A thermodynamic measure of the Magento-electric coupling in the 3D topological insulator

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We show that the magneto-electric coupling in 3D (strong) topological insulators is related to a second derivative of the bulk magnetization. The formula we derive is the non-linear response analog of the Streda formula for Hall conductivity (P. Streda, J. Phys. C: Solid State Physics, 15, 22 (1982)), which relates the Hall conductivity to the derivative of the magnetization with respect to chemical potential. Our finding allows one to extract the magneto-electric coefficient by measuring the magnetization, while varying the chemical potential and one more perturbing field. Such an experimental setup could circumvent many of the current difficulties with measuring the magneto-electric response in 3D topological insulators. The relation we find also makes transparent the effect of disorder on the magnetoelectric response, which occurs only through the density of states, and has no effect when the system is gapped.

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For many years after the discovery of the Quantum Hall effect[1] (QHE), finding an analog of it in a 3D system had remained an unrealized dream of the condensed matter community. Recently, however, this has changed. The discovery of the topological insulator[2–4], and specifically the 3D strong topological insulator (STI)[5,6], have finally realized the dream of a 3D analog of the QHE. Streda et al.[7,8] were able to show that the Hall conductivity characterizing the Integer QHE, is related to a thermodynamic derivative

$$\sigma_{xy} = -\left.\frac{\partial n}{\partial B}\right|_\mu = -\left.\frac{\partial M}{\partial \mu}\right|_B , \qquad (1)$$

where n is the particle density, M the orbital magnetization per unit volume (perpendicular to the 2D system), B is the external magnetic field, and μ the chemical potential. Here and throughout the manuscript we use units where $c = e = \hbar = 1$. Motivated by the analogy between 2D QHE and 3D STI, in this paper we show that the magneto-electric coefficient characterizing the STI, is also related to a thermodynamic derivative.

The magneto-electric coupling[9,10] P_3, appears in an anomalous term in the action for the electro-magnetic fields in an insulator

$$S_{EB} = \frac{1}{2\pi} \int d\vec{r} dt \vec{E} \cdot \vec{B} P_3 . \qquad (2)$$

Under inversion $\vec{E}$ is odd and under time reversal $\vec{B}$ is odd, so P_3 is odd under both. Ref. 9 showed that P_3 takes on values modulo 1, and so in a material with either time reversal or inversion symmetry (or both), it can take on the values $P_3 = 0, \frac{1}{2}$. The value $P_3 = \frac{1}{2}$ then characterizes the STI. This value can in principal be measured[10] as

$$P_3 \delta_{ab} = 2\pi \frac{\partial M_a}{\partial E^b} = 2\pi \frac{\partial P_a}{\partial B^b} , \qquad (3)$$

where the Latin letters $a, b = x, y, z$ denote spatial directions. Here and throughout the manuscript we will use the Einstein summation convention.

At this point in time, a number of materials have been identified as topological insulators using spectroscopy to characterize their unique surface states[11–15] (an odd number of Dirac points). However, thus far measuring the magneto electric coefficient has proved challenging. The materials by and large have proven rather poor insulators, with significant carrier concentration, in some cases even a bulk Fermi surface appearing[16,17]. In a bulk metal DC electric fields are screened, making it impossible to measure (3) directly.

Many other indirect ways have been proposed to detect the magneto-electric effect, Most of them relying on the surface states in the STI[9,10,18–28], and on the Witten effect[9,29,30]. The magnetoelectric effect at the surface appears as a consequence of the material boundary, where P_3 has a sharp jump, and the Witten effect appears as a consequence of a flux monopole entering the STI. Our motivation in this work is to generalize the measurable effects of the magneto-electric coupling, beyond the surface and Witten effects, to response in the bulk. This can be achieved, as we explain below, by using a field ϕ imitating the 4th vector potential component in 4D A_4, and replacing P_3. With this extra field ϕ, we will find a thermodynamic relation similar to (1). Formulated in this way, we will also be able to talk about magnetoelectric effects in gapless systems, as was recently explored in Refs. 31,32.

Since the STI is the $d = 3$ analog of the QHE, we look to $d = 2$ for inspiration. First, the analog of magneto electric coupling in a gapless metal[31,32] is the intrinsic anomalous Hall effect (AHE)[33]: in metals where time-reversal is broken, a large clean limit contribution to the Hall conductivity appears. The general expression for the intrinsic AHE contribution to the Hall conductivity becomes quantized once the chemical potential is in a gap of the band structure, giving the IQHE. In a metal the effect of disorder cannot be neglected, and there are additional contributions to the Hall conductivity[34]. The interplay of the intrinsic AHE and disorder can be understood using the Bastin formula[7,35,36] for the electric conductivity tensor. This form distinguishes between a Fermi surface
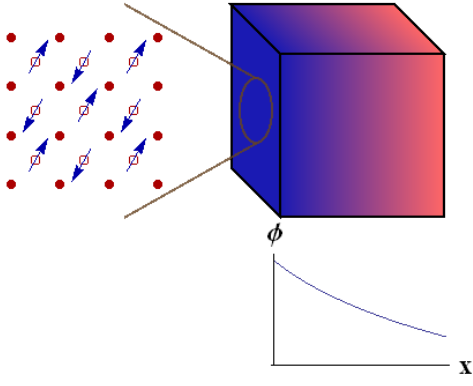
FIG. 1: Measuring the topological magneto-electric response with anti-ferromagnetic (AFM) order assuming the role of the auxiliary field ϕ, odd under both inversion and time-reversal. At the microscopic level, some of the ions are non-magnetic (denoted by full circles), while others are magnetic (denoted by open circles), and form AFM order (denoted by the arrows). A slow gradient in ϕ in combination with the electromagnetic field generate a magneto-electric response. The ϕ gradient indicated in the graph at the bottom is represented in the image of the material by a change of shade (light red to light blue).

contribution σ^I and other contributions σ^{II}

$$
\sigma_{ab}^I = \frac{i}{2} Tr \left[v_a G_R \big|_{\epsilon=0} v_b \delta(H) - v_a \delta(H) v_b G_A \big|_{\epsilon=0} \right]
$$

$$
\sigma_{ab}^{II} = -\frac{1}{4\pi} \int_{-\infty}^{+\infty} d\epsilon f(\epsilon) Tr \left[v_a G_R v_b \frac{\partial G_R}{\partial \epsilon} \right.
$$
$$
\left. - v_a \frac{\partial G_R}{\partial \epsilon} v_b G_R - v_a G_A v_b \frac{\partial G_A}{\partial \epsilon} + v_a \frac{\partial G_A}{\partial \epsilon} v_b G_A \right],
\tag{4}
$$

where v_a are the velocity operators, $f(\epsilon)$ is the Fermi Dirac distribution, $\delta(x)$ is the Dirac delta function, and $G_{R,A} = [\epsilon \pm i\delta - H]^{-1}$ are the retarded and advanced Green's functions, which can include any random potential. The chemical potential is included in $H = \ldots - \mu$, so that the Fermi energy is at $\epsilon = 0$. Finally, the trace is over all degrees of freedom of the system - real (or momentum) space coordinates, and internal degrees of freedom. From inspection it is evident that σ^{II} is antisymmetric in its indices $\sigma_{ab}^{II} = -\sigma_{ba}^{II}$ so that it gives only a Hall conductivity contribution.

Streda et al. [7,8] were able to show that the σ^{II} contribution can be related to a derivative of the orbital magnetization

$$
\sigma_{\text{Hall}}^{II} = -\frac{\partial n(\mu)}{\partial B}\bigg|_{\mu} = -\frac{\partial M}{\partial \mu}\bigg|_{B}.
\tag{5}
$$

Here M, B are the orbital magnetization and magnetic field, respectively, ignoring Zeeman coupling to the electron spin. The formula holds in both gapped and gapless systems, and for an insulator, $\sigma^I = 0$, and the total Hall conductivity is reduced to (1). Then one can show that the Hall conductivity is quantized[8]. Finally, the effects of disorder on (5) are

entirely included in the density of states (DOS) $D(\epsilon)$ through the particle density $n(\mu) = \int d\epsilon f(\epsilon) D(\epsilon)$.

The result (5) can be anticipated from the following considerations. In an insulator, with no dissipative currents, the only currents possible are persistent currents related to the orbital magnetization $\mathbf{J} = \nabla \times \mathbf{M}$. The electric field is found from $\mathbf{E} = -\nabla\mu(\mathbf{x})$. Assuming the magnetization is an entirely *local* function of the intensive thermodynamic quantities $M_a = M_a(T, \mathbf{B}, \mu(\mathbf{x}))$, we find

$$
J^a = \epsilon^{abc} \partial_b M_c = \epsilon^{abc} \frac{\partial M_c}{\partial \mu} \frac{\partial \mu}{\partial x^b} = -\epsilon^{abc} \frac{\partial M_c}{\partial \mu} E_b,
\tag{6}
$$

resulting in $\sigma_{xy} = -\frac{\partial M_z}{\partial \mu}$. The second equality in (5) is due to a Maxwell relation[37,38].

Interestingly, the Streda formula (5) suggests we can measure the topological contribution to the Hall conductivity, by doing a thermodynamic measurement - vary the chemical potential through a back gate, and measure the magnetization of the sample. Calculating the derivative of the magnetization with respect to the gate voltage should give the σ^{II} contribution. However, the measured magnetization will include both the orbital and Zeeman contributions to the magnetization, while (5) involves the *orbital* magnetization alone. For an insulator one can argue that the magnetization due to Zeeman coupling does not vary with chemical potential, and therefore measuring the derivative of the total magnetization, will give the same result as if we were measuring the orbital magnetization alone. For a metal on the other hand, the Zeeman effect magnetization can depend on the chemical potential, for instance in Pauli paramagentism. Therefore, measuring the total magnetization will only give a quantitatively accurate measure of σ^{II} in an insulator. Still, it will be useful in finding qualitative differences. While such a measurement is conceptually straightforward, in practice it is is more difficult than measuring Hall effect through electric currents. Still, it has been carried out[39,40]. Next we will present the analog of (5) in the $d = 3$ STI, and we will use it to propose a thermodynamic measurement of the magnetoelectric coupling.

In order to deal with a possibly gapless spectrum, as well as with disorder, we will have to formulate the magneto-electric coupling in a slightly different way from Refs. 9,10. As explained in Ref. 31, the magneto-electric effect in $d = 3$ is the descendant of a more faithful analog of the IQHE in $d = 4$[41,42]. The dimensional reduction is accomplished by replacing the extra momentum and vector potential components by an auxiliary field $q_4 + A_4 \rightarrow Q + \phi$. Just like $q_4 + A_4$, $Q + \phi$ is odd under both inversion and time reversal symmetry. The auxiliary field consists of a homogeneous part Q (the analog of q_4), and an inhomogeneous part ϕ (the analog of A_4). We take ϕ as an external field, and Q as a parameter of the system, even though in reality both can be realized by the same external field. Also, we will want to maintain time-reversal symmetry, and the values Q can assume are restricted because of this. Like q_4 in $d = 4$, the Q could have been restricted to a Brillouin Zone $0 \leq Q \leq 2\pi$, and take on the values $Q = 0, \pi$, or it could be defined in the continuum $-\infty \leq Q \leq \infty$, and take on only the value $Q = 0$. The $d = 4$

Chern form $S \sim \int d\vec{r} dt A_\alpha F_{\beta\gamma} F_{\delta\eta} \epsilon^{\alpha\beta\gamma\delta\eta}$ is then replaced by

$$S_{EB} = \chi(Q) \frac{1}{8\pi} \int_{\mathbf{r},t} \epsilon^{\nu\lambda\tau\mu} A_\nu F_{\lambda\tau} \partial_\mu \phi$$
$$= \chi(Q) \frac{1}{2\pi} \int d\vec{r} dt \vec{E} \cdot \vec{B} \phi \ . \tag{7}$$

Here we have used the electromagnetic field strength $F_{\mu\nu} = \partial_\mu A_\nu - (\mu \leftrightarrow \nu)$, and the Greek letters $\mu\nu\lambda\tau$ denoting space-time indices in $d = 3$, while $\alpha\beta\gamma\delta\eta$ denote space-time indices in $d = 4$. The transport coefficient χ is the quantity we want to calculate. Taking ϕ to be dimensionless, χ is dimensionless as well. Comparing (2) and (7), we would naively identify $P_3 = \phi\chi$, a combination of the external field ϕ and the response coefficient χ. In fact one should identify[9] $P_3 = \int_{-\infty}^{0} dQ \chi(Q)$, where dQ replaced ϕ, as we will show explicitly later. The precise value of χ depends on how the field ϕ is defined and couples to the system, and therefore by itself will *not* attain a universal quantized value. This is the one sacrifice we have to make in the alternate formulation of the magneto electric response. On the other hand, it will prove a more robust quantity to measure, in a system that may be gapless, and most importantly it will be quantized in an insulator - the key qualitative feature we are after.

We will now derive the analog of (5) in the magnetoelectric response. The derivation in the body of this manuscript is not rigorous, and does not apply to gapless systems. It is presented here for the sake of brevity and clarity. In the supplementary material A we will derive the result with some assumptions, while a general rigorous derivation is left for a future publication. From the term in the action (7) we can find the macroscopic current

$$J^\mu = \chi \frac{1}{4\pi} \epsilon^{\mu\nu\lambda\tau} F_{\nu\lambda} \partial_\tau \phi \ . \tag{8}$$

The density $n = -J^0$ is given by

$$n = -\chi \frac{1}{4\pi} \epsilon^{abc} F_{ab} \partial_c \phi = -\chi \frac{1}{2\pi} B^c \partial_c \phi \ , \tag{9}$$

where we have used $\epsilon^{abc} F_{ab} = 2B^c$ (we use the Minkowski metric sign $(-,+,+,+)$ here). Taking derivatives with respect to the magnetic field B^c, and the auxiliary field gradient $\partial_c \phi = h_c$, we now find

$$\chi \delta_a^b = -2\pi \frac{\partial^2 n}{\partial B^a \partial h_b} = -2\pi \frac{\partial^2 M_a}{\partial \mu \partial h_b} \ , \tag{10}$$

where we used the same Maxwell relation as in (5). Note that the magneto-electric response is found from the magnetization *parallel* to the direction of the auxiliary field gradient. This should not be surprising as the magnetoelectric field should not care about whether the system is isotropic or not. In an isotropic system, the absence of any other directionality necessitates this outcome. The result (10) can also be derived from (6), by realizing that when the system is time-reversal invariant, the magnetization to lowest order is linear in ϕ. We take $\phi = x_a h^a$ (and $Q = 0$), and assume the magnetization has only a dependence on h. We then have

$M_a(h_d, \mu(\mathbf{x})) \approx \left. \frac{\partial M_a}{\partial h_d} \right|_{h=0} h_d$, where here M is the (orbital) magnetization, and we arrive at

$$J^a = -\epsilon^{abc} \left. \frac{\partial^2 M_c}{\partial \mu \partial h_d} \right|_{h=0} E_b h_d \ . \tag{11}$$

From (8) we then find

$$J^a = \frac{\chi}{4\pi} 4 \epsilon^{ab0c} F_{b0} \partial_c \phi = \frac{\chi}{2\pi} \epsilon^{abc} E_b \partial_c \phi \ , \tag{12}$$

where we used $F_{a,0} = \partial_a A_0 - \partial_0 A_a = -\partial_a \Phi - \partial_t A_a = E_a$. Comparing with (11), this allows us to identify $\chi \delta_c^d = -2\pi \left. \frac{\partial^2 M_c}{\partial \mu \partial h_d} \right|_{h=0}$ precisely (10).

A rigorous proof of (10), as well as a generalization to gapless systems can be derived with some effort. Following standard response theory techniques[43], we can find the nonlinear response analog of (4)

$$\chi^I = \frac{4\pi}{4!} \epsilon^{abc} Re \left\{ Tr \left[\delta(H) \left(v_b G_R v_\phi - v_\phi G_R v_b \right) G_R v_c G_R v_a \right] \right\}$$
$$\chi^{II} = 2\pi \frac{\epsilon^{\mu\nu\lambda\tau}}{4!} \int_{-\infty}^{+\infty} \frac{d\epsilon}{2\pi i} f(\epsilon)$$
$$Tr \left[v_\phi G_R v_\mu G_R v_\nu G_R v_\lambda G_R v_\tau G_R \right] + c.c. \ , \tag{13}$$

where in the expression for the contribution χ^{II}, all Green's functions depend on the frequency ϵ, while in the expression for χ^I, all Green's functions have $\epsilon = 0$. The velocity v_ϕ is the conjugate operator to the auxiliary field $H = H_0 + \int_\mathbf{x} \phi(\mathbf{x}) v_\phi$. The full details of this derivation we leave for a future publication. In the supplementary material A we provide a limited derivation, appropriate for an insulator, with the field $\phi = h_a x^a$ coupled to a momentum independent v_ϕ.

Much like (4), the form (13) distinguishes between Fermi surface contributions χ^I, which vanish for an insulator, and the contribution χ^{II}, which turns out to be the second derivative of the orbital magnetization, satisfiying (10)

$$\chi^{II} = -\frac{2\pi}{3} \frac{\partial^2 M_a}{\partial \mu \partial h_a} \ , \tag{14}$$

where the $1/3$ factor appears after we sum over the indices in (10). The effect of disorder on χ^{II} is entirely contained in the DOS, regardless of the disorder strength, a very useful fact for carrying out theoretical calculations. Disorder will reduce the effective gap in the spectrum, compared with the clean limit[44], but otherwise will not change anything, as long as the chemical potential remains in the gap.

Our result suggests that even in a gapless topological metal, where $\chi^I \neq 0$, we could still obtain χ^{II}, by measuring the 2nd derivative of the magnetization. As noted earlier, at least in the insulating case, the Zeeman contribution to the magnetization should not vary with the chemical potential, and measuring the full magnetization instead of the orbital magnetization alone, will yield the same result. It is then conceptually straightforward to measure magnetization, and vary the chemical potential. The auxiliary field gradient h_a, on the

other hand, is at this point an abstract object we defined for our theoretical needs. We turn our attention now to exploring how ϕ can be realized. First, given that ϕ must be odd under time reversal and inversion, it can appear when anti-ferromagnetic (AFM) order is present in the material. It is not unimaginable that a topological insulator material could be stuffed with magnetic atoms that realize AFM order in the material. Second, we need ϕ to vary (slowly) in space, as illustrated in Fig. 1. This can occur naturally in AFM order, as it tends to form magnetic domains. More difficult will be controlling and varying the strength of the AFM field. This can be done by changing the temperature of the system, and for better control of it, to be sufficiently close to the critical temperature of the AFM order.

We now turn to a concrete example, based on the band structure of Bi_2Se_3. Using the effective model derived for Bi_2Se_3 in Ref. 45, we have

$$H_0 = C(\mathbf{q}) + M(\mathbf{q})\gamma_5 + B_0 q_3 \gamma_4 + A_0(q_2\gamma_1 - q_1\gamma_2) + o(q^3) \,, \tag{15}$$

where $C(\mathbf{q}) = C_0 - \mu + C_1 q_3^2 + C_2(q_1^2 + q_2^2)$, and $M(\mathbf{q}) = M_0 + M_1 q_3^2 + M_2(q_1^2 + q_2^2)$. The gamma matrices are taken as $\gamma_{a=1,2,3} = \sigma_a \tau_1$, $\gamma_4 = \tau_2$, and $\gamma_5 = \tau_3$, where σ_a are the Pauli matrices of the electron spin, and τ_a are the Pauli matrices describing two orbitals. It is noteworthy that the model (15) with different values for the parameters can be used to describe the model proposed in Ref. 5 for a 3D STI. Next we will use a spatially-varying Zeeman field as a realization of the auxiliary field ϕ. The 2 orbitals originate in the p-orbitals of different atoms (Bi and Se respectively). As a consequence, the two orbitals in general will have a different gyromagnetic ratio when coupled to a Zeeman field. Indeed, if the magnetic field is applied in the z-direction (the trigonal axis of the Bi_2Se_3 crystal), Ref. 45 finds $H_1 = b\sigma_3(g_0 + g_3\tau_3)$ If the magnetic field b varies on the length scale of atomic distances, it will effectively break inversion symmetry in the crystal and allow a more general Zeeman coupling to occur

$$H_1 = b_{FM}\sigma_3(g_0 + g_3\tau_3) + b_{AFM}\sigma_3(g_1\tau_1 + g_2\tau_2) \,. \tag{16}$$

Here b_{FM} and b_{AFM} are "ferromagnetic" (FM) and "anti-ferromagnetic" (AFM) fields, respectively. The field b_{AFM} is odd under *both* time-reversal and inversion, and is therefore a suitable realization of ϕ. Generating it may require anti-ferromagnetic order, though a ferrimagnetic field would also suffice to get $b_{AFM} \neq 0$. Also, one could imagine breaking inversion symmetry in Bi_2Se_3 by the application of pressure, and then an ordinary Zeeman field would suffice. We also note in passing that we neglect the orbital coupling of the magnetic field we apply here. With a sufficiently weak Zeeman field the flux through a unit cell of the solid will be small, and we can safely neglect it. Ref. 45 has calculated $g_0 \approx -21.3\mu_B/4 \approx -3.1 \times 10^{-4}T^{-1}eV$, and $g_3 \approx -29.5\mu_B/4 \approx 4.3 \times 10^{-4}T^{-1}eV$. We will estimate $g_{1,2}$ to have comparable values $g_{1,2} = 3.5 \times 10^{-4}T^{-1}eV$ (and propose a method of measuring it in the supplementary material A1). The remaining parameters in (15), take on the values $A_0 = 3.33eV\text{Å}, B_0 = 2.26eV\text{Å}, C_0 = -0.0083eV, C_1 = 5.74eV\text{Å}^2, C_2 = 30.4eV\text{Å}^2, M_0 = -0.28eV, M_1 = 6.86eV\text{Å}^2, M_2 = 44.5eV\text{Å}^2$.

Taking the model Hamiltonian (15) coupled to the Zeeman fields in (16), we have $H(b) = H_0 + b\sigma_3\left(\sum_{j=0}^3 g_j\tau_j\right)$. Using (13), at temperature $T = 0$, with $v_\phi = \frac{\partial H(b)}{\partial b}$, we find

$$\chi^{II}(b=0) = -g_1 4i A_0^2 B_0 \int_0^\infty \frac{2\pi q dq}{(2\pi)^2} \int_{-\infty}^0 d\epsilon \int_{-\infty}^{+\infty} \frac{dz}{2\pi}$$

$$\times \frac{[M_0 - M_2 q^2 - M_1 z^2]}{\left[M(q,z)^2 + A_0^2 q^2 + B_0^2 z^2 - (\epsilon + i\delta - C(q,z))^2\right]^3} + c.c. \,, \tag{17}$$

where we denote $q^2 = q_1^2 + q_2^2, z = q_3$. Note here that χ depends only on g_1. It is only a very special coupling that produces the completely anti-symmetric magnetoelectric response, and this observation tells us that even if we have both b_{FM} and b_{AFM}, χ can be measured since it is a response only to b_{AFM}. We perform the energy integral first

$$\lim_{\delta \to 0} Im\left[\int_{-\infty}^0 \frac{d\epsilon}{(E^2 - (\epsilon - C + i\delta)^2)^3}\right]$$
$$= \frac{3\pi}{16E^5}\left[\frac{2}{\pi}Im\left[\tanh^{-1}\left(\frac{-C}{E}\right)\right] - 1\right] = -\frac{3\pi\Theta(E^2 - C^2)}{16E^5} \,, \tag{18}$$

where $E^2 = M(q,z)^2 + A_0^2 q^2 + B_0^2 z^2$, and we have used

$$\frac{2}{\pi}Im\left[\tanh^{-1}(x)\right] = \begin{cases} 1 & |x| > 1 \\ 0 & |x| < 1 \end{cases} = \Theta(x^2 - 1).$$

We are now left with

$$\chi^{II}(b=0) = -g_1\frac{3\pi}{2}A_0^2 B_0 \int_0^\infty \frac{2\pi q dq}{(2\pi)^2} \int_{-\infty}^{+\infty} \frac{dz}{2\pi}$$
$$\times \Theta\left(E^2 - C(q,z)^2\right)\frac{[M_0 - M_2 q^2 - M_1 z^2]}{E^5} \,. \tag{19}$$

For $\mu = 0$, and taking $g_1 = 3.5 \times 10^{-4}T^{-1}eV$ we get $\chi^{II} \approx 4 \times 10^{-4}T^{-1}$. Note that the combination $\chi^{II}\phi = \chi^{II}b_{AFM}$ is dimensionless, as we required. Varying the chemical potential, we find the values plotted in Fig. 2. The most striking feature in plotting χ^{II} versus chemical potential is the *plateau* in its value while μ is in the gap. Once the chemical potential is outside the gap, the value of χ^{II} changes continuously. This will be the most easily discernible experimental signature of the topological insulator - a plateau in the transport coefficient χ - even though its value is not universal.

As we mentioned earlier, formulated in this way no universal value of χ^{II} is manifest. However, there is one theoretical quantity that will be universal, and quantized. For this we need to consider $\chi^{II}(Q)$, calculated for the entire range of values of Q

$$\chi^{II}(Q) = 2\pi\frac{1}{4!}\epsilon^{\mu\nu\lambda\tau}\int_{-\infty}^{+\infty}\frac{d\epsilon}{2\pi i}f(\epsilon)$$
$$Tr\left[v_\phi G_R(Q)v_\mu G_R(Q)v_\nu G_R(Q)v_\lambda G_R(Q)v_\tau G_R(Q)\right] + c.c. \,, \tag{20}$$

where now $G_R(Q) = [\omega + i\delta - H_0 - v_\phi Q]^{-1}$. Coupled to the field ϕ, the Hamiltonian is $H(Q) = H_0 +$
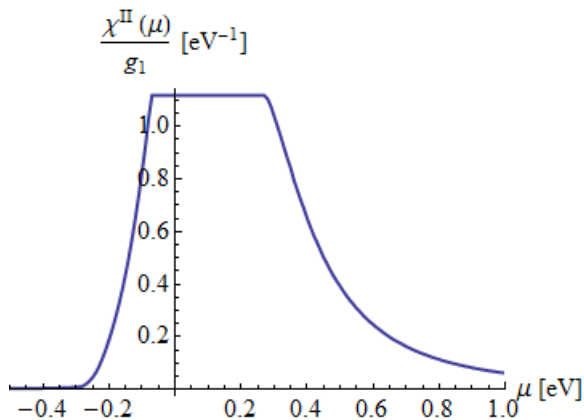
FIG. 2: Plot of χ^{II}/g_1 for numerically Bi$_2$Se$_3$. The χ^{II} value is quantized as long as the chemical potential μ is in the bulk gap. Once μ is outside the gap, χ^{II} is no longer quantized.

$\int_{\mathbf{x}} v_\phi (Q + \phi(\mathbf{x}))$, and can now be mapped directly onto a $d = 4$ Hamiltonian $H_{4D} = H_0 + \int_{\mathbf{x}} v_\phi (q_4 + A_4(\mathbf{x}))$. In $d = 4$ there exists a nonlinear transport coefficient $C_2^{9,41,42}$ of $J^\mu = \frac{C_2}{8\pi^2}\epsilon^{\mu\nu\lambda\tau\rho}\partial_\nu A_\lambda\partial_\tau A_\rho$ which in an insulator is quantized to integer values $C_2 = N$. The expression for C_2 turns out to be $C_2 = \int_{-\infty}^{+\infty} dQ \chi^{II}(Q)$ 9see Ref. 9) In an inversion symmetric system, we can easily show that $\chi^{II}(Q) = \chi^{II}(-Q)$, by noting that under inversion $v_{1,2,3,\phi}$ are odd, v_0 is even, and $G_R(Q) \to G_R(-Q)$. We then have $C_2 = 2\int_{-\infty}^{0} dQ \chi^{II}(Q) = 2P_3$, and therefore $P_3 = \frac{N}{2}$ assumes *half* integer values.

In conclusion, we have found that the magneto-electric coupling in topological insulators and their gapless counterparts, can be related to a third derivative of a thermodynamic potential. Most interestingly, this implies that the topological effects could be measured by probing either charge-

density or Magnetization in equilibrium, rather than from non-equilibrium transport properties of the surface. Our result (10), suggests a conceptually simple way to measure the magneto-electric response, by measuring magnetization, while varying the chemical potential and the auxiliary field. Moreover, our formula holds regardless of whether the system is gapless or gapped, clean or disordered. The measurement we propose, however, is challenging. First and foremost, realizing the auxiliary field is difficult, in the case of Bi$_2$Se$_3$, requiring the introduction of microscopic AFM order to the bulk of the material, and carefully controlling it. Controlling the chemical potential may also be challenging, given that we wish to probe 3D systems. Varying the chemical potential is needed not only to calculate the derivative in (10), but also to detect the most clear cut evidence for a topological state - the plateau in χ^{II}, as illustrated in Fig. 2. Finally, the magnetization in our formula is the *orbital* magnetization, ignoring the Zeeman contributions to the magnetization. In a metal, the Zeeman contribution can vary with the chemical potential, but in an insulator, it will not. Therefore measuring the full magnetization, instead of the orbital magnetization, will yield χ^{II} in the insulating state, but in the metal it will yield χ^{II} plus some corrections. However, the key qualitative feature is the plateau in χ^{II} in the insulating state, which will still show up when measuring the total magnetization instead of the orbital magnetization. Despite these difficulties, our findings allow a unique conceptual approach to measuring the magneto-electric coupling, and it is our sincere hope this insight will be put to use in the lab.

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Appendix A: Supplementary material

1. Method of measuring Zeeman coupling to AFM order

The Zeeman coupling to the AFM field g_1 used in (16) is unknown. While it should be possible to calculate it, a better approach may be to measure it experimentally, in the following manner. Starting from zero, increase the auxiliary field gradient in the bulk, until zero modes appear in the bulk. This will have a distinct spectroscopic signature. Take our model for Bi_2Se_3 , (15), with $C_0 \approx 0$ and keep only terms to linear order in q,

$$H = M_0\gamma_5 + B_0q_3\gamma_4 + A_0(q_2\gamma_1 - q_1\gamma_2) + g_1b_{AFM}(\mathbf{x})\gamma_3 + o(q^2) , \tag{A1}$$

where we have used $\gamma_3 = \sigma_3\tau_1$. Squaring the Hamiltonian, and assuming b_{AFM} varies only in the x direction we find

$$H^2 = M_0^2 + A_0(q_1^2 + q_2^2) + B_0^2q_3^2 + (g_1b_{AFM})^2 \\ + iA_0g_1\gamma_2\gamma_3\partial_x b_{AFM}(x) . \tag{A2}$$

From this we can find

$$\left[H^2 - \left(M_0^2 + A_0(q_1^2 + q_2^2) + B_0^2q_3^2 + (g_1b_{AFM})^2\right)\right]^2 \\ = A_0^2g_1^2 \left(\partial_x b_{AFM}(x)\right)^2 . \tag{A3}$$

The term on the right hand side is $o(b_{AFM}^2)$, while the last term on the left hand side is $o(b_{AFM}^4)$, and we neglect it. If we now look for $E = 0$ solutions we find these are possible only when

$$|\partial_x b_{AFM}(x)| \approx \frac{M_0}{A_0g_1} = \frac{1}{\xi g_1} . \tag{A4}$$

We identify $\xi = \frac{A_0}{M_0}$ as the skin depth of the Jackiw-Rebbi surface state solutions[46], and in this way we see that as the gradient is increased, when it hits the value $g_1|\nabla b_{AFM}(x)| \approx \xi^{-1}$ gapless states appear tied to this gradient. This would suggest that as we increase the gradient we could observe spectral flow, and this could perhaps be measured by absorption experiments.

2. Nonlinear response

In this section we will briefly describe how one derives the response function to the product of two fields. The external fields $F_j(t)$ are coupled to operators X_j. Coupling an imaginary time action with 3 fields $F_{j=1,2,3}$, we have a partition function $Z = Tr\left[e^{-S-\delta S}\right]$ where

$$\delta S = -\int_\tau \sum_{j=1}^3 X_j(\tau)F_j(\tau) . \tag{A5}$$

Here the operators $X_j(\tau)$ are in the Heisenberg representation in imaginary time. Here we assume that the real time action

can be converted to an imaginary time action with no difficulty - that we encounter no poles in the partition function in the continuation of time t to the complex plane.

The expectation value of the operator X_1 is given by

$$
\begin{aligned}
\langle X_1 \rangle &= \left. \frac{\delta \log(Z)}{\delta F_1} \right|_{F_1=0} \\
&= \text{equilibrium} + \text{linear response} + \text{quadratic response} \\
&= 0 + \mathcal{O}(F_2 + F_3) + \mathcal{O}(F_2 F_3) + \dots .
\end{aligned}
\tag{A6}
$$

The quadratic response coefficient will be given by

$$
\begin{aligned}
u &= \frac{1}{2} \left[\frac{\delta^2 \langle X_1 \rangle}{\delta F_2 \delta F_3} + \frac{\delta^2 \langle X_1 \rangle}{\delta F_3 \delta F_2} \right] \\
&= \frac{1}{2} \left. \frac{\delta^3 \log(Z)}{\delta F_1 \delta F_2 \delta F_3} \right|_{F_j=0} + (F_2 \leftrightarrow F_3) \\
&= \frac{1}{2Z} \left. \frac{\delta^3 Z}{\delta F_1 \delta F_2 \delta F_3} \right|_{F_j=0} + (F_2 \leftrightarrow F_3) ,
\end{aligned}
\tag{A7}
$$

where the last equality follows from $\left. \frac{\delta Z}{\delta F_j} \right|_{F_j=0} = 0$ - the expectation value for $X_{1,2,3}$ are assumed to vanish in equilibrium. Therefore, we can immediately relate the response coefficient u to a correlation function

$$
\begin{aligned}
u &= \frac{1}{2Z} Tr\left[X_1 X_2 X_3 e^{-S} \right] + (2 \leftrightarrow 3) \\
&= \frac{1}{2} \left[\langle X_1 X_2 X_3 \rangle + \langle X_1 X_3 X_2 \rangle \right] .
\end{aligned}
\tag{A8}
$$

Deriving this response function using real time instead of imaginary time, the correlation function would consist of a double commutator.

$$
u \sim \langle [[X_1, X_2], X_3] \rangle .
\tag{A9}
$$

The imaginary time formulation is more convenient as it eliminates the commutator.

The correlation function will only depend on the time differences, and we shall therefore Fourier transform from imaginary time to (bosonic) Mastubara frequency. The correlation function we want to calculate is then

$$
u(i\omega, i\omega') = \frac{1}{2} \langle X_1(-i\omega - i\omega') X_2(i\omega) X_3(i\omega') \rangle + (2 \leftrightarrow 3) ,
\tag{A10}
$$

described by the Feynman diagram in Fig. 3. Using the Green's function $G^{-1}(iE_n) = iE_n - H$, we have

$$
\begin{aligned}
u(i\omega, i\omega') =& T \sum_n Tr\Big[X_1 G(iE_n) X_2 G(iE_n + i\omega) \\
& X_3 G(iE_n + i\omega + i\omega') \Big] + (2 \leftrightarrow 3) \\
=& T \sum_n P(iE_n, iE_n + i\omega, iE_n + i\omega + i\omega') ,
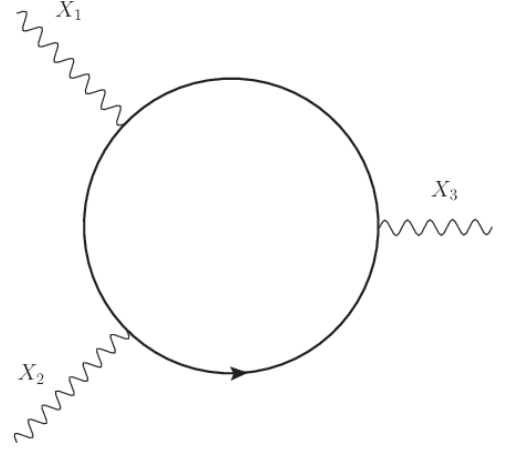\end{aligned}
\tag{A11}
$$

FIG. 3: Nonlinear response from the 3-legged bubble. From the particle physics point of view, two bosons are coming in, getting absorbed by a fermion with vertices $X_{2,3}$, and one boson being emitted by the fermion from vertex X_1. From the response theory point of view, two perturbing fields couple to a fermionic system through the operators $X_{2,3}$ and produce an expectation value for the operator X_1.

where E_n are fermionic Matusbara frequencies, and the trace is over all degrees of freedom in the Hamiltonian. In addition, X_j are now in the Schroedinger picture, and have no time or frequency dependence.

The response function u in real time must be causal, and therefore we will have to take $i\omega \to \omega + i\delta$ and $i\omega' \to \omega' + i\delta$. The intuitive way to understand this is that the quadratic response must be to two perturbations in the past, and therefore both external fields must be retarded. One should think of the process described in the diagram as 2 bosons coming in with frequencies ω, ω', being absorbed by fermions, and one boson coming out with frequency $\omega + \omega'$.

We will now switch from imaginary to real frequencies. The single particle Green's function

$$
G(iE_n) = [iE_n - H]^{-1} ,
\tag{A12}
$$

gets replaced by

$$
G(z) = [z - H + i\delta \, sgn(Im(z))]^{-1} ,
\tag{A13}
$$

with the branch cut at $Im(z) = 0$ obviated by the new term involving $0 < \delta \to 0$. It is worth noting at this point, that even for a dressed Green's function, we will require the same branch cut, since it is the manifestation of causality. The form of the Green's function, with no self-energy, holds strictly only for a non-interacting Hamiltonian, but for our needs this will suffice. Using the Matsubara sum identity

$$
T \sum_{E_n} h(iE_n) = \frac{-1}{2\pi i} \oint dz f(z) h(z) ,
\tag{A14}
$$

where $f(z) = \left[1 + e^{\beta(z-\mu)} \right]^{-1}$ is the Fermi-Dirac distribution, and assuming that the current vertex does not have any branch cuts, the Matsubara summation has to be broken up to 4 contours in different domains, divided by the 3 branch cuts
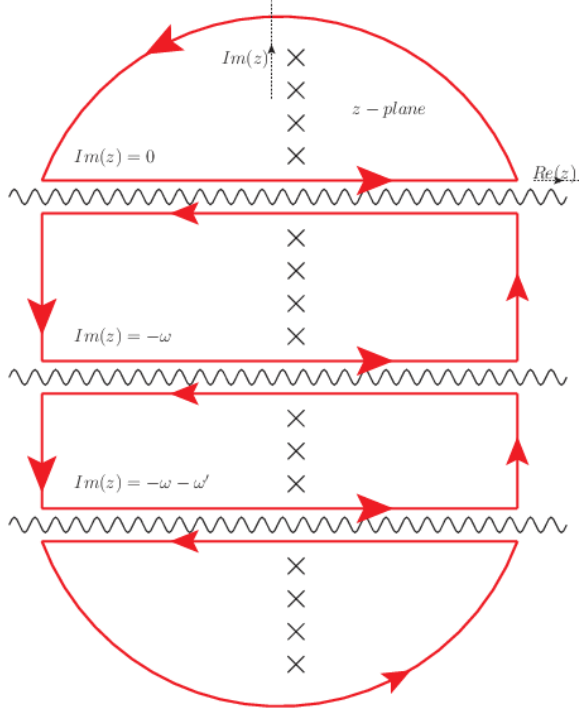
FIG. 4: Integration contours in the complex plane for the frequency z. Fermionic Matsubara frequencies are the poles marked by (blue) crosses, the three branch cuts are denoted by a wavy (black) line, and the 4 integration contours are marked by the (red) loops with arrows.

at $Im(z) = 0$, $Im(z + i\omega) = 0$ and $Im(z + i\omega + i\omega') = 0$. In each domain all of the poles not in $f(z)$ are outside the domain, since the imaginary part of the denominator in the Green's function never vanishes in each domain. The X_j operators do not have any poles, as they are independent of frequency for a non-interacting Hamiltonian. Therefore, the Matsubara sum in the 4 separate domains can be deformed to contour integrals over the entire extent of each domain (see Fig. 4). Assuming without loss of generality $\omega > 0, \omega' > 0$ (since we will be sending them to zero at the end) this yields for us

$$
\begin{aligned}
u(i\omega, i\omega') &= \sum_{j=1}^{4} \oint_{C_j} \frac{idz}{2\pi} f(z) P(z, z + i\omega, z + i\omega + i\omega') \\
&= \int_{-\infty}^{+\infty} \frac{id\epsilon}{2\pi} \Bigg[\Big[P(\epsilon + i\delta, \epsilon + i\omega, \epsilon + i\omega + i\omega') \\
&\quad - P(\epsilon - i\delta, \epsilon + i\omega, \epsilon + i\omega + i\omega') \Big] f(\epsilon) \\
&\quad + \Big[P(\epsilon - i\omega, \epsilon + i\delta, \epsilon + i\omega') \\
&\quad - P(\epsilon - i\omega, \epsilon - i\delta, \epsilon + i\omega') \Big] f(\epsilon - i\omega) \\
&\quad + \Big[P(\epsilon - i\omega - i\omega', \epsilon - i\omega', \epsilon + i\delta) \\
&\quad - P(\epsilon - i\omega - i\omega', \epsilon - i\omega', \epsilon - i\delta) \Big] f(\epsilon - i\omega - i\omega') \Bigg].
\end{aligned}
$$
(A15)

Since ω and ω' are bosonic Matsubara frequencies, we have $f(\epsilon - i\omega) = f(\epsilon)$ and $f(\epsilon - i\omega - i\omega') = f(\epsilon)$. This, together with the Wick rotations $i\omega \to \omega + i\delta$ and $i\omega' \to \omega' + i\delta$ then yields

$$
\begin{aligned}
u(\omega, \omega') &= \int_{-\infty}^{+\infty} \frac{id\epsilon}{2\pi} f(\epsilon) \Bigg[\\
&\quad \Big[P(\epsilon + i\delta, \epsilon + \omega + i\delta, \epsilon + \omega + \omega' + i\delta) \\
&\quad - P(\epsilon - i\delta, \epsilon + \omega + i\delta, \epsilon + \omega + \omega' + i\delta) \Big] \\
&\quad + \Big[P(\epsilon - \omega - i\delta, \epsilon + i\delta, \epsilon + \omega' + i\delta) \\
&\quad - P(\epsilon - \omega - i\delta, \epsilon - i\delta, \epsilon + \omega' + i\delta) \Big] \\
&\quad + \Big[P(\epsilon - \omega - \omega' - i\delta, \epsilon - \omega' - i\delta, \epsilon + i\delta) \\
&\quad - P(\epsilon - \omega - \omega' - i\delta, \epsilon - \omega' - i\delta, \epsilon - i\delta) \Big] \Bigg].
\end{aligned}
$$
(A16)

Now we can identify

$$
\begin{aligned}
&P(\epsilon + i\delta, \epsilon + \omega + i\delta, \epsilon + \omega + \omega' + i\delta) \\
&= P_{RRR}(\epsilon, \epsilon + \omega, \epsilon + \omega + \omega') \\
&= \frac{1}{2} Tr \Big[X_1 G_R(\epsilon) X_2 G_R(\epsilon + \omega) X_3 G_R(\epsilon + \omega + \omega') \Big] \\
&\quad + (2 \leftrightarrow 3),
\end{aligned}
$$
(A17)

as involving 3 retarded Greens functions, and in similar ways identify all the other terms, as products of retarded and advanced Green's functions. Shifting the integration variable in the 2nd and 3rd terms we can arrive at

$$
\begin{aligned}
u(\omega, \omega') &= \int_{-\infty}^{+\infty} \frac{id\epsilon}{2\pi} \Big[f(\epsilon)(P_{RRR} - P_{ARR}) \\
&\quad + f(\epsilon + \omega)(P_{ARR} - P_{AAR}) \\
&\quad + f(\epsilon + \omega + \omega')(P_{AAR} - P_{AAA}) \Big],
\end{aligned}
$$
(A18)

where all P-functions depend on the trio $(\epsilon, \epsilon+\omega, \epsilon+\omega+\omega')$. Grouping together the terms by the number of retarded and advanced Green's function, we find

$$
\begin{aligned}
u(\omega, \omega') &= \int_{-\infty}^{+\infty} \frac{id\epsilon}{2\pi} \Big[(f(\epsilon + \omega) - f(\epsilon)) P_{ARR} \\
&\quad + (f(\epsilon + \omega + \omega') - f(\epsilon + \omega)) P_{AAR} \\
&\quad + [f(\epsilon) P_{RRR} - f(\epsilon + \omega + \omega') P_{AAA}] \Big].
\end{aligned}
$$
(A19)

This is the most general form of nonlinear response to two independent fields.

3. Derivation of the thermodynamic relation

In the previous section, we analyzed the general expression (A19) for quadratic response to two fields (in our case F_{ab} and

h_c), captured by the Feynman diagram of Fig 3. In this section we will use (A19) to prove the relation (10).

We will only be interested in the low frequency limit, and in fact we will keep terms only to linear order in the frequencies ω, ω'. We first shift the integration variable in the last term in(A19), $\epsilon \to \epsilon - \omega$ to get

$$
\begin{aligned}
[f(\epsilon)P_{RRR} - f(\epsilon + \omega + \omega')P_{AAA}] \to \\
f(\epsilon - \omega)P_{RRR}(\epsilon - \omega, \epsilon, \epsilon + \omega') \\
-f(\epsilon + \omega')P_{AAA}(\epsilon - \omega, \epsilon, \epsilon + \omega') ,
\end{aligned} \tag{A20}
$$

and then expanding in ω, ω' we reach

$$
u(\omega, \omega') \approx \int_{-\infty}^{+\infty} \frac{id\epsilon}{2\pi}
$$

$$
\left\{ f'(\epsilon)\Big[\omega\left(P_{ARR}(\epsilon, \epsilon, \epsilon) - P_{RRR}(\epsilon, \epsilon, \epsilon)\right) \right.
$$

$$
+ \omega'\left(P_{AAR}(\epsilon, \epsilon, \epsilon) - P_{AAA}(\epsilon, \epsilon, \epsilon)\right)\Big]
$$

$$
\left. + f(\epsilon)\Big[P_{RRR}(\epsilon - \omega, \epsilon, \epsilon + \omega') - P_{AAA}(\epsilon - \omega, \epsilon, \epsilon + \omega')\Big] \right\}
$$

$$
\approx \int_{-\infty}^{+\infty} \frac{id\epsilon}{2\pi} \left\{ \vphantom{\int} \right.
$$

$$
f'(\epsilon)\Big[\omega\left(P_{ARR} - P_{RRR}\right) + \omega'\left(P_{AAR} - P_{AAA}\right)\Big]
$$

$$
+ f(\epsilon)\Big[\frac{\omega'}{2}Tr\left[X_1 G_R(X_2 G_R X_3 + X_3 G_R X_2)\partial_\epsilon G_R\right]
$$

$$
- \frac{\omega}{2}Tr\left[X_1 \partial_\epsilon G_R(X_2 G_R X_3 + X_3 G_R X_2)G_R\right]
$$

$$
\left. + P_{RRR} - (R \to A)\Big] \right\} , \tag{A21}
$$

where in the final form all Green's functions depend on the energy ϵ, $G_{R,A} = G_{R,A}(\epsilon)$ and $P_{RRR} = P_{RRR}(\epsilon, \epsilon, \epsilon)$. Now we split this expression into terms involving a derivative of the Fermi-Dirac function u^I, and all the rest $u^{II} = u - u^I$. The two contributions are

$$
u^I(\omega, \omega') = \omega \int_{-\infty}^{+\infty} \frac{id\epsilon}{2\pi} f'(\epsilon)\left[P_{ARR}(\epsilon, \epsilon, \epsilon) - P_{RRR}(\epsilon, \epsilon, \epsilon)\right]
$$

$$
+ \omega' \int_{-\infty}^{+\infty} \frac{id\epsilon}{2\pi} f'(\epsilon)\left[P_{AAR}(\epsilon, \epsilon, \epsilon) - P_{AAA}(\epsilon, \epsilon, \epsilon)\right]
$$

$$
u^{II}(\omega, \omega') = \int_{-\infty}^{+\infty} \frac{id\epsilon}{2\pi} f(\epsilon)
$$

$$
\left[\frac{\omega'}{2}Tr\left(X_1 G_R(X_2 G_R X_3 + X_3 G_R X_2)(\partial_\epsilon G_R)\right) \right.
$$

$$
- \frac{\omega}{2}Tr\left(X_1(\partial_\epsilon G_R)(X_2 G_R X_3 + X_3 G_R X_2)G_R\right)
$$

$$
\left. + P_{RRR} - (R \to A)\right] . \tag{A22}
$$

At zero temperature $f'(\epsilon) = -\delta(\epsilon)$, leading to

$$
\begin{aligned}
u^I|_{T=0} = \frac{\omega}{2\pi i}\left[P_{ARR}(0,0,0) - P_{RRR}(0,0,0)\right] \\
+ \frac{\omega'}{2\pi i}\left[P_{AAR}(0,0,0) - P_{AAA}(0,0,0)\right] .
\end{aligned} \tag{A23}
$$

Using the identity

$$
G_A(\epsilon) - G_R(\epsilon) = \frac{1}{2\pi i}\delta(H - \epsilon) , \tag{A24}
$$

we can write

$$
\begin{aligned}
u^I|_{T=0} = \frac{\omega}{2}\left[X_1 \delta(H) X_2 G_R(0) X_3 G_R(0)\right] \\
- \frac{\omega'}{2}\left[X_1 G_A(0) X_2 G_A(0) X_3 \delta(H)\right] \\
+ (2 \leftrightarrow 3) ,
\end{aligned} \tag{A25}
$$

and we see that this term involves contributions only from the Fermi surface. For an insulator, there is zero density of states at the Fermi energy $\epsilon = 0$, and this contribution will vanish. We can already see that this is reminiscent of the σ^I contribution to the conductivity in (4). More generally, at low temperature and frequency u^I depends only on states close to the Fermi energy.

Now we specialize the calculation to our problem. Consider a band structure perturbed by a random scalar potential,

$$
H = H_0(\mathbf{p}) + V(\mathbf{x}) , \tag{A26}
$$

and couple to an auxiliary field gradient $\phi = x_c h_c$ (introduced in (7)) as well as to an electric field, using the gauge $A_b = \frac{1}{i\omega}e^{-i\omega t}E_b$

$$
H_1 = x_c v_\phi h^c + \frac{1}{i\omega}e^{-i\omega t}E^b v_b . \tag{A27}
$$

We will calculate the current response

$$
J_a = u\epsilon_{abc}E^b h^c . \tag{A28}
$$

Comparing this with (8), we identify $u = \frac{\chi}{2\pi}$. Note that $v_b = \frac{\partial H_0}{\partial p^b}$, and that we assume v_ϕ is independent of momentum, and thus commutes with x_a. We will have to anti-symmetrize in the indices a, b, c, and take $\omega \to 0$ for the DC limit. As mentioned above, in the insulator case we have $u^I = 0$, and we need only calculate u^{II}.

We identify $X_1 = v_a$, $X_2 = \frac{1}{i\omega}v_b$ and $X_3 = x_c v_\phi$. The P_{RRR} term will vanish since is symmetric under $a \leftrightarrow b$

$$
\epsilon^{abc}P_{RRR}
$$

$$
\to \frac{\epsilon^{abc}}{2i\omega}Tr\left[v_a G_R v_b G_R x_c v_\phi G_R + v_a G_R x_c v_\phi G_R v_b G_R\right]
$$

$$
= \frac{\epsilon^{abc}}{i\omega}Tr\left[(v_a G_R v_b + v_b G_R v_a)G_R x_c v_\phi G_R\right] . \tag{A29}
$$

We are then left with

$$u = \frac{\epsilon^{abc}}{3!} \int_{-\infty}^{+\infty} \frac{id\epsilon}{2\pi} f(\epsilon) \left[\frac{\omega}{2} Tr \left(v_a G_R x_c v_\phi G_R \frac{v_b}{i\omega} (\partial_\epsilon G_R) \right) \right.$$
$$\left. - \frac{\omega}{2} Tr \left(v_a (\partial_\epsilon G_R) \frac{v_b}{i\omega} G_R x_c v_\phi G_R \right) - (R \to A) \right] .$$

(A30)

Swapping $a \leftrightarrow b$ in the second term we get

$$u = \frac{\epsilon^{abc}}{3!} \int_{-\infty}^{+\infty} \frac{d\epsilon}{2\pi} f(\epsilon)$$
$$Tr \left[v_a G_R x_c v_\phi G_R v_b (\partial_\epsilon G_R) \right] - (R \to A) .$$

(A31)

We shall now integrate by parts, to get

$$u = -\frac{\epsilon^{abc}}{3!} \int_{-\infty}^{+\infty} \frac{d\epsilon}{2\pi} f(\epsilon)$$
$$Tr \left[v_a \left((\partial_\epsilon G_R) x_c v_\phi G_R + G_R x_c v_\phi (\partial_\epsilon G_R) \right) v_b G_R \right]$$
$$- \frac{\epsilon^{abc}}{3!} \int_{-\infty}^{+\infty} \frac{d\epsilon}{2\pi} f'(\epsilon) Tr \left[v_a G_R x_c v_\phi G_R v_b G_R \right] - (R \to A) .$$

(A32)

This can be reorganized into

$$u = \frac{\epsilon^{abc}}{3!} \int_{-\infty}^{+\infty} \frac{d\epsilon}{2\pi} f(\epsilon) Tr \left[G_R x_c v_\phi G_R v_b G_R v_a G_R \right.$$
$$\left. + G_R v_b G_R v_a G_R x_c v_\phi G_R \right]$$
$$- \frac{\epsilon^{abc}}{3!} \int_{-\infty}^{+\infty} \frac{d\epsilon}{2\pi} f'(\epsilon) Tr \left[x_c v_\phi G_R v_b G_R v_a G_R \right] - (R \to A) .$$

(A33)

Using the relation $v_a = -i [x_a, H] = +i [x_a, G^{-1}]$, for either $G = G_{R,A}$, we find

$$G v_a G v_b G - (a \leftrightarrow b) = i G x_a v_b G + x_a G x_b - (a \leftrightarrow b) .$$

(A34)

Using this identity, as well as $x_a x_b - (a \leftrightarrow b) 0$ and the fact that v_ϕ commutes with x_a, we can show that

$$u = -\frac{\epsilon^{abc}}{3!} \int_{-\infty}^{+\infty} \frac{id\epsilon}{2\pi} f(\epsilon)$$
$$Tr \left[G_R x_c v_\phi G_R x_a v_b G_R + G_R x_a v_b G_R x_c v_\phi G_R \right]$$
$$+ \frac{\epsilon^{abc}}{3!} \int_{-\infty}^{+\infty} \frac{id\epsilon}{2\pi} f'(\epsilon) Tr \left[x_c v_\phi G_R x_a v_b G_R \right] - (R \to A) ,$$

(A35)

where we have also swapped a, b.

With the further observation that with a Hamiltonian of the form

$$H = H_0(\mathbf{p}) + V(\mathbf{x}) + v_a A^a + v_\phi x_c h^c ,$$

(A36)

where the vector potential is $A^a = -\frac{1}{2} \epsilon^{abc} x_b B_c$, and the auxiliary field is $\phi = x_c h^c$, we can show

$$\frac{\partial H}{\partial B_c} = -\frac{\partial G^{-1}}{\partial B_c} = -\frac{1}{2} \epsilon^{abc} v_a x_b = +\frac{1}{2} \epsilon^{abc} x_a v_b$$
$$\frac{\partial H}{\partial h^c} = -\frac{\partial G^{-1}}{\partial h^c} = v_\phi x_c = x_c v_\phi .$$

(A37)

After some more algebra, using $\partial G = -G \partial G^{-1} G$, we can show that

$$\frac{\partial^2 G}{\partial B_d \partial h^c} = G \frac{\partial H}{\partial B_d} G \frac{\partial H}{\partial h^c} G + G \frac{\partial H}{\partial h^c} G \frac{\partial H}{\partial B_d} G ,$$

(A38)

from which we can find

$$Tr \left[\frac{\partial^2 G}{\partial B_c \partial h^c} \right]$$
$$= \frac{1}{2} \epsilon^{abc} Tr \left[G x_a v_b G x_c v_\phi G + G x_c v_\phi G x_a v_b G \right] .$$

(A39)

Using this, we arrive at

$$u = \frac{2}{3!} \int_{-\infty}^{+\infty} \frac{d\epsilon}{2\pi i} f(\epsilon) Tr \left[\frac{\partial^2 (G_R - G_A)}{\partial B_c \partial h^c} \right]$$
$$- \frac{2}{3!} \int_{-\infty}^{+\infty} \frac{d\epsilon}{2\pi i} f'(\epsilon) Tr \left[x_c v_\phi \frac{\partial (G_R - G_A)}{\partial B_c} \right] .$$

(A40)

Using $G_A - G_R = 2\pi i \delta(\epsilon - H)$ we arrive at

$$u = -\frac{1}{3} \frac{\partial^2}{\partial B_c \partial h^c} \int_{-\infty}^{+\infty} d\epsilon f(\epsilon) Tr \left[\delta(\epsilon - H) \right]$$
$$+ \frac{1}{3} \frac{\partial}{\partial B_c} \int_{-\infty}^{+\infty} d\epsilon f'(\epsilon) Tr \left[x_c v_\phi \delta(\epsilon - H) \right] .$$

(A41)

The last term at $T = 0$ becomes

$$-\frac{1}{3} \frac{\partial}{\partial B_c} Tr \left[x_c v_\phi \delta(H) \right] ,$$

(A42)

and vanishes for an insulator. We are then left with

$$u = -\frac{1}{3} \frac{\partial^2 n}{\partial B_c \partial h^c} ,$$

(A43)

which gives us

$$\chi = 2\pi u = -\frac{2\pi}{3} \frac{\partial^2 n}{\partial B_c \partial h^c} ,$$

(A44)

proving our main result, (14).