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Berry-phase effects in dipole density and Mott relation

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We provide a unified semiclassical theory for thermoelectric responses of any observable represented by an operator $\hat{\theta}$ that is well-defined in periodic crystals. The Einstein and Mott relations are established generally, in the presence of Berry-phase effects, for various physical realizations of $\hat{\theta}$ in electronic systems, including the familiar case of the electric current as well as the currently controversial cases of the spin polarization and spin current. The magnetization current, which has been proven indispensable in the thermoelectric response of electric current, is generalized to the cases of various $\hat{\theta}$. In our theory the dipole density of a physical quantity emerges and plays a vital role, which contains not only the statistical sum of the dipole moment of $\hat{\theta}$ but also a Berry-phase correction.

The Mott relation [1, 2] was originally proposed as a fundamental link between the measurable electric current responses to the electric field and to the temperature gradient in independent-electron systems with elastic scattering off static disorder. Since the rapid extension of the fields of spintronics and spin-caloritronics [3], the question whether the Mott relation still holds for thermoelectric responses related to the electronic spin degree of freedom in spin-orbit coupled systems has attracted intensive debates [4–6]. In particular, despite the recent experimental observation of the spin Nernst effect [7–10] the thermal counterpart of the spin Hall effect [12, 13], the puzzle whether the Mott relation exists between these two effects has not been settled theoretically [14–19]. Besides, whether the Edelstein effects (nonequilibrium spin polarization) induced by the electric field [12, 20] and by the temperature-gradient [21] are linked by the Mott relation is also a controversial issue [22, 23].

In the presence of band-structure spin-orbit coupling, various Berry-phase effects on thermoelectric responses appear [12, 13, 24–26]. In particular, the identification of the orbital magnetization including a Berry-phase correction has been proven vital in validating the Mott relation between the anomalous Nernst and anomalous Hall effects in ferromagnets [4]. In this Letter we provide a unified semiclassical theory for thermoelectric responses of any observable represented by an operator $\hat{\theta}$ that is well-defined in periodic crystals. We establish the Einstein and Mott relations in the presence of Berry-phase effects for various physical realizations of $\hat{\theta}$, including the known case of the electric current [4], as well as the intensively debated cases of the conventional spin current (defined as the anti-commutator of the spin and velocity operators) [14–19] and the spin polarization [22, 23]. The magnetization current, which has been proven indispensable in the thermoelectric response of electric current [4], is generalized to various $\hat{\theta}$. As a generalization of the orbital magnetization in the case of the electric current, in our theory the dipole density of a physical quantity ($\hat{\theta}$) emerges and plays a vital role. It contains not only the statistical sum of the dipole moment of $\hat{\theta}$ [27] but also a Berry-phase correction.

In the strategy of the semiclassical theory [28], one considers a grand canonical ensemble of dynamically independent semiclassical Bloch electrons, each of which is physically identified as a wave-packet $|\Phi(\mathbf{q}_c, \mathbf{r}_c, t)\rangle$ that is constructed from the Bloch states in a particular nondegenerate band and is localized around a central position \mathbf{r}_c and a mean crystal momentum \mathbf{q}_c . Within the validity of the uncertainty principle, the phase-space occupation function $f_{tot}(\mathbf{q}_c, \mathbf{r}_c, t)$ can be defined, and the density-of-states $D(\mathbf{q}_c, \mathbf{r}_c)$ has to be introduced [29]. The number of states within a small phase space volume is hence given by $Df_{tot}d\mathbf{r}_cd\mathbf{q}_c/(2\pi)^3$. $f_{tot} = f + \delta f$, where f is the local equilibrium Fermi distribution, and δf is a small deviation originating from scattering processes.

In this paper, we consider Bloch electrons in a crystal under small electric field, spatially inhomogeneous chemical potential and temperature. We keep our result to the first order of the gradients of the electrostatic potential and chemical potential μ as well as temperature T . The electron wave-packet in such a system is described by the following Hamiltonian:

$$\hat{H} = \hat{H}_0(\hat{\mathbf{p}} + \mathbf{q}_c, \hat{\mathbf{r}}; w(\mathbf{r}_c)) - e\phi(\mathbf{r}_c), \quad (1)$$

where the electrostatic potential $\phi(\mathbf{r}_c) = -\mathbf{E} \cdot \mathbf{r}_c$ is explicitly shown with \mathbf{E} the electric field, and $w(\mathbf{r}_c)$ represent other possible mechanical perturbation fields [30]. We focus on the static case such that $w(\mathbf{r}_c)$ does not depend on time. All these fields vary slowly on the scale of the wave-packet. Thus their original $\hat{\mathbf{r}}$ dependence is replaced by the \mathbf{r}_c dependence under the local approximation. The eigenstate of \hat{H} is the same as that of \hat{H}_0 while the eigenenergy is shifted by $-e\phi(\mathbf{r}_c)$. We denote $\varepsilon(\mathbf{q}_c, \mathbf{r}_c)$ and $|u(\mathbf{q}_c, \mathbf{r}_c)\rangle$ as the eigenenergy and eigenstate (periodic part of Bloch function) of \hat{H}_0 . Then the phase-space density-of-states reads: $D(\mathbf{q}_c, \mathbf{r}_c) = 1 + \Omega_{q_c r_c^i}$ [29], where $\Omega_{\lambda_i \lambda_j} = 2 \text{Im} \langle \partial_{\lambda_j} u | \partial_{\lambda_i} u \rangle$ are the Berry curvatures, $\lambda_i = r_c^i$ or $q_{c,i}$, i and j are Cartesian indices. Summation over repeated indices is implied henceforth.

The local density of a physical observable $\hat{\theta}$ (generally a tensor operator) is defined as [27]

$$\rho_{tot}^{\theta}(\mathbf{r}) \equiv \int [d\mathbf{q}_c] d\mathbf{r}_c D f_{tot} \langle \Phi | \hat{\theta} \delta(\hat{\mathbf{r}} - \mathbf{r}) | \Phi \rangle. \quad (2)$$

We further divide it into two parts: $\rho_{tot}^\theta = \rho_{loc}^\theta + \delta\rho_{loc}^\theta$, where ρ_{loc}^θ is the contribution from f and $\delta\rho_{loc}^\theta$ is from δf . In the following, we focus on ρ_{loc}^θ while the discussion of $\delta\rho_{loc}^\theta$ is postponed to the end of the paper. Hereafter the symmetrization between operators that do not commute to each other is implied. $[d\mathbf{q}_c]$ is shorthand for $\sum_n d\mathbf{q}_c / (2\pi)^d$ with d the spatial dimensionality (we use the convention $\hbar = 1$). First-order Taylor expansion of $\hat{\mathbf{r}}$ with respect to \mathbf{r}_c in the Dirac delta function yields [24]

$$\rho_{loc}^\theta(\mathbf{r}) = \int [d\mathbf{q}_c] Df \langle \Phi | \hat{\boldsymbol{\theta}} | \Phi \rangle |_{\mathbf{r}_c=\mathbf{r}} - \nabla \cdot \int [d\mathbf{q}_c] f \langle \Phi | \hat{\boldsymbol{\theta}} (\hat{\mathbf{r}} - \mathbf{r}) | \Phi \rangle |_{\mathbf{r}_c=\mathbf{r}}, \quad (3)$$

which is the basis of the following discussion. Henceforth we will omit the center position label c , and the notation \int without integral variable is shorthand for $\int [d\mathbf{q}_c]$, unless otherwise noted. We consider $\rho_{loc}^\theta(\mathbf{r})$ up to the first order, thus it is sufficient to set $D = 1$ in the second term of $\rho_{loc}^\theta(\mathbf{r})$. This term is related to the dipole moment of $\hat{\boldsymbol{\theta}}$ [24, 27]:

$$m^{i\theta} = \langle \Phi | \hat{\boldsymbol{\theta}} (\hat{\mathbf{r}} - \mathbf{r})^i | \Phi \rangle, \quad (4)$$

whose physical meaning is shown in Fig.1. Whereas the first term of $\rho_{loc}^\theta(\mathbf{r})$ is just the conventional semiclassical expression [1].

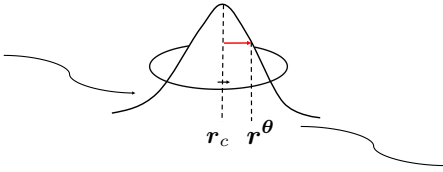


FIG. 1. A schematic picture of $m^{i\theta}$ which is proportional to the difference between the θ -center \mathbf{r}^θ and the usual probability center \mathbf{r}_c (the red arrow), where the θ -center is defined as $\mathbf{r}^\theta \equiv \frac{\langle \Phi | \hat{\mathbf{r}} \hat{\boldsymbol{\theta}} | \Phi \rangle}{\langle \Phi | \hat{\boldsymbol{\theta}} | \Phi \rangle}$. By definition (3), $m^{i\theta} = \langle \Phi | \hat{\boldsymbol{\theta}} | \Phi \rangle (\mathbf{r}^\theta - \mathbf{r}_c)^i$. For “conserved” $\hat{\boldsymbol{\theta}}$ that commutes with the Hamiltonian \hat{H}_0 , the θ -center coincides with the probability center such that the θ dipole moment vanishes.

Given the complexity of the present subject, we first look into the special case when $\hat{\boldsymbol{\theta}} = -e\hat{\mathbf{v}}$ and the electric current is calculated. Here we stress that, as will be discussed later, the following derivation is not a repetition of what has been done in Ref. [4], but is a novel approach and provides a different perspective which eventually inspires a general method applicable to observables other than the electric current. The case of electric current is special because, the first term in Eq. (3) is now simply $-e\langle \Phi | \hat{\mathbf{v}} | \Phi \rangle = -e\dot{\mathbf{r}}$ where $\dot{\mathbf{r}}$ is the velocity of the wave-packet and is given by the equations of motion [30]

$$\begin{aligned} \dot{\mathbf{r}} &= \partial_{\mathbf{q}} \varepsilon_{tot} - \Omega_{\mathbf{q}\mathcal{T}}, \\ \dot{\mathbf{q}} &= -\partial_{\mathbf{r}} \varepsilon_{tot} - e\mathbf{E} + \Omega_{\mathbf{r}\mathcal{T}}. \end{aligned} \quad (5)$$

ε_{tot} is the total wave-packet energy from \hat{H}_0 : $\varepsilon_{tot} = \varepsilon + \Delta\varepsilon$ with $\Delta\varepsilon = \text{Im}\langle \partial_{q_i} u | \varepsilon - \hat{H} | \partial_w u \rangle \partial_{r_i} w$ the contribution from the gradient of $w(\mathbf{r}_c)$ [30]. The Berry curvature term reads $\Omega_{\lambda\mathcal{T}} = \Omega_{\lambda\mathbf{r}}\dot{\mathbf{r}} + \Omega_{\lambda\mathbf{q}}\dot{\mathbf{q}} + \Omega_{\lambda t}$ with \mathcal{T} denoting the total time (t) derivative. $\Omega_{\lambda t}$ vanishes in the static case studied here.

Therefore, the local electric current density \mathbf{j}_{loc} reads

$$\mathbf{j}_{loc} = -e \int Df (\partial_{\mathbf{q}} \varepsilon_{tot} - \Omega_{\mathbf{q}\mathcal{T}}) + \nabla \times \int f \mathbf{m}. \quad (6)$$

Here $\mathbf{m} = e \text{Im}\langle \partial_{\mathbf{q}} u | \times (\varepsilon - \hat{H}) | \partial_{\mathbf{q}} u \rangle$ is the vector form of the antisymmetric tensor m^{ij} with the index j coming from the three components of $\hat{\boldsymbol{\theta}} = -e\hat{\mathbf{v}}$, and is known as the orbital magnetic moment of the wave-packet [30]. Substituting the equations of motion into the $\Omega_{\mathbf{q}\mathcal{T}}$ term, after some algebra [31] we find that \mathbf{j}_{loc} can be divided into two parts:

$$\mathbf{j}_{loc} = \mathbf{j}_{eq} + \mathbf{j}_{neq}. \quad (7)$$

The equilibrium part \mathbf{j}_{eq} exists irrespective of the electric field and statistical force (temperature gradient and chemical potential gradient), while the non-equilibrium part \mathbf{j}_{neq} is induced by them. The two parts read:

$$\mathbf{j}_{eq} = \nabla \times \mathbf{M}, \quad \mathbf{j}_{neq} = \boldsymbol{\sigma}^i (E_i + \partial_i \mu / e) - \boldsymbol{\alpha}^i \partial_i T, \quad (8)$$

where the Hall and Nernst conductivities are given by $\boldsymbol{\sigma}^i = e^2 \int f \Omega_{q_i \mathbf{q}}$ and $\boldsymbol{\alpha}^i = -\frac{e}{T} \int \Omega_{q_i \mathbf{q}} [(\varepsilon - \mu) f - g]$, respectively. For \mathbf{j}_{neq} , the Einstein relation is evident, which states that the electric field and the gradient of chemical potential $\nabla \mu / e$ are equivalent in inducing the electric current. The Mott relation is also easy to obtain, which reads $\boldsymbol{\alpha}^i = \frac{\pi^2}{3} \frac{k_B^2 T}{e} \frac{\partial \boldsymbol{\sigma}^i(\varepsilon)}{\partial \varepsilon} |_{\varepsilon=\mu}$ at low temperature [4], where $\boldsymbol{\sigma}^i(\varepsilon)$ is the Hall conductivity at zero temperature with ε the Fermi energy. As for \mathbf{j}_{eq} , we obtain

$$\mathbf{M} = \int (f \mathbf{m} - e \Omega g), \quad (9)$$

where $(\Omega)_k = \frac{1}{2} \Omega_{q_i q_j} \epsilon_{ijk}$ is the vector form of the antisymmetric tensor $\Omega_{\mathbf{q}\mathbf{q}}$, and $g = -\frac{1}{\beta} \ln[1 + e^{-(\varepsilon - \mu)}]$ is the grand potential density for a particular state. A key observation is that \mathbf{M} coincides with the orbital magnetization [4, 32, 33], namely the dipole density of the electric current, hence \mathbf{j}_{eq} is just the magnetization current.

It is important to note that, in the previous semiclassical transport approach [4] \mathbf{M} is obtained separately from its thermodynamic definition $\mathbf{M} = -\partial G_{tot} / \partial \mathbf{B}$ with G_{tot} the grand potential density and \mathbf{B} the magnetic field, whereas the form of the magnetization current $\nabla \times \mathbf{M}$ is known from the electrodynamics. Thereby, to generalize this approach to other physical quantities θ , e.g., spin and spin current, is difficult because the generalizations of the magnetization current in these cases are not known. In fact, this is a main theoretical difficulty in the study of the thermoelectric responses of spin

and spin current. Moreover, inhomogeneities from mechanical perturbation fields w , which are usually present in practical materials, cannot be incorporated into the previous theory [4]. On the other hand, in the present approach both the dipole density and its contribution to the electric current emerge automatically just through the manipulation of \mathbf{j}_{loc} itself, in the presence of w . Thus, if one can generalize this approach to the thermoelectric responses of physical quantities other than the electric current, the generalization of the magnetization current can be obtained.

Applying the above new approach in these cases is not straightforward because the perturbed wave-packet (by gradients of w and ϕ) is needed to calculate the $\langle \Phi | \hat{\boldsymbol{\theta}} | \Phi \rangle$ term of Eq. (3) [34] (the electric current is special since $\langle \Phi | \hat{\mathbf{v}} | \Phi \rangle = \dot{\mathbf{r}}$ is already given by the equations of motion). Trying to overcome this difficulty, we note that one may introduce an auxiliary coupling term $e\hat{\mathbf{v}} \cdot \mathbf{A}$ (\mathbf{A} is the vector potential) in the wave-packet Lagrangian, so that $\langle \Phi | \hat{\mathbf{v}} | \Phi \rangle$ and \mathbf{j}_{loc} can also be obtained by the variation of the action with respect to the field \mathbf{A} . Then we are faced with a field-variational problem.

This observation stimulates the generic idea that, to obtain $\rho_{loc}^{\boldsymbol{\theta}}(\mathbf{r})$ we consider the Hamiltonian:

$$\hat{\mathcal{H}} = \hat{H}_0 + \hat{\boldsymbol{\theta}} \cdot \mathbf{h}(\mathbf{r}_c, t) - e\phi(\mathbf{r}_c), \quad (10)$$

where \mathbf{h} is the slowly-varying field that couples to the considered physical observable $\hat{\boldsymbol{\theta}}$, and thus has an unambiguous physical meaning determined by that of $\hat{\boldsymbol{\theta}}$. For instance, when $\hat{\boldsymbol{\theta}}$ are the spin and electric current, \mathbf{h} are the Zeeman field and vector potential, respectively. In some realizations of $\hat{\boldsymbol{\theta}}$, the explicit form of \mathbf{h} may not be familiar, e.g., when $\hat{\boldsymbol{\theta}}$ is the conventional spin current \mathbf{h} is the so-called spin-dependent vector potential [18, 35]. This does not matter since knowing the explicit form of \mathbf{h} is not necessary in our method. This is because the auxiliary term $\hat{\boldsymbol{\theta}} \cdot \mathbf{h}$ is introduced to acquire the thermoelectric response of $\hat{\boldsymbol{\theta}}$ and is set to zero ($\mathbf{h} = 0$) at the last of the calculation. In general, both $\hat{\boldsymbol{\theta}}$ and \mathbf{h} are tensors and the product denotes the contraction between them.

Next we consider the dynamics of wave-packet $|\Phi\rangle$ constructed from Hamiltonian $\hat{\mathcal{H}}$. The action for the wave-packet state is [24]:

$$S = \int dt L, \quad L = \langle \Phi | i\partial_t - \hat{\mathcal{H}} | \Phi \rangle, \quad (11)$$

where L is the wave-packet Lagrangian [31]. It can be easily verified that the variation of S with respect to $\langle \Phi |$ gives the Schrodinger equation satisfied by the wave-packet. The variation with respect to \mathbf{h} instead gives

$$\frac{\delta S}{\delta \mathbf{h}}|_{onshell} = - \int dt \langle \Phi | \frac{\delta \hat{\mathcal{H}}}{\delta \mathbf{h}} | \Phi \rangle|_{onshell} \quad (12)$$

for on-shell wave-packet states (states that satisfy the Schrodinger equation). By the definition of the field

variation [31], the right hand side of Eq. (12) is simply $-\langle \Phi | \hat{\boldsymbol{\theta}} \delta(\hat{\mathbf{r}} - \mathbf{r}) | \Phi \rangle$. Notice that $|\Phi\rangle$ becomes the wave-packet from the original Hamiltonian \hat{H} (1) in the limit $\mathbf{h} \rightarrow 0$. Combining Eqs. (2) and (12) we get the following vital relation after summing over all wave-packets:

$$\rho_{loc}^{\boldsymbol{\theta}} = - \int [d\mathbf{q}] d\mathbf{r} Df \frac{\delta S}{\delta \mathbf{h}}|_{onshell}^{\mathbf{h} \rightarrow 0}. \quad (13)$$

In the following, we omit the label $\mathbf{h} \rightarrow 0$ for simplicity, but all results are evaluated in this limit.

Starting from Eq. (13), a straightforward derivation [31] yields the important result

$$\rho_{loc}^{\boldsymbol{\theta}} = \int Df (\partial_{\mathbf{h}} \varepsilon_{tot} - \Omega_{\mathbf{h}\mathcal{T}}) - \partial_{r_i} \int f m^{i\boldsymbol{\theta}}. \quad (14)$$

We note that this equation indicates $\langle \Phi | \hat{\boldsymbol{\theta}} | \Phi \rangle = \partial_{\mathbf{h}} \varepsilon_{tot} - \Omega_{\mathbf{h}\mathcal{T}}$ with $\Omega_{\mathbf{h}\mathcal{T}} = \Omega_{\mathbf{h}\mathbf{r}} \dot{\mathbf{r}} + \Omega_{\mathbf{h}\mathbf{q}} \dot{\mathbf{q}} + \Omega_{\mathbf{h}t}$. Notwithstanding the similar form to Eq. (6), there is a basic difference: the \mathbf{q} derivative in Eq. (6) is replaced by the derivative with respect to the field \mathbf{h} that couples to the considered observable $\boldsymbol{\theta}$. In fact, Eq. (6) can be reinterpreted from the view point of the field-variation as the special case of Eq. (14) when $\hat{\boldsymbol{\theta}} = -e\hat{\mathbf{v}}$ and $\mathbf{h} = -\mathbf{A}$: Since the vector potential is always minimally coupled into the Hamiltonian in the combined form $\mathbf{q} + e\mathbf{A}$, the \mathbf{h} derivative is proportional to the \mathbf{q} derivative with a factor $-e$.

The dipole moment of $\boldsymbol{\theta}$ takes the form of $m^{i\boldsymbol{\theta}} = \text{Im} \langle \partial_{q_i} u | \varepsilon - \hat{\mathcal{H}} | \partial_{\mathbf{h}} u \rangle$. It is related to the gradient correction of the wave-packet energy in the way that $\Delta\varepsilon = \text{Im} \langle \partial_{q_i} u | \varepsilon - \hat{\mathcal{H}} | \partial_w u \rangle \partial_{r_i} w + m^{i\boldsymbol{\theta}} \cdot \partial_{r_i} \mathbf{h}$. Thus the gradient correction can be generally interpreted as the potential energy of the dipole moment in an external field.

Starting from Eq. (14) and taking some technical steps similar to those from Eq. (6) to Eq. (7) [31], we obtain

$$\rho_{eq}^{\boldsymbol{\theta}} = \partial_{\mathbf{h}} G_{tot} - \partial_i M^{i\boldsymbol{\theta}}, \quad (15)$$

$$\rho_{neq}^{\boldsymbol{\theta}} = \sigma^{i\boldsymbol{\theta}} (E_i + \partial_i \mu / e) - \alpha^{i\boldsymbol{\theta}} \partial_i T. \quad (16)$$

Here $\rho_{eq}^{\boldsymbol{\theta}}$ is the equilibrium part. In the case of the electric current, its first term vanishes since the \mathbf{q} variable has already been integrated out, and its second term gives the magnetization current. $G_{tot} = \int Dg (\varepsilon_{tot}) = G + \Delta G$, where $G = \int g(\varepsilon)$ is the local part and $\Delta G = \int [f \Delta\varepsilon + \Omega_{q_i r_i} g]$ is induced by inhomogeneity.

$$M^{i\boldsymbol{\theta}} = \int (f m^{i\boldsymbol{\theta}} + g \Omega_{q_i \mathbf{h}}) \quad (17)$$

is recognized as the dipole density of $\boldsymbol{\theta}$ since

$$M^{i\boldsymbol{\theta}} = \frac{\partial G_{tot}}{\partial (\partial_{r_i} \mathbf{h})}, \quad (18)$$

which is the thermodynamical definition of the dipole density of a physical quantity. This definition reduces to

the orbital magnetization [4, 33] and the spin dipole density (whose antisymmetric part is called spin toroidization) [23, 36] when $\boldsymbol{\theta}$ is the electric current ($\mathbf{h} = -\mathbf{A}$) and the spin (\mathbf{h} is the Zeeman field), respectively. The fact that the divergence of $M^{i\boldsymbol{\theta}}$ contributes to the $\boldsymbol{\theta}$ density also verifies its physical meaning.

Equation (16) describes the general linear response to the electric field and statistical force, with the coefficients

$$\sigma^{i\boldsymbol{\theta}} = -e \int f \Omega_{q,\mathbf{h}}, \quad \alpha^{i\boldsymbol{\theta}} = \frac{1}{T} \int \Omega_{q,\mathbf{h}} [(\varepsilon - \mu)f(\varepsilon) - g(\varepsilon)]. \quad (19)$$

The Einstein relation is apparent in Eq. (16). The generalized Mott relation can be also proved [31]:

$$\alpha^{i\boldsymbol{\theta}} = \frac{1}{e} \int d\varepsilon \frac{\partial f}{\partial \varepsilon} \frac{\varepsilon - \mu}{T} \sigma^{i\boldsymbol{\theta}}(\varepsilon), \quad (20)$$

where $\sigma^{i\boldsymbol{\theta}}(\varepsilon)$ is the zero-temperature value of $\sigma^{i\boldsymbol{\theta}}$ with Fermi energy ε . At low temperatures much less than the distances between the chemical potential and band edges, the Sommerfeld expansion is legitimate [37], yielding the standard Mott relation $\alpha^{i\boldsymbol{\theta}} = -\frac{\pi^2 k_B^2 T}{3e} \frac{\partial \sigma^{i\boldsymbol{\theta}}(\varepsilon)}{\partial \varepsilon} \Big|_{\varepsilon=\mu}$, which relates $\alpha^{i\boldsymbol{\theta}}$ to the energy derivative of $\sigma^{i\boldsymbol{\theta}}$ around the chemical potential.

For the convenience of calculation, one can express the dipole moment and Berry curvatures involving \mathbf{h} derivatives in a more explicit form:

$$m^{i\boldsymbol{\theta}} = \text{Im} \sum_{m \neq n} \frac{\langle u_n | \hat{v}^i | u_m \rangle \langle u_m | \hat{\boldsymbol{\theta}} | u_n \rangle}{\varepsilon_n - \varepsilon_m},$$

$$\Omega_{q,\mathbf{h}} = -2 \text{Im} \sum_{m \neq n} \frac{\langle u_n | \hat{v}^i | u_m \rangle \langle u_m | \hat{\boldsymbol{\theta}} | u_n \rangle}{(\varepsilon_n - \varepsilon_m)^2}, \quad (21)$$

where n is the index of the band we are considering. In obtaining these two expressions the \mathbf{h} derivatives have been done, followed by setting $\mathbf{h} = 0$, thus both terms exist only if $\hat{\boldsymbol{\theta}}$ does not commute with the genuine Hamiltonian \hat{H}_0 . Therefore, the dipole density and the linear response coefficients we discussed before is a property pertaining to such ‘‘nonconserved’’ quantities. It is also worthwhile to mention that our results apply to any operator $\hat{\boldsymbol{\theta}}$ that is well-defined in the Bloch representation. For the conventional spin current operator, $\Omega_{q,\mathbf{h}}$ is just the quantity sometimes referred to as the ‘‘spin Berry curvature’’ in first-principles literatures [38, 39].

Having identified the generalization of the magnetization current $-\partial_i M^{i\boldsymbol{\theta}}$, we can now understand the thermoelectric response of $\boldsymbol{\theta}$ in a direct way when inhomogeneities come only from temperature and chemical potential [4]. In this simple case the local density (3) reduces to

$$\rho_{loc}^{\boldsymbol{\theta}} = \int f \langle u | \hat{\boldsymbol{\theta}} | u \rangle + \sigma^{i\boldsymbol{\theta}} E_i - \partial_{r,i} \int f m^{i\boldsymbol{\theta}}, \quad (22)$$

where the $\sigma^{i\boldsymbol{\theta}} E_i$ term arises from the interband mixing of Bloch states induced by the electric field [27, 40], whereas

$$-\partial_i M^{i\boldsymbol{\theta}} = -\partial_{r,i} \int f m^{i\boldsymbol{\theta}} - \sigma^{i\boldsymbol{\theta}} \partial_i \mu / e + \alpha^{i\boldsymbol{\theta}} \partial_i T. \quad (23)$$

Hence the nonequilibrium part of $\rho_{loc}^{\boldsymbol{\theta}} - (-\partial_i M^{i\boldsymbol{\theta}})$, which corresponds to the subtraction of the magnetization current from the local electric current density in [4], just gives the thermoelectric response satisfying the Einstein and Mott relations. In this picture, contributions from the dipole moment $m^{i\boldsymbol{\theta}}$ cancel out in the linear response, while the Berry-phase correction to the dipole density plays the vital role in validating both relations.

$\sigma^{i\boldsymbol{\theta}}$ contains a Streda term $\sigma^{i\boldsymbol{\theta},\text{II}}$ [12, 25, 41] whose zero temperature value is related to the dipole density as:

$$M^{i\boldsymbol{\theta}} = \frac{1}{e} \int d\varepsilon f(\varepsilon) \sigma^{i\boldsymbol{\theta},\text{II}}(\varepsilon). \quad (24)$$

This relation can be derived from Eq. (17) by the same procedure in [42]. $\sigma^{i\boldsymbol{\theta},\text{II}}(\varepsilon)$ has the following form [41]:

$$\sigma^{i\boldsymbol{\theta},\text{II}}(\varepsilon) = \text{Re} \int_{-\infty}^{\varepsilon} \frac{d\varepsilon'}{2\pi} \text{Tr} [\hat{\boldsymbol{\theta}} \hat{G}^{R'} \hat{j}_e^i \frac{d\hat{G}^{R'}}{d\varepsilon'} - \hat{\boldsymbol{\theta}} \frac{d\hat{G}^{R'}}{d\varepsilon'} \hat{j}_e^i \hat{G}^{R'}]. \quad (25)$$

Here $\hat{G}^{R'}$ is the bare retarded Green’s function. This connection is useful in model calculations. For instance, in the two-dimensional Rashba model with both Rashba subbands partially occupied [12], the zero-temperature Streda term of the conventional spin Hall conductivity is $\sigma_s^{xy,\text{II}}(\varepsilon) = \frac{-e}{8\pi} \left[\frac{k_R}{k_0(\varepsilon)} - \frac{k_0(\varepsilon)}{k_R} \right] \Theta(-\varepsilon)$, where Θ is the step function, $k_0(\varepsilon) = \alpha_R^{-1} \sqrt{\varepsilon_R^2 + 2\varepsilon_R \varepsilon}$ with α_R the Rashba coefficient, $k_R = m\alpha_R/\hbar^2$ (m is the effective mass) the Rashba wave-vector and $\varepsilon_R = \alpha_R k_R$ the Rashba energy. Thus the zero-temperature dipole density of the conventional spin current is obtained as $M_s^{xy} = -\frac{\varepsilon_R}{12\pi}$.

Finally, for completeness, we demonstrate that the Einstein and Mott relations still hold in the presence of elastic scattering on weak static disorder. As mentioned before, the total local density has a term $\delta\rho_{loc}^{\boldsymbol{\theta}} = \int \delta f \langle \Phi | \hat{\boldsymbol{\theta}} | \Phi \rangle$. δf in steady states is determined by the linearized Boltzmann equation [1] ($P_{\mathbf{k}\mathbf{q}}$ is the scattering rate in the Born approximation)

$$\dot{\mathbf{r}} \cdot \partial_{\mathbf{r}} f + \dot{\mathbf{k}} \cdot \partial_{\mathbf{k}} f = \int P_{\mathbf{k}\mathbf{q}} (f_{tot}(\mathbf{q}) - f_{tot}(\mathbf{k})). \quad (26)$$

The left hand side is simply $\mathbf{F} \cdot \partial_{\mathbf{k}} f$, where $\mathbf{F} = -e\mathbf{E} - \partial_{\mathbf{r}} \mu - \frac{\varepsilon_0 - \mu}{T} \partial_{\mathbf{r}} T$ [1]. Thus $\delta f \propto \mathbf{F} \cdot \partial_{\mathbf{k}} f$ in the linear response [43], validating the Einstein and Mott relations [28]. In systems with Berry-phase corrections, it is well known that two extrinsic effects called skew scattering and coordinate-shift need also be incorporated into the Boltzmann equation [44, 45]. We show in Supplemental Material [31] that these two effects do not break the Einstein and Mott relations. Besides modifying the occupation function, disorder also alters $\langle \Phi | \hat{\boldsymbol{\theta}} | \Phi \rangle$ by inducing

interband mixing of Bloch states [40]. This contribution, known as side-jump velocity for $\hat{\theta} = \hat{v}$ [40, 46], is averaged by $\delta f \propto \mathbf{F} \cdot \partial_{\mathbf{k}} f$, hence does not go against the Einstein or Mott relation.

The proposed approach provides a unified description for the anomalous and spin Nernst effects, the thermally induced spin and spin-orbit torque [26]. It also applies to or can be extended in several directions of current great interest. First, it can be further generalized to a framework of linear thermoelectric responses of dipole densities. In the present paper we are limited to linear responses of operator $\hat{\theta}$ that is well-defined in periodic crystals, and only the equilibrium dipole density of $\hat{\theta}$ is needed. We extend [47] the variational approach to non-linear responses of $\hat{\theta}$ and then obtain the linear response of $\hat{\theta}$ -dipole. This extension enables to, for example, analyze the temperature gradient induced orbital magnetization, thus paving the way for thermal generation and control of magnetization via the orbital degree of freedom, which is especially important in low-symmetry valley systems. Second, by allowing for the second order spatial derivative of the \mathbf{h} field, the variational approach yields a general theory for various quadrupole densities ($r_i r_j \theta_l$), such as the orbital magnetic quadrupole [48] which serves as a order parameter of systems with combined time-reversal and inversion symmetry. Third, the generalization into the case of degenerate bands, i.e., a non-abelian formalism [49], can also be pursued. Fourth, the field-variational approach applies to bosonic systems as well. Indeed the idea of our work has been shown recently to work in the thermal spin generation and spin Nernst effect of magnons in noncollinear antiferromagnetic insulators [50].

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