Bulk photospin effect

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We compute the electric spin susceptibility of Bloch electrons with spin-orbit coupling to second order. We find that it is possible to generate a nonequilibrium spin polarization in the bulk of non-magnetic inversion-symmetric materials using linearly polarized electric fields, but the process depends on interband coherence and produces heating. It may be possible to avoid heating with circular polarization in certain scenarios. The standard Edelstein effect and spin orientation effects are recovered in appropriate limits within the formalism. Finally, the electric spin susceptibility of metals has contributions proportional to spin multipole moments of the Fermi sea that dominate the low frequency spin response.

I. INTRODUCTION AND MAIN RESULTS

An electric field can exert torque on an electron’s spin through the field of the ions. This spin-orbit coupling (SOC) can be large in materials that break inversion symmetry. The idea of using electric fields to establish a nonequilibrium spin polarization has been extensively explored.\textsuperscript{1\textendash}15 The subsequent evolution of the spin ensemble and the path to reach equilibrium is determined by the balance between spin-injection and spin-relaxation processes. Manipulation of an individual electron’s spin or spin ensembles could potentially find applications ranging from information storage to energy-efficient electronics and quantum computation.\textsuperscript{6,13}

In the presence of a static $E_0$ and an optical $E$ electric field, we can expand the time-independent (dc) spin polarization in powers of the electric fields as

$$\mathbf{S}_{dc} = \zeta^{(1)}_e E_0 + \zeta^{(2)}_e E_0^2 + \zeta^{(2)}_{bpse} E^2 + \cdots,$$

where $\zeta^{(1)}_e$ is the linear dc spin susceptibility, $\zeta^{(2)}_e$ is the quadratic dc spin susceptibility, and $\zeta^{(2)}_{bpse}$ is the bulk photospin effect (BPSE) susceptibility. In metals, the linear term gives the leading contribution. In insulators, the quadratic term gives the leading contribution.

Since, under spatial inversion, the spin magnetization is even but the electric field is odd, the linear spin susceptibility vanishes if there is inversion symmetry (IS). To have a nonzero linear susceptibility, IS must be broken. Indeed, a spin polarization can be established, to linear order, by a static electric field in non-magnetic metals with broken IS, known as the spin Edelstein effect.\textsuperscript{3,4} This phenomenon can be understood on the basis of the SOC provided by the field of the ions.\textsuperscript{2} The Edelstein effect has been observed experimentally in GaAs\textsuperscript{9\textendash}11 and studied in topological insulators,\textsuperscript{13,16\textendash}20 van der Waals heterostructures,\textsuperscript{21,22} Weyl semimetals\textsuperscript{23,24} and superconductors.\textsuperscript{25,26}

The Edelstein effect is usually associated with metals where the Fermi surface (FS) dominates the spin response at low frequencies. Here we find that the FS contribution to the $m$-th order electric spin susceptibility can be thought, more intuitively, as the average $m$-th spin multipole of the Fermi sea

$$\zeta^{(m)}_e = \frac{e_m}{\hbar m V} \sum_{nk} f_n s_n^{a,bc...}.$$

The notation is defined in Appendix A. For example, to first order, the dc spin polarization of metals is given by the spin dipole of the Fermi sea. These spin moments are analogous to the $m$-th order Drude conductivity in the sense that they have the same structure, albeit with the spin operator replacing the velocity operator.

More important, we find that contrary to the linear response, a nonlinear spin polarization can be generated in the bulk of homogenous materials without interfaces. This \textit{bulk photospin effect} (BPSE) is characterized by the quadratic electric spin susceptibility. It is useful to separate the BPSE susceptibility into its symmetric and antisymmetric parts

$$\mathbf{S}_{dc,bpse} = \nu_2 |\mathbf{E}|^2 + \nu_2 \mathbf{E} \times \mathbf{E}^*, \quad (3)$$

where $\nu_2$ is symmetric in the electric field indices and $\nu_2$ is antisymmetric. $|\mathbf{E}|^2$ indicates (schematically) a symmetric combination of field indices. The BPSE is analogous to the photovoltaic effect\textsuperscript{27\textendash}31 (BPVE), whereby a constant current is generated in materials that lack IS. Since the current is odd under spatial inversion, but the electric field is even, the BPVE vanishes if the point group of the material has IS. To have a nonzero BPVE, the material has to break IS. In the BPSE, on the other hand, both the spin magnetization and the electric field are even under spatial inversion, and hence no restrictions are imposed by IS (to second order). Under the time reversal operation, the spin magnetization and current are both odd, and hence time reversal symmetry (TRS) imposes the same restrictions on both the BPVE and BPSE.

In the BPSE, $\nu_2$ characterizes the spin response to fields with circular polarization. $\nu_2$ processes have been extensively studied in the context of spin orientation phenomena\textsuperscript{1,6,14} and are usually associated with angular momentum transfer from circularly polarized light to electrons’ spin. $\nu_2$, on the other hand, characterizes the generation of spin polarization with linearly polarized light. $\nu_2$ processes have received less attention,\textsuperscript{8,12} perhaps because it is unclear where the spin angular momentum comes from. Since linear polarized photons do
not carry angular momentum, and the material does not break TRS by assumption, an internal torque appears in the system that transfers angular momentum to other degrees of freedom, e.g., charge, phonons, excitons, etc. For example, an internal torque could lead to current loops and dissipation. Alternatively, in the absence of an external torque, a spin polarization may be accompanied by a rotation of the sample as a whole (Einstein-de Haas effect).

In this paper, we present a microscopic derivation of $\nu_2$ and $\nu_3$ for insulators and metals for any configuration of external field frequencies in terms of generic Bloch matrix elements. We find that $\nu_2$ depends on the off-diagonal elements of the density matrix and hence requires quantum coherence. $\nu_2$ vanishes when field frequencies are lower than the energy gap (it is resonant), and hence the system absorbs energy and heats up. $\nu_2$, on the other hand, has resonant and nonresonant contributions. The former depends on the diagonal elements of the density matrix and gives the usual spin orientation phenomena extensively studied in the literature. The latter means that it is possible to generate spin polarization with circularly polarized light without producing heat.

We consider a classical homogenous electric field

$$E^\beta(t) = \sum_\beta E^\beta_\beta e^{-i\omega_\beta t},$$

with $\omega_\beta$ frequency components acting on an ensemble of non-interacting Bloch electrons characterized by the density matrix

$$\rho_{mn} \equiv \langle a^*_m a_n \rangle.$$  \hspace{1cm} (5)

The density matrix evolves according to the Boltzmann equation

$$\frac{\partial \rho_{mn}}{\partial t} + i\omega_{mn} \rho_{mn} - \frac{e^2}{\hbar^2} \sum_b E^b_b (\rho_{ml} v^b_{ln} - r^b_{ml} \rho_{ln}) = \frac{e}{\hbar} \sum_b E^b_b \rho_{mn,b} = -\frac{1}{\tau} (\rho_{mn} - \rho_{mn}^{(0)}).$$ \hspace{1cm} (6)

The notation is given in Appendix A. The left hand side describes coherent motion due to the electric field. It is obtained from the equation of motion of $\hat{\rho}$ with the Hamiltonian provided in Appendix A. The right hand side is added phenomenologically to describe dissipative processes. It is a collision integral in the relaxation time approximation. Eq. 6 incorporates interband and intraband matrix elements on an equal footing. This guarantees, among other things, Maxwell’s equation $d\textbf{P}/dt = \textbf{J}$ holds in the Bloch basis. Also, Eq. 6 takes into account interband coherence important to recover, e.g., the Hall conductivity, shift current, etc. If only intraband processes are important, $\rho_{nm} \to \delta_{nm} \rho_{nn}$, Eq. 6 reduces (as expected) to the one-band semiclassical Boltzmann equation

$$\frac{\partial \rho_{nn}}{\partial t} + \frac{e}{\hbar} \textbf{E} \cdot \nabla \rho_{nn} = \frac{1}{\tau} (\rho_{nn} - \rho_{nn}^{(0)}).$$ \hspace{1cm} (7)

Momentum relaxation produces spin relaxation via SOC mechanism, e.g., Dyakonov-Perel’, but the details of such process are not considered here. Our relaxation time does not depend on momentum or energy. We solve Eq. (6) in powers of the electric field as

$$\rho_{mn} = \rho_{mn}^{(0)} + \rho_{mn}^{(1)} + \rho_{mn}^{(2)} + \cdots,$$ \hspace{1cm} (8)

where $\rho_{mn}^{(0)}$ is the density matrix in the absence of fields and $\rho_{mn}^{(n)}$ are higher order terms. In the long-time limit we obtain

$$\rho_{mn}^{(0)} = \delta_{nm} f_n,$$ \hspace{1cm} (9)

$$\rho_{mn}^{(1)} = \sum_{b} \rho_{mn,b}^{(1)} E^b_\beta e^{-i\omega_\beta t},$$ \hspace{1cm} (10)

$$\rho_{mn}^{(2)} = \sum_{b\beta\sigma} \rho_{mn,b}^{(2)} E^b_\beta E^\sigma_\alpha e^{-i\omega_\alpha t},$$ \hspace{1cm} (11)

where $\omega_\Sigma \equiv \omega_\beta + \omega_\alpha$.  

The paper is organized as follows. In Sec. II, we solve the Boltzmann equation for the density matrix up to second order in the electric field. These solutions are then used to construct the general first-order susceptibility (Sec. IV), and apply it to special cases (Sec. V), in particular, we the provide an example from a TI in an electric field (Sec. VI). We then construct the general second-order susceptibility (Sec. VII), apply it to special cases (Sec. VIII), in particular, the dc quadratic Edelstein susceptibility (Sec. IX), the BPSE in insulators (Sec. X) and metals (Sec. XI). Then we give an example of a spin quadrupole in a TI under a magnetic and an electric field (Sec. XII), and of optical spin coherence of conduction bands (Sec. XIII). A final discussion is presented in Sec. XIV.
A. First order density matrix

To linear order we find

\[ \tilde{\rho}^{(1)}_{mn} = \tilde{\rho}^{(1e)}_{mn} + \tilde{\rho}^{(1i)}_{mn}, \]

(12)

where

\[ \tilde{\rho}^{(1e)}_{mn} = \frac{e}{\hbar} \frac{r_{mn} f_{nm}}{\omega_{mn} - \omega_\beta}, \]

(13)

and

\[ \tilde{\rho}^{(1i)}_{mn} = \delta_{nm} \frac{e}{\hbar} \frac{f_{mn}}{\omega_\beta}. \]

(14)

Here \( f_n = [e^{(E_n - \mu)/k_B T} + 1]^{-1} \) is the Fermi distribution function at temperate \( T \) and chemical potential \( \mu, E_n = \mathcal{E}_n(k) \) is the energy dispersion of Bloch electrons in band \( n \), and \( \omega_\beta \equiv \omega_\beta + i \tau \) (see also Appendix A). The superscripts \( e \) and \( i \) indicate interband and intraband processes, respectively.

Note that Eq.(13) gives the Hall conductivity (Appendix D) in the dc and \( \tau \to \infty \) limits, and Eq.(14) gives the semiclassical Drude conductivity. Only when both are taken into account can we recover the full quantum mechanical conductivity to linear order (Appendix C).

B. Second order density matrix

To second order we obtain

\[ \tilde{\rho}^{(2)}_{mn} = \tilde{\rho}^{(2e)}_{mn} + \tilde{\rho}^{(2i)}_{mn}, \]

(15)

where

\[ \tilde{\rho}^{(2e)}_{mn} = \frac{ie}{\hbar (\omega_{mn} - \omega_\Sigma)} \left[ \tilde{\rho}^{(1e)}_{mn,\Sigma} \right] + i \sum_l \left[ \tilde{\rho}^{(1e)}_{ml,\Sigma} (r_{ln} - r_{ln}) \tilde{\rho}^{(1e)}_{ln,\Sigma} \right], \]

(16)

and

\[ \tilde{\rho}^{(2i)}_{mn} = \frac{e^2}{\hbar^2} \frac{1}{i \omega_\Sigma} \frac{r_{mn} f_{nm,\Sigma}}{\omega_{mn} - \omega_\Sigma} + \delta_{nm} \frac{e^2}{\hbar^2} \frac{1}{i \omega_\beta} \frac{f_{nm}}{i \omega_\Sigma}. \]

(17)

We defined \( \omega_\Sigma \equiv \omega_\beta + i / \tau, \omega_\Sigma \equiv \omega_\Sigma + i / \tau, \) and \( \omega_\Sigma \equiv \omega_\beta + i \omega_\Sigma \). The terms in Eq.(17) are FS contributions, since they contain derivatives of the distribution function \( f_n \). In particular, the first term in Eq.(17) involves transitions from the FS to other bands.38,39 FS contributions to higher orders can be computed in a similar way. For example, to \( n \)th order there will always be a FS contribution proportional to the \( n \)th derivative of \( f_n \).

III. GROUND STATE SPIN POLARIZATION

Each Bloch electron contributes

\[ s_{nm} = \frac{\hbar}{2} \langle nk | \sigma | mk \rangle \]

(18)

to the total spin expectation value

\[ S = \frac{1}{V} \sum_{nm} \rho_{nn} s_{nm}. \]

(19)

Here \( n = (n_\beta) \) labels band index \( n \) and spinor index \( i_\beta = 1, 2, \) and \( \sigma = (\sigma_x, \sigma_y, \sigma_z) \) are the Pauli spin matrices. In the ground state \( \rho_{nn}^{(0)} = \delta_{nm} f_n \), and the spin magnetization is

\[ S_0 = \frac{1}{V} \sum_{nk} f_n s_n, \]

(20)

where we defined \( s_n \equiv s_{nn} \). If there is TRS, we can choose \( s_{nm}(-k) = -s_{mn}(k) \), \( f(E_n(-k)) = f(E_n(k)) \), and hence \( S_0 = 0 \), as expected. \( \bar{n} \) is time reversed spin state of \( n \).

IV. FIRST ORDER SPIN POLARIZATION: SPIN EDELSTEIN EFFECT

To first order the induced spin

\[ \mathcal{S}^{(1)} = \sum_{k} \zeta^{(1)ab}_{n,k} (-\omega_\beta; \omega_\beta) f_{b} e^{-i \omega_\beta t}, \]

(21)

oscillates at the frequency of the external field. It is convenient to analyze the Fermi surface (FS) and non-FS (nFS) contributions separately. To this end, we write

\[ \zeta^{(1)} = \zeta^{(1)}_{n,FS} + \zeta^{(1)}_{n,nFS}, \]

(22)

where

\[ \zeta^{(1)ab}_{n,FS} = \frac{e}{\hbar V} \sum_{m,n} \frac{f_{mn} r_{mn} s_{mn}^a}{\omega_{mn} - \omega_\beta}, \]

(23)

and

\[ \zeta^{(1)ab}_{n,nFS} = \frac{e}{\hbar V} \sum_{n,k} \frac{f_{nk} s_{nk}^a}{\omega_{nk}}, \]

(24)

If there is IS, the FS and nFS contributions vanish. To see this, let \( k \to -k \) in the integrands, and note that we can choose \( r_{mn}(-k) = -r_{nm}(k) \) if there is IS. The spin texture at the FS determines \( \zeta^{(1)}_{n,FS} \), but an integration by parts shows that we can also think of Eq.(24) as the average spin dipole (momentum derivative of the spin) of the Fermi sea

\[ \zeta^{(1)ab}_{n,FS} = -\frac{e}{\hbar V} \sum_{n,k} \frac{f_{nk} s_{nk}^a}{\omega_{nk}}. \]

(25)

In general, an inhomogeneous spin texture in momentum space generates a spin polarization in real space.

V. SPECIAL CASES OF THE LINEAR SPIN SUSCEPTIBILITY

Eqs.(23) and (24) can be specialized to any frequency configuration of external fields. For example, for a
monochromatic field with components $\omega_\beta = \pm \omega$ or a static field, we have

$$
\zeta^{(1)ac} \equiv \zeta^{(1)}(-\omega, \omega),
$$

$$
\zeta^{(1)ce} \equiv \zeta^{(1)}(0, 0),
$$

which are the well-known ac and dc Edelstein spin susceptibilities. Explicitly

$$
\zeta^{(1)ab}_{ac} = \frac{e}{hV} \sum_{n\Omega k} f_{nm} r_{\beta \alpha}^{b} \frac{\omega_{mn}}{\omega_{mn} - \omega},
$$

$$
\zeta^{(1)ab}_{ce} = -\frac{e\tau}{hV} \sum_{nk} f_{n;\beta} s_{n;\alpha}.
$$

To obtain Eq.(29) we assumed TRS and large $\tau$. These expressions agree with, e.g., Kubo formula results.\textsuperscript{40–42}

VI. EXAMPLE: TI IN AN ELECTRIC FIELD

Consider the electrons at the surface of the topological insulator (TI).\textsuperscript{8} Such electrons have, in a sense, maximal SOC. The spin forms a vortex (antivortex) in the conduction (valence) band with a center at Dirac point $k = 0$. The conduction and valence bands have conical shape with apices meeting at the Dirac point, Fig. 1(a). An effective Hamiltonian near the Dirac point is

$$
H_{TI} = v\hbar (k^x\sigma_y - k^y\sigma_x),
$$

where $v$ is the slope of quasiparticles. Let us assume the Fermi level $E_F$ lies in the conduction band, Fig. 1(a). For a monochromatic linearly polarized light incident perpendicular to the surface $E = 2\hat{z}E_0 e^{-i\omega t} + c.c.$ of frequency $\omega$, Eq.(21) becomes

$$
S^{(1)} = S^{(1)}_{nFS} + S^{(1)}_{FS},
$$

where

$$
S^{(1)}_{nFS} = \frac{e}{\hbar} \text{ArcCot} \left( \frac{2\Omega_F\tau}{1 - i\omega\tau} \right) (\hat{z} \times \vec{E}_0) e^{i\omega t} + c.c.,
$$

$$
S^{(1)}_{FS} = \frac{e}{\hbar} (\hat{z} \times \vec{E}_0) \frac{4\Omega_F\tau}{\omega^2 \tau^2 + 1} (\omega\tau \sin(\omega t) + \cos(\omega t)).
$$

We defined $E_0 = E_0/32\pi v$ and $\Omega_F \equiv v k_F$. The order of magnitude of the spin polarization is given by $S_{nFS} \equiv \epsilon E_0/32\pi v$ and has units of spin/m$^2$. Note that only the transverse components of the susceptibilities are nonzero. The nFS spin susceptibility is shown in Fig. 1(b). Its real part has a maximum at $\omega = 2\Omega_F$, i.e., as interband transitions become possible. Its imaginary part has a step-like feature at $\omega = 2\Omega_F$ as energy absorption becomes favorable. The FS contribution to the spin susceptibility has a decaying behavior as a function of frequency, similar to the Drude conductivity. Note that both the FS and nFS spin components depend on the dimensionless parameters $\Omega_F\tau$, which parameterize the density/cleanness of the surface.

Interestingly, the spin polarization is perpendicular to the electric field. Intuitively,\textsuperscript{13,43} the spin and velocity are related by $s_c = (\hbar/2e) \hat{z} \times \vec{v}_c$, and hence when the electronic velocity gets a nonzero expectation value (in the direction of the electric field), so does the spin polarization (perpendicular to it). Eq.(25) makes this statement more precise because the spin polarization is also the average spin dipole

$$
s_{c;x} = \frac{\hbar k}{2k} \sin \theta,
$$

$$
s_{c;y} = -\frac{\hbar k}{2k} \cos \theta,
$$

over the Fermi sea, Fig. 1(a). Here, $\hat{k} = (\cos \theta, \sin \theta)$ is the unit vector along momentum and $\theta$ is the angle of $\vec{k}$ with the $x$-axis. The spin vortex texture in this specific case gives a transverse spin polarization. Finally, with a static electric field, only the FS term contributes ($\Omega_F\tau \gg 1$) and we obtain

$$
S^{(1)}_{dc} = \frac{\epsilon}{\hbar} \frac{4\Omega_F\tau}{\omega^2 \tau^2 + 1} (\hat{z} \times \vec{E}_0).
$$

A significant spin polarization ratio could be achieved. For example, if $E_0 = 10^4$ V/m and $v = 10^6$ m/s we obtain $2S_{nFS}/\hbar \sim 5 \times 10^4$ Bohr magnetons per mm$^2$, i.e., roughly the equivalent of $5 \times 10^4$ fully polarized electrons per mm$^2$. Typical surface electron density is $10^{10}$ mm$^{-2}$. If the density can be brought to, e.g., $10^6$ mm$^{-2}$ or less, the spin polarization would be 5% or more.

VII. SECOND ORDER SPIN POLARIZATION

To second order, the induced spin

$$
S^{(2)a} = \sum_{\Omega_\Sigma \beta \sigma} \zeta^{(2)abc} (-\omega_\Sigma, \omega_\beta, \omega_\sigma) E_0 b^{(0)} E_0 c^{(0)} e^{-i\omega_\Sigma t},
$$

FIG. 1. (a) Spin textures of conduction band $s_c \sim \hat{z} \times \hat{k}$ and spin dipoles at the Fermi surface. (b) Non-FS contribution to electric spin susceptibility in TIs in units of ($e/16\pi v$) and for $\Omega_F\tau = 3$.\textsuperscript{27}
oscillates at the frequency $\omega_\Sigma = \omega_\beta + \omega_\sigma$ in the long-time limit. It has two contributions, which we label as intraband and interband

$$\zeta^{(2)} = \zeta^{(2\text{e})} + \zeta^{(2\text{i})},$$

(38)

because they arise from Eq.(13) and Eq.(14), respectively.

A. Second order intraband contribution

To second order, Eqs.(13) and (14) branch out to produce intraband and interband when substituted into the Boltzmann equation. Let us dub second-order intraband those terms which originate from Eq.(14). From Eq.(17) we can separate the 2nd order intraband terms further into intraband and interband processes as

$$\zeta^{(2\text{i})} = \zeta^{(2\text{ie})} + \zeta^{(2\text{ii})},$$

(39)

where

$$\zeta^{(2\text{ie})}_{abc} = \frac{ie^2}{\hbar^2} \frac{1}{\bar{\omega}_\Sigma} \sum_{nmk} s_{n,m}^a f_{m,n}^{b\text{ie}} f_{n,m;c}^{b\text{ie}} - \frac{ie^2}{\hbar^2} \frac{1}{\bar{\omega}_\Sigma} \sum_{nmk} s_{n,m}^a f_{n,i;cb}^b f_{m,n}^{b\text{ie}},$$

(40)

$$\zeta^{(2\text{ii})}_{abc} = \frac{ie^2}{\hbar^2} \frac{1}{\bar{\omega}_\Sigma} \sum_{nmk} s_{n,m}^a f_{m,n}^{b\text{ii}} f_{n,m;c}^{b\text{ii}}. $$

(41)

These expressions still need to be symmetrized with respect to the exchange of indices $\beta \leftrightarrow \sigma$. Note that $\zeta^{(2\text{ii})}$ is proportional to the spin quadrupole moment, vanishes if there is TRS, but does not necessarily if there is IS.

B. Second order interband contribution

The interband contribution to second order is

$$\zeta^{(2\text{e})}_{abc} = \frac{ie^2}{\hbar^2} \sum_{nmk} s_{n,m}^a \sum_{\omega, \bar{\omega}} \zeta_{nm}^{(1\text{e})} f_{m,n}^{b\text{e}} f_{n,m;c}^{b\text{e}} \left( r_{mn}^{(1\text{e})} \beta \bar{\omega} - r_{mn}^{(1\text{e})} \beta \omega \right),$$

(42)

This expression still needs to be symmetrized with respect to exchange $b\beta \leftrightarrow c\sigma$.

VIII. SPECIAL CASES OF THE SECOND ORDER SPIN SUSCEPTIBILITY

Eq.(37) can be specialized to particular configurations of fields. For example, we can construct quadratic susceptibilities

$$\zeta^{(2)}_{e} = \zeta^{(2)}_{(0,0,0)},$$

(43)

$$\zeta^{(2)}_{\text{bpse}} = \zeta^{(2)}_{(0,\omega,-\omega)},$$

(44)

$$\zeta^{(2)}_{\text{e,oc}} = \zeta^{(2)}_{(-\omega,0,-\omega)},$$

(45)

$$\zeta^{(2)}_{\text{shg}} = \zeta^{(2)}_{(2\omega,\omega,\omega)},$$

(46)

with an optical monocromatic source and a dc static field. Eq.(43) is the dc quadratic correction to the Edelstein susceptibility shown in Eq.(1) (see Sec. IX). Eq.(44) is the bulk photospin susceptibility (see Sec. X and XI). Eq.(45) corresponds to the Edelstein susceptibility modulated by an ac field. Eq.(46) is the generation of second harmonics in the spin polarization.

IX. QUADRATIC EDELSTEIN SUSCEPTIBILITY

Direct calculation of Eq.(43) yields intraband and interband terms. However, if we assume TRS, all terms vanish except for the FS contribution Eq.(40) and we obtain

$$\zeta^{(2\text{e})}_{abc} = -\frac{e^2}{\hbar^2 V} \sum_{nmk} \sum_{\nu} \sum_{\omega} s_{n,m}^a \sum_{\omega} \sum_{\bar{\omega}} \zeta_{nm}^{(2\text{e})} \left( f_{m,n}^{b\text{e}} f_{n,m;c}^{b\text{e}} \right).$$

(47)

See Appendix A for notation. Note that Eq.(47) is real and symmetric under exchange of the indices $b \leftrightarrow c$. From this result we conclude that there is no second-order dc Edelstein susceptibility in insulators.

X. BULK PHOTOSPIN EFFECT IN INSULATORS

We now consider an insulator with fully occupied valence bands and fully empty conduction bands so that Eq.(40) and Eq.(41) vanish. Let us assume there is a monochromatic optical field of the form $E = E(\omega)e^{-i\omega t} + c.c.$. The static induced spin is

$$S^{(2)\text{b, static}}_{\text{bpse},in} = 2 \sum_{bc} \zeta^{(2\text{e})}_{abc} (0; \omega, -\omega) E(\omega) E^c(-\omega).$$

(48)

From Eq.(42), $\zeta^{(2\text{e})}_{abc}$ can be further decomposed into 2-band and 3-band contributions

$$\zeta^{(2\text{e})}_{abc} = \zeta^{(2\text{e})}_{2\text{b}} + \zeta^{(2\text{e})}_{3\text{b}},$$

(49)

where

$$\zeta^{(2\text{e})}_{2\text{b}} = -\frac{ie^2}{2\hbar^2 V} \sum_{nmk} \sum_{\nu} \sum_{\omega} \sum_{\bar{\omega}} \zeta_{nm}^{(2\text{e})} \left( f_{m,n}^{b\text{e}} f_{n,m;c}^{b\text{e}} \right),$$

(50)

$$\zeta^{(2\text{e})}_{3\text{b}} = \frac{e^2}{2\hbar^2 V} \sum_{nmk} \sum_{\nu} \sum_{\omega} \sum_{\bar{\omega}} \zeta_{nm}^{(2\text{e})} \left( f_{m,n}^{b\text{e}} f_{n,m;c}^{b\text{e}} \right),$$

(51)

and $\bar{\omega} \equiv \omega + i/\tau$ and $\bar{\omega}_{nm} = \omega_{nm} + i/\tau$. We define the BPSE tensor for insulators as the symmetric and antisymmetric parts of $\zeta^{(2\text{e})}_{abc}$

$$\nu^{abc}_{2,\text{in}} = (\zeta^{(2\text{e})}_{abc} + \zeta^{(2\text{e})}_{abc})/2,$$

(52)

$$\nu^{abc}_{2,\text{in}} = (\zeta^{(2\text{e})}_{abc} - \zeta^{(2\text{e})}_{abc})/2.$$

(53)
Eqs. (50) and (51) are the most general for any $\tau$. However, in the limit of large $\tau$, we can set $\tilde{\omega}_{nm} = \omega_{nm} + i/\tau \rightarrow \omega_{nm}$ when $n \neq m$ in denominators. In this case, many terms simplify if there is no TRS. For example, the symmetric part becomes

$$
\nu_{2,\text{in}}^{abc} = -\frac{\pi e^2}{2\hbar^2 V} \sum_{nmk} f_{nm} \left( \frac{s^a_{nm}}{\tilde{\omega}_{nm}}, r^b_{mn} \right) \delta_{\tau}(\omega_{nm} - \omega) + \frac{i e^2}{2\hbar^2 V} \sum_{nmk} f_{nm} \left( \frac{s^a_{nm}}{\tilde{\omega}_{nm}}, r^b_{mn} \right) D_1(\omega_{ml}, \omega) + i \tau e^2 \sum_{nmk} f_{nm} \left( \frac{s^a_{nm}}{\tilde{\omega}_{nm}}, r^b_{mn} \right) H_m(\omega_{mn}, \omega),
$$

which is real and resonant, i.e., vanishes for field frequencies smaller than the energy gap. The notation is defined in Appendix A. Note that $\nu_{2,\text{in}}$ depends on the off-diagonal elements of the density matrix and hence is a pure quantum effect. In particular, the first term in Eq. (54) comes from Eq. (50) whose $m = n$ term vanishes. The second term in Eq. (54) comes from Eq. (51) with the $n = m$ term excluded. The $n = m$ term of Eq. (51) in fact is the resonant part of $\nu_{2,\text{in}}$

$$
\nu_{2,\text{in}}^{abc} = \frac{\pi e^2}{2\hbar^2 V} \sum_{nmk} f_{nm} \left( s^a_{nm} - s^a_{m}, r^b_{mn} \right) \delta_{\tau}(\omega_{nm} - \omega) + \frac{i e^2}{2\hbar^2 V} \sum_{nmk} f_{nm} \left( s^a_{nm} - s^a_{m}, r^b_{mn} \right) H_m(\omega_{mn}, \omega) + \frac{e^2}{2\hbar^2 V} \sum_{nmk} f_{nm} \left( s^a_{nm} - s^a_{m}, r^b_{mn} \right) H_m(\omega_{ml}, \omega).
$$

$\nu_{2,\text{in}}$ is pure imaginary and contains both resonant and nonresonant contributions. The resonant part is proportional to $\tau$, meaning a spin injection can be obtained from simple Fermi’s golden applied to the diagonal elements of the density matrix, e.g., Eq. (4) of Ref. 44. Alternatively, the resonant term of $\nu_{2,\text{in}}$ could have been derived from the effective equation of motion

$$
\frac{d}{dt} S^{(2)} = \left( \frac{d}{dt} S^{(2)} \right)_{\text{source}} - \frac{1}{\tau} S^{(2)} + \frac{1}{\tau} S^{(2)},
$$

with recombination and spin relaxation times equal to $\tau$. Interestingly, the last two terms in Eq. (55) are nonresonant; i.e., they are nonzero even for subgap frequencies. This means a permanent spin polarization is possible with circularly polarized photons even if energy is not absorbed and heat is not produced. This is important for spintronic applications. However, a more detailed model of dissipation is needed to understand the evolution of interband coherence.

### XI. BULK PHOTOSPIN EFFECT IN METALS

We define the BPSE response tensor for metals as the symmetric and antisymmetric parts of $\zeta^{(2)abc}$

$$
\nu_{2,m} = \frac{(\zeta^{(2)})^{abc} + (\zeta^{(2)})^{abc}}{2},
$$

$\nu_{2,m} = \frac{(\zeta^{(2)})^{abc} - (\zeta^{(2)})^{abc}}{2},
$$

which, in addition to the interband contributions, now include FS contributions specific to metals. Assuming TRS, we find that only Eq. (40) survives, and

$$
\nu_{2,m} = \nu_{2,\text{in}} + e \nu_{2,FS},
$$

$$
\nu_{2,m} = \nu_{2,\text{in}} + e \nu_{2,FS},
$$

where the metallic contributions are

$$
\nu_{2,FS} = \frac{-i \tau e^2}{2\hbar^2 V} \frac{1}{1 + \omega^2 \tau^2} \sum_{nmk} \left( \frac{s^a_{nm}}{\tilde{\omega}_{nm}} \right) \left( r^b_{mn}, f_{nm; c} \right),
$$

$$
\nu_{2,FS} = \frac{i \tau e^2}{2\hbar^2 V} \frac{\omega \tau}{1 + \omega^2 \tau^2} \sum_{nmk} \left( \frac{s^a_{nm}}{\tilde{\omega}_{nm}} \right) \left( r^b_{mn}, f_{nm; c} \right).
$$

### XII. EXAMPLE: TI IN AN ELECTRIC AND MAGNETIC FIELD

We consider the electrons at the surface of a TI subject to an Zeeman field

$$
H = \hbar(k^x \sigma_y - k^y \sigma_x) + m \sigma_z.
$$

The Zeeman field breaks TRS and now the spin quadrupole Eq. (41) does not vanish. Let us assume an electric field linearly polarized in the plane of the TI surface with magnitude $E_0$ and frequency $\omega$. The induced spin point out of the plane and has magnitude

$$
S^{(2)} = -\frac{e^2 E_0}{4\pi \hbar^2} \frac{s_z^z(k_F)}{\tilde{\omega}^2 \tau^2 + 1} \left( 1 - \frac{m^2}{E_F^2} \right),
$$

where $s_z^z = h \hbar / 2 \mathcal{E}_c$ is the $z$-component of the spin in the conduction band and $\mathcal{E}_F \equiv \mathcal{E}_c(k_F) > m$ is the Fermi level assumed to lie in the conduction band. If $\mathcal{E}_F \gg m$ and the electric field is static, the spin quadrupole is given by

$$
S^{(2)} = -\frac{e^2 E_0}{4\pi \hbar^2} s_z^z(k_F) \quad \omega = 0.
$$

### XIII. EXAMPLE: COHERENCE OF SPIN-SPLIT CONDUCTION BANDS

At very short times, interband coherence of conduction bands plays an important role in insulators that break IS. Here we recover the equations describing this effect starting from Eq. (42). To include the coherence of pairs of conduction bands close in energy, instead of
taking the diagonal elements of Eq. (50) (which give zero) and Eq. (51), we consider the diagonal elements of Eq. 50 and the first and fourth terms of Eq. (51)

\[
\zeta^{(2)}_{ch} = \frac{e^2}{2\hbar^2V} \sum_{nmkl} \frac{s_{nm}^{a} y_{ml}^{b} r_{ln}^{c}}{\bar{\omega}_{nm}} \left[ f_{ln} - \frac{f_{in}}{\omega_{nl} - \omega} \right],
\]

(66)

and let \( n = c' \) and \( m = c \) label conduction bands spin-split by SOC but very close in energy. Now write \( \omega_{cc'} = \omega_{cv} - \omega_{cc} \) and expand in powers of the small parameter \( \omega_{cc} \). To lowest order, we obtain

\[
\zeta^{(2)}_{ch} \bigg|_{n = c', m = c} = \frac{\tau \pi e^2}{2\hbar^2V} \sum_{cc'k} s_{cc}^{a} y_{cc'}^{b} r_{cc}^{c} \left[ \delta_{T} (\omega_{cc'} - \omega) + \delta_{T} (\omega_{cc} - \omega) \right],
\]

(67)

which was originally derived in Ref. 44 by other methods.

XIV. DISCUSSION AND CONCLUSIONS

We calculated the electric spin susceptibility to second order in the electric field for a system of non-interacting Bloch electrons with SOC. We dub this response the bulk photo-spin effect (BPSE) to emphasize spin polarization is generated in the bulk of the materials without need of interfaces. Our expressions for the BPSE tensors depend on generic Bloch matrix elements and hence are amenable for use in large-scale first-principles numerical codes. In appropriate limits, we recover the linear Edelstein and spin orientation phenomena.

We can draw some general conclusions from the form of the BPSE susceptibility: (a) The symmetric part of the BPSE susceptibility in insulators is resonant; i.e., light of linear polarization cannot induce spin polarization unless the frequency of light is at least equal to the energy gap, and hence energy is absorbed by the electron ensemble.

(b) The symmetric part of the BPSE susceptibility in insulators depends on the off-diagonal elements of the density matrix; i.e., spin polarization with linearly polarized light requires quantum coherence. Since quantum coherence can be feeble, this kind of spin polarization may be harder to observe in experiments.

(c) The antisymmetric part of the BPSE susceptibility in insulators has both resonant and nonresonant contributions. The former is given by diagonal elements of the density matrix and reproduces the standard spin orientation effects which requires energy absorption. Interestingly, the existence of the nonresonant contributions means that spin polarization is possible with circularly polarized light, even if the system does not absorbs energy.

(d) Non-magnetic metals have additional contributions to the spin polarization. The symmetric and antisymmetric parts of the metallic response are nonzero at all frequencies and hence produce heating. Although linear or circular polarization of light can induce spin polarization this requires the existence quantum coherence.

We also pointed out that the low-frequency spin response of metals is dominated by spin multipoles of the Fermi sea. These terms are analogous to the semiclassical Drude conductivities, but with the velocity operator replacing the spin operator. For example, the linear and quadratic (see Appendix E) dc Drude conductivities are

\[
\sigma^{(1)}_{dc} = -\frac{e^2}{\hbar V} \sum_{nk} f_{n} v_{n;cb}^{a},
\]

(68)

\[
\sigma^{(2)}_{dc} = -\frac{e^2 \tau^2}{\hbar^2 V} \sum_{nk} f_{n} v_{n;bc}^{a}.
\]

(69)

which we could think of as the average inverse mass tensor of the Fermi sea or the average jerk (two derivatives of the velocity) of the Fermi sea, respectively. Finally, we did not consider the orbital magnetization of electrons, which also contributes to the overall magnetization of the system. The orbital magnetization requires special care and will be considered separately.

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Appendix A: Definitions

\[ e = \text{signed electron charge} \] (A1)

\[ \hat{H} = \frac{p^2}{2m} + V(r) + \mu_B^2 e \cdot (\hat{p} \times \sigma) \] (A2)

\[ \sigma = (\sigma_x, \sigma_y, \sigma_z) \] Pauli spin matrices (A3)

\[ (r|n) = (r|u_n)e^{ikr} \] Bloch state \((nk)\), (A4)

\[ E_n = \langle nk|\hat{H}|nk \rangle, \] energy of state \((nk)\) (A5)

\[ \hbar \omega_n = E_n \] (A6)

\[ \rho_{nm} = \langle a_n^\dagger a_m \rangle, \] density matrix Bloch basis (A7)

\[ f_n = f(E_n) = \rho_{nn}^{(0)}, \] Fermi function (A8)

\[ \omega_{nm} = \omega_n - \omega_m \] (A9)

\[ f_{nm} = f_n - f_m \] (A10)

\[ \xi_{nm} = \langle u_n|\nabla_k|u_m \rangle, \] Berry connection (A11)

\[ r_{nm} = (1 - \delta_{nm})\xi_{nm} \] (A12)

\[ \rho_{nm:b} \equiv \left[ \frac{\partial}{\partial k_b} - i(\xi_{m:n}^b - \xi_{n:m}^b) \right] \rho_{mn} \] (A13)

\[ f_{n:b} = \frac{\partial f_n}{\partial k_b} \] (A14)

\[ \omega_{n:b} \equiv \frac{\partial \omega_n}{\partial k_b} \] (A15)

\[ f_{nm:b} \equiv f_{n:b} - f_{m:b} \] (A16)

\[ v_{nm} = \langle nk|\mathbf{v}|mk \rangle \] (A17)

\[ v_n^b = v_{nm}^b = \omega_n^b \] (A18)

\[ s_{nm} = \hbar \langle nk|\sigma|mk \rangle \] (A19)

\[ s_n = s_{nm}, \] spin of state \((nk)\) (A20)

\[ \tau = \text{appropiate relaxation time} \] (A21)

\[ \omega_\beta = \text{frequency component of E-field} \] (A22)

\[ \omega_\Sigma = \omega_\beta + \omega_\tau + \cdots \] (A23)

\[ \tilde{\omega}_\beta = \omega_\beta + i/\tau \] (A24)

\[ \Omega_{nm}^{ab} = \frac{\partial \xi_{mn}^b}{\partial k^a} - \frac{\partial \xi_{mn}^a}{\partial k^b} \] (A25)

\[ \Omega_n = \nabla \times \xi_{nn} \] Berry curvature (A26)

For any scalar functions \(f(b)\) and \(g(c)\) of Cartesian indices \(b\) and \(c\), we defined the symmetric and antisymmetric combinations

\[ \{f(b), g(c)\} \equiv f(b)g(c) + f(c)g(b), \] (A27)

\[ [f(b), g(c)] \equiv f(b)g(c) - f(c)g(b). \] (A28)

We also defined broadened delta functions as

\[ \delta_{\tau}(x) = \frac{1}{\pi} \frac{\tau^{-1}}{x^2 + \tau^{-2}}, \] (A29)

\[ P_{\tau} \] (A30)

\[ H_\pm(\omega_{mn}, \omega) = \frac{P_{\tau}}{\omega_{mn} - \omega} \pm \frac{P_{\tau}}{\omega_{mn} + \omega}. \] (A31)

\[ D_\pm(\omega_{mn}, \omega) = \delta_{\tau}(\omega_{mn} - \omega) \pm \delta_{\tau}(\omega_{mn} + \omega). \] (A32)

Appendix B: Useful relations

An operator \(\hat{Q}\) in Bloch basis can be projected into diagonal and off-diagonal components as

\[ \langle nk|\hat{Q}|mk \rangle = \delta_{nm}Q_{nn} + (1 - \delta_{nm})Q_{nm}. \] (B1)

When \(\hat{Q}\) is a commutator that involves the position matrix elements52,53

\[ \langle nk|\mathbf{r}|mk'\rangle = \delta_{nm}[\delta_{kk'}\xi_{nn} + i\nabla_k\delta_{k,k'}] 
+ (1 - \delta_{nm})\delta_{k,k'}\xi_{nm}, \] (B2)

the result are expressions that relate position, velocity, energy, current, and their derivatives. The most common are

\[ v_{nm}^b = \delta_{nm}\omega_n^b + i\omega_n^b r_{nm}^b \] (B3)

\[ v_{nm,a}^b = \hbar \delta_{ab}\delta_{nm} + \sum_l (r_{nl}^a r_{lm}^b - v_{nl}^a r_{lm}^b) \] (B4)

\[ \Omega_n^{ba} = -i\sum_l (r_{nl}^a r_{lm}^b - r_{nl}^b r_{lm}^a), \] (B5)

\[ r_{nm:b} - r_{nm:a}^b = -i\sum_l (r_{nl}^a r_{lm}^b - r_{nl}^b r_{lm}^a), \] (B6)

\[ \omega_{n:ab} = \hbar \delta_{ab} - \sum_l \omega_l (r_{nl}^a r_{lm}^b + r_{nl}^b r_{lm}^a), \] (B7)

\[ r_{nm:a} = \frac{1}{\omega_{nm}}(r_{nm}^a \omega_{mn:b} + r_{nm}^b \omega_{mn:a}) 
+ \frac{i}{\omega_{nm}} \sum_l (\omega_l r_{nl}^a r_{lm}^b - \omega_l r_{nl}^b r_{lm}^a). \] (B8)

The original derivations are presented in Ref. 54. (B3-B6) can be derived simply by taking matrix elements of

\[ [r^a, \hat{H}] / \hbar = \hat{u}^a, \] (B9)

\[ [r^a, \hat{p}^b] / \hbar = \hat{d}_{ab}, \] (B10)

\[ [r^a, r^b] = 0. \] (B11)

It is reassuring that the well-known double momentum derivative of energies55 Eq.(B7) is recovered in this approach. We can also take (covariant) derivatives of any of these to form new ones. For example, we could obtain Eq.(B7) and Eq.(B8) by substituting Eq.(B3) into
Eq. (B4) eliminating the velocity, and carefully separating diagonal from off-diagonal terms. Alternatively, Eq. (B7) is just the $n = m$ special case of Eq. (B4). Note that Eq. (B6) and Eq. (B8) are valid only when the right hand side is evaluated for $n \neq m$. More properly, there should be a factor of $(1 - \delta_{nm})$ multiplying the right hand side of these expressions. Note that we implicitly assumed differentiable Bloch wave functions and the periodic gauge $\psi_n(k + \mathbf{G}, \mathbf{r}) = \psi_n(k, \mathbf{r})$.

Finally, we comment that taking two momentum derivatives of the gauge-dependent $\langle u_n | \hat{H}_k | u_m \rangle = \delta_{nm} E_n$, where $\hat{H}_k = e^{-i \mathbf{k} \cdot \mathbf{r}} \hat{H} e^{i \mathbf{k} \cdot \mathbf{r}}$, gives a similar expression to Eq. (B8) but with additional term. Caution should be exercised when taking derivatives of matrix elements that depend on the phase of the Bloch wave functions and when using approximate tight-binding Hamiltonians. In our case B3-B8 are fixed by the commutation relations Eqs. (B9)-(B11) and, in particular, do not depend on the form of the Hamiltonian.

Appendix C: FS contributions to linear order conductivity

We now show that the FS contribution of Eq. (14) recovers the semiclassical Drude conductivity of metals in the relaxation time approximation. This suggest that the spin dynamics arising from the FS is essentially semiclassical. The current to linear order is

$$J^{(1)} = \text{tr}[\hat{\mathcal{A}}^{(1)} \hat{\mathcal{V}}] = J^{(1)i} + J^{(1)e}. \quad \text{(C1)}$$

Using Eq. (14) and (13) we obtain

$$J^{(1)i} = \frac{e^2}{\hbar} \sum_{nk} \sum_{b\beta} v^a_n f_{ab} E^b_{\beta} e^{-i \omega_{\beta} t}, \quad \text{(C2)}$$

$$J^{(1)e} = \frac{e^2}{\hbar} \sum_{nmk} \sum_{b\beta} \frac{\omega_{nm} \delta_{\beta} f_{ab} E^b_{\beta}}{\omega_{nm} - \omega_{\beta}} e^{-i \omega_{\beta} t}. \quad \text{(C3)}$$

For monochromatic light, the conductivity, defined by

$$J^{(1)a} = \sum_b \sigma^{(1)ab}(\omega) E^b(\omega) e^{-i \omega t} + c.c., \quad \text{(C4)}$$

has two contributions

$$\sigma^{(1)ab} = \sigma_i^{(1)ab} + \sigma_e^{(1)ab}, \quad \text{(C5)}$$

where

$$\sigma_i^{(1)ab} = \frac{e^2}{\hbar} \frac{1}{\omega} \sum_{nk} v^a_n f_{ab}, \quad \text{(C6)}$$

$$\sigma_e^{(1)ab} = \frac{e^2}{\hbar} \sum_{nmk} \frac{v^a_{nm} v^b_{mn}}{\omega_{mn} - \omega}. \quad \text{(C7)}$$

Eq. (C6) can be written as\(^{55}\)

$$\sigma_i^{(1)ab} = \frac{e^2}{V} \sum_{nk} v^a_n v^b_n \frac{1}{\tau - i \omega} \left( \frac{\partial f_n}{\partial \epsilon_n} \right), \quad \text{(C8)}$$

which is the Drude linear conductivity with a momentum-independent relaxation time. The full quantum mechanical result is usually presented as\(^{55}\)

$$\sigma_i^{(1)ab} = -\frac{e^2}{\hbar} \frac{1}{\omega} \sum_{nk} \left[ \frac{\delta_{ab}}{m} \delta_{nm} - \sum_{i \neq n} \left( \frac{v^a_{nm} v^b_{in}}{\omega_{ln} - \omega} + \frac{v^a_{in} v^b_{nm}}{\omega_{ln} + \omega} \right) \right]. \quad \text{(C9)}$$

To recover this result, note that Eq. (C6) can also be written as

$$\sigma_i^{(1)ab} = -\frac{e^2}{\hbar} \frac{1}{\omega} \sum_{nk} \omega_{nm} f_n, \quad \text{(C10)}$$

and using Eq. (B7) and Eq. (C7) we obtain, after some algebra, Eq. (C9). Dissipation in the relaxation time approximation enters by broadening all frequencies in the denominators. In the small frequency limit, interband transitions become the anomalous velocity contribution. Hence, including only the FS term may miss Berry curvature effects.

Appendix D: Interband contribution in the dc-limit: Hall conductivity

The interband term Eq. (C3) contributes to both the dc limit and the finite frequency limit. In the dc limit Eq. (C3) gives the familiar Hall conductivity. This term can be obtained in many ways, but the above formalism allows us to see in a more transparent way various limiting cases. For example, using the identities Eq. (B3) and Eq. (B5), and considering the dissipationless limit $\tau \to \infty$, and the dc limit $\omega \to 0$, we obtain

$$J^{(1)e} = -\frac{e^2}{\hbar} \frac{1}{\omega} \sum_{nk} f_n \mathbf{E}_0 \times \mathbf{\Omega}_n, \quad \text{(D1)}$$

which is the the standard Hall current. This result could have been obtained more easily from the intraband current, e.g., Eq. (56) of Ref. 35, which includes all contributions to the dc conductivity, including Berry phases, FS contributions, (e.g., $\propto f_{nm,e}$) to any order in a homogeneous electric field.

Appendix E: Second order Drude conductivity

In the relaxation time approximation, the semiclassical distribution in Eq. (7) can be written in close form, e.g., Eq. (13.19) of Ref. 55. To obtain the second-order
Drude conductivity, simply parametrize the momentum by $k(t') = k + eE_0(t - t')/\hbar$, expand velocity $v^b_n(k(t'))$ to first power of $E_0$, and perform the integrations to obtain the second order semiclassical distribution function

$$g_n^{(2)} = -\frac{e^2r^2}{\hbar} \sum_{bc} \left(-\frac{\partial f_n}{\partial E_n}\right) v^b_n(E_0) V^b_n.$$  

(E1)

Now substitute into the current

$$j_{dc}^{(2)a} = \frac{e}{V} \sum_{nk} v^a_n g_n^{(2)} = \sum_{bc} \sigma_{dc}^{(2)abc} E^c_0 E^b_0$$

(E2)

where the conductivity is

$$\sigma_{dc}^{(2)abc} = \frac{e^2r^2}{h^2V} \sum_{nk} v^a_n v^b_n \cdot (\nabla^c)$$

(E3)

or after integration by parts gives Eq.(69).

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