}^S

In the velocity gauge there is a (small) “diamagnetic” contribution from the vertex operator $\frac{q^2}{m_0} \mathbf{A}_{\text{cl}}$ to the generation matrix $G_{mn'}$, which is usually neglected. In linear order with respect to \mathbf{B} , this contribution reads

$$\begin{aligned} \delta G_n^{(\mathbf{B}, \text{dia})}(\mathbf{k}) &= I \frac{\pi q^3}{\omega^3 m_0^3 \epsilon_0 c \eta} B_\beta \epsilon_{\beta\nu\gamma} \sum_{\substack{n' \\ \Omega = \pm\omega}} [f_{n',0}(\mathbf{k}) - f_{n,0}(\mathbf{k})] \delta[E_{n'}(\mathbf{k}) - E_n(\mathbf{k}) - \Omega] \text{sgn}(\Omega) \\ &\times \{ \text{Re}(\langle n, \mathbf{k} | p_\mu | n', \mathbf{k} \rangle \langle n', \mathbf{k} | p_\nu | n, \mathbf{k} \rangle) \text{Im}(e_{\mu,\Omega}^* e_{\nu,\Omega}) + \text{Im}(\langle n, \mathbf{k} | p_\mu | n', \mathbf{k} \rangle \langle n', \mathbf{k} | p_\nu | n, \mathbf{k} \rangle) \text{Re}(e_{\mu,\Omega}^* e_{\nu,\Omega}) \}. \quad (\text{B1}) \end{aligned}$$

This result is obtained in the same way as $G_n^{(0)}$ in Eqs. (22) and (23) by taking into account the terms linear in \mathbf{B} in the product of the matrix elements $\langle n, \mathbf{k} | p_\mu - \frac{q}{2}(\mathbf{B} \times \mathbf{r})_\mu | n', \mathbf{k} \rangle$ $\langle n', \mathbf{k} | p_\nu - \frac{q}{2}(\mathbf{B} \times \mathbf{r})_\nu | n, \mathbf{k} \rangle$ of the vertex operator. Note that the phase factor contained in the approximation (17) is responsible for transforming the gauge-dependent field \mathbf{A}_{cl} into the gauge-independent term $\frac{1}{2} \mathbf{B} \times \mathbf{r}$ in the vertex operator. Subsequently, the matrix element of the position operator \mathbf{r} is replaced by that of the momentum operator \mathbf{p} using the identity $\langle n, \mathbf{k} | \mathbf{r} | m, \mathbf{k} \rangle = \frac{1}{i m_0} \langle n, \mathbf{k} | \mathbf{p} | m, \mathbf{k} \rangle / [E_n(\mathbf{k}) - E_m(\mathbf{k})]$, which holds for $E_n(\mathbf{k}) \neq E_m(\mathbf{k})$. Moreover, only odd terms in \mathbf{k} contribute, i.e., terms containing $\text{Im}(\langle n, \mathbf{k} \dots n, \mathbf{k} \rangle) \text{Re}(e_{\mu,\Omega}^* e_{\nu,\Omega})$, giving a contribution to \mathbf{R}^S but

not to \mathbf{R}^A . Following the same route as for \mathbf{P}^A [see Eqs. (33)–(37)], we obtain

$$R_{\alpha\beta\mu\nu}^{S,\text{dia}} = I \frac{q^4}{4\pi^2 \omega^3 m_0^3 \epsilon_0 c \eta} \epsilon_{\beta\nu\gamma} \sum_{\substack{n',n \\ \Omega=\pm\omega}} \int_{1.BZ} d^3k [f_{n',0}(\mathbf{k}) - f_{n,0}(\mathbf{k})] \delta[E_{n'}(\mathbf{k}) - E_n(\mathbf{k}) - \Omega] \\ \times \tau_n v_{n,\alpha}(\mathbf{k}) (\delta_{v,n} + \delta_{c,n}) \text{Im}(\langle n, \mathbf{k} | p_\mu | n', \mathbf{k} \rangle \langle n', \mathbf{k} | p_\nu | n, \mathbf{k} \rangle) \text{sgn}(\Omega). \quad (\text{B2})$$

Remarkably, result (B2) can be linked to \mathbf{P}^A by Eq. (37),

$$R_{\alpha\beta\mu\nu}^{S,\text{dia}} = \frac{e}{\omega m_0} \epsilon_{\beta\nu\gamma} P_{\alpha\mu\gamma}^A. \quad (\text{B3})$$

Hence, diamagnetic contributions to \mathbf{R}^S exist only in nongyrotropic media, yet a different spectral dependence may be expected.

For a crude estimate we consider parabolic valence and conduction bands and disregard the angular dependence of \mathbf{k} in Eqs. (B2) and (43). Near the energy gap Δ , we have

$$|\mathbf{R}^{S,\text{dia}}| \approx |\mathbf{R}^S| \left(1 - \frac{\Delta}{\omega}\right), \quad \omega \geq \Delta.$$

This result supports the usual approximation to neglect the diamagnetic contribution near the gap. Nevertheless, it should be taken into account in numerical calculations covering a wide frequency range.

APPENDIX C: NUMERICAL APPLICATION TO GaP

The expressions for the response coefficients, Eqs. (32), (38), (43), (48), and (52), involve band energies and momentum matrix elements which are directly available or can be obtained from band structure calculations. With respect to the shift mechanism, n -doped GaP is a particularly favorable system. Optical transitions occur from the bottom of the conduction band (near the X point) to the next upper band which is separated by a small gap of $\Delta = 355$ meV. The latter is solely due to the noninversion symmetry of the crystal. Previous calculations [14] for the absorption coefficient and linear photogalvanic tensor component P_{xyz} proved to be in almost perfect agreement with experimental results.

GaP belongs to the symmetry group $\bar{4}3m$. For \mathbf{P}^S there is only a single independent element, P_{xyz} , whereas \mathbf{P}^A vanishes identically because GaP is nongyrotropic. In this symmetry, a fourth-rank axial tensor has three independent components, which are R_{xxyy}^S , R_{xyxy}^S , and R_{xyxy}^A .

To keep the presentation simple, we use the results for GaP from a local pseudopotential calculation [14]. The conduction band and next upper band near the X point are nondegenerate, and there are six pockets with equal occupation. Band energies are modeled analytically, whereas the \mathbf{k} dependence of the momentum matrix elements [14] will be neglected. $\langle c, \mathbf{k} | p_\nu | c^*, \mathbf{k} \rangle$ ($\nu \hat{=} x, y$) is solely different from zero in the pockets on the \mathbf{k}_x and \mathbf{k}_y axes. At room temperature the electron system for $n = 2.4 \times 10^{16} \text{ cm}^{-3}$ is nondegenerate.

Within this approximation (rotationally symmetric energy surfaces) R_{xxyy}^S vanishes, whereas R_{xyxy}^S is nonvanishing, and a momentum relaxation time of $\tau = 5.0 \times 10^{-14} \text{ s}$ has been assumed.

To determine $R_{xyxy}^{A,\text{shift}}$, the \mathbf{Q}_i derivatives ($i = 1, 2$) have first to be calculated. The dominant contribution results from a sum of products whose two factors are first derivatives with respect to \mathbf{Q}_i . One factor contains the Fermi functions and the δ function, while the second factor results from products of matrix elements $M_{xy}^{vc/cv}$. The \mathbf{Q}_i derivatives of the latter are determined using $\mathbf{k} \cdot \mathbf{p}$ perturbation theory. There is no contribution from $\mathbf{R}^{A,\text{bal}}$ because GaP is nongyrotropic, $R_{xyxy}^A = R_{xyxy}^{A,\text{shift}}$. Numerical results are displayed in Fig. 1. The comparatively small numerical values for R_{xxyy}^S and R_{xyxy}^A are due to the low electron concentration n .

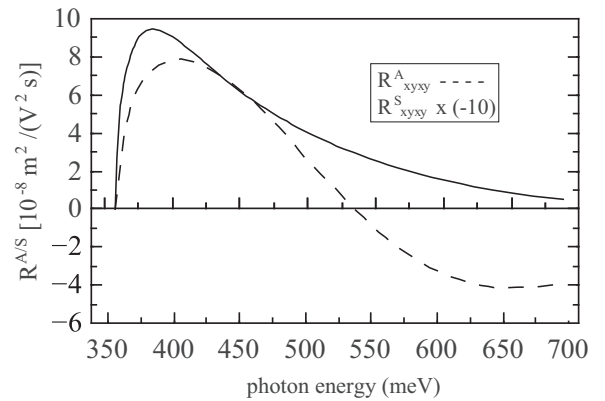


FIG. 1. Tensor components R_{xyxy}^A and R_{xyxy}^S .

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