Editors' Suggestion

Spin-Derived Electric Polarization and Chirality Density Inherent in Localized Electron Orbitals

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In solid state physics, any phase transition is commonly observed as a change in the microscopic distribution of charge, spin, or current. However, there is an exotic order parameter inherent in the localized electron orbitals that cannot be primarily captured by these three fundamental quantities. This order parameter is described as the electric toroidal multipoles connecting different total angular momenta under the spin-orbit coupling. The corresponding microscopic physical quantity is the spin current tensor on an atomic scale, which induces spin-derived electric polarization aligned circularly and the chirality density of the Dirac equation. Here, elucidating the nature of this exotic order parameter, we obtain the following general consequences that are not restricted to localized electron systems; chirality density is indispensable to unambiguously describe electronic states and it is a species of electric toroidal multipoles, just as the charge density is a species of electric multipoles. Furthermore, we derive the equation of continuity for chirality and discuss its relation to chiral anomaly and optical chirality. These findings link microscopic spin currents and chirality in the Dirac theory to the concept of multipoles and provide a new perspective for quantum states of matter.

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Introduction.—In strongly correlated electron systems, the spin and orbital degrees of freedom of nearly localized electrons are activated by electronic correlations, resulting in various intriguing phenomena, such as heavy electrons, unconventional superconductivity, and exotic magnetic orders. These quantum states are commonly characterized by the spatial distribution of the fundamental microscopic physical quantities, charge, spin, and current. They have been systematically studied using the concept of multipole expansions [1–12]. These multipoles are classified into four categories (electric, magnetic, magnetic toroidal, and electric toroidal) according to spatial parity and time reversal [12]. Such a classification is useful for elucidating exotic orders and predicting novel response to external fields.

In particular, electric toroidal multipole ordering has recently attracted much attention as a novel nonmagnetic degree of freedom [13–17], which has not been strongly recognized so far. In localized electron systems, such degrees of freedom are inherent in the components connecting different total angular momenta under the spin-orbit coupling $\lambda\boldsymbol{\ell}\cdot\boldsymbol{s}$. The simplest rank-1 electric toroidal dipole is written as $\boldsymbol{G}(1)=\boldsymbol{\ell}\times\boldsymbol{s}$ [15,18–20]. When considering this electric toroidal dipole in analogy to a magnetic toroidal dipole [21], we would expect the electric polarization to be circularly aligned. The ordinary electric polarization $\boldsymbol{P}(\boldsymbol{r})=\boldsymbol{r}\rho(\boldsymbol{r})$ (ρ is a charge density), however, cannot capture the toroidal structure, as $\boldsymbol{P}(\boldsymbol{r})$ is a simple charge distribution. What physical quantity characterizes the nature of electric toroidal multipoles microscopically?.

In the following, we clarify the underlying fundamental physical quantity using the knowledge of the relativistic quantum mechanics. It is shown that the electric polarization $\boldsymbol{P}_S(\boldsymbol{r})$ induced by the spin degrees of freedom is responsible for the electric toroidal moment. The spin-derived electric polarization $\boldsymbol{P}_S(\boldsymbol{r})$ is also associated with the microscopic spin current tensor, which is regarded as one of the fundamental physical quantities analogous to charge, spin, and electric current. The relation between electric polarization and spin current has been discussed in the context of spintronics based on weak-coupling itinerant Fermi liquid description [22]. We further find the relation between the electric toroidal multipole, spin current, and chirality of the Dirac equation by employing the localized electron picture. This chirality degree of freedom is intimately related to the diagonal part of the spin current, and is a more fundamental quantity corresponding to electric toroidal multipoles. We thus link microscopic spin currents and chirality in Dirac theory to the concept of multipoles. Finally, we derive the equation of continuity for

TABLE I. List of the multipole distribution function $f(\boldsymbol{r}; p_\eta, \gamma)$ ($p = 2q$ or $p = 2q+1$) defined in Eq. (3) where $f = \rho, M_{S\mu}, j_\mu, P_{S\mu}, \tau^{Z,X,Y}$, and $\boldsymbol{\nabla}\cdot\boldsymbol{P}_S$. The label "nonzero" ("0") for each cell indicates a nonzero (zero) multipole distribution function in the leading-order contribution of the nonrelativistic limit. The signs of the spatial inversion $\mathcal{P}$ and time reversal Θ indicated in the third column and the second row are defined as $\mathcal{P}f(\boldsymbol{r})\mathcal{P}^{-1} = \pm f(-\boldsymbol{r})$ and $\Theta f(\boldsymbol{r})\Theta^{-1} = \pm f(\boldsymbol{r})$.

			ρ	$\boldsymbol{M}_S$	$\boldsymbol{j}$	$\boldsymbol{P}_S$	τ^Z	τ^X $(\sim\rho)$	$\tau^Y(\sim\boldsymbol{\nabla}\cdot\boldsymbol{M}_S)$	$\boldsymbol{\nabla}\cdot\boldsymbol{P}_S$
Multipole	Type	SI/TR	$+/+$	$+/-$	$-/-$	$-/+$	$-/+$	$+/+$	$-/-$	$+/+$
Electric toroidal	$(2q+1)_d$	$+/+$	0	0	0	Nonzero	Nonzero	0	0	0
Magnetic toroidal	$(2q)_d$	$+/-$	0	Nonzero	0	0	0	0	0	0
Electric	$(2q)_{a,b,c}$	$+/+$	Nonzero	0	0	Nonzero	0	Nonzero	0	Nonzero
Magnetic	$(2q+1)_{a,b,c}$	$+/-$	0	Nonzero	Nonzero	0	0	0	Nonzero	0

chirality density and discuss its relation to chiral anomaly and optical chirality.

Definition of multipoles.—Let us start with the definition of multipoles in localized electron orbitals with the angular momentum ℓ. The multipole operators are defined as a complete matrix basis set to describe all operators of the type $c^\dagger_{m\sigma}c_{m'\sigma'}$, where $c_{m\sigma}$ is the annihilation operator of the electron with the magnetic quantum number $m \in [-\ell, \ell]$ and spin $\sigma = \uparrow, \downarrow$. Under strong spin-orbit coupling, the multipole operators are usually considered only for a ground-state $j = \ell \pm 1/2$ multiplet. We here consider the full space containing different j multiplets. The classification scheme recently formulated for $\ell = 1$ case [20] is applied to the general ℓ [23]. In this case, the generic rank-p multipole is written as

$$X^\gamma(p_\eta) = \sum_{mm'\sigma\sigma'} c^\dagger_{m\sigma}\mathcal{O}^\gamma_{m\sigma,m'\sigma'}(p_\eta)c_{m'\sigma'}, \qquad (1)$$

where $p = 0, \ldots, 2\ell+1$, and $\mathcal{O}$ is a matrix representation of the multipole. γ is a label to distinguish $2p+1$ degeneracies. We have separated the rank-p multipole into several pieces denoted by the η index: $\eta = a$, b denotes the intra-j multiplet component, and $\eta = c$, d corresponds to a component connecting a different j multiplet [27]. For $\eta = a$, b, c, the even ($p = 2q$) or odd ($p = 2q+1$) rank coincides with the even or odd time-reversal (TR) symmetry, but this relation is reversed for d components. Note that in the present intra-ℓ case, the parity of spatial inversion (SI) is always even. In addition, the type $\eta = d$ multipoles are categorized as the toroidal multipoles from its symmetry [19]. These results are summarized in the left three columns ("Multipole," "Type," "SI/TR") of Table I.

Charge and current distribution.—Since the multipoles obtained above were defined based on localized electron orbitals, they can be described as microscopic charge or current distributions in continuous space. With the field operator $\psi_\sigma(\boldsymbol{r})$, the microscopic charge density is given by $\rho_0 = e\psi^\dagger\psi$, and the current density and magnetization operators by

$$\boldsymbol{j} = \frac{e}{2m}\psi^\dagger\overleftrightarrow{\boldsymbol{p}}\psi, \qquad \boldsymbol{M}_S = \frac{\hbar e}{2mc}\psi^\dagger\boldsymbol{\sigma}\psi, \qquad (2)$$

where $\boldsymbol{p} = -i\hbar\boldsymbol{\nabla}$, and $A\overleftrightarrow{\partial}B = A\partial B - (\partial A)B$. The spin summation is implicitly performed. We expand the operator by the atomic orbitals as $\psi_\sigma(\boldsymbol{r}) = \sum_m R(r)Y_{\ell m}(\hat{\boldsymbol{r}})c_{m\sigma}$. Then, for example, the current operator is written as

$$\boldsymbol{j}(\boldsymbol{r}) = \sum_{p\eta\gamma} X^\gamma(p_\eta)\boldsymbol{j}(\boldsymbol{r}; p_\eta, \gamma). \qquad (3)$$

Namely, once the multipoles are given, the spatial distribution of the current can be visualized through the product with the distribution function, $\boldsymbol{j}(\boldsymbol{r}; p_\eta, \gamma)$ for each set of (p_η, γ). Similar expansions are possible for other microscopic physical quantities.

However, as will be shown later, there is no primary change in the spatial distributions of $\rho_0(\boldsymbol{r}), \boldsymbol{j}(\boldsymbol{r})$, and $\boldsymbol{M}_S(\boldsymbol{r})$ in the ordered state of electric toroidal dipole $\boldsymbol{G}(1)$. In order to obtain another microscopic quantity having primary change, we start with the basic Hamiltonian $\mathcal{H}$ with relativistic corrections. Then the current and charge are obtained by $\boldsymbol{j}_{\rm tot} = -\delta\mathcal{H}/(\delta\boldsymbol{A}/c)$ and $\rho_{\rm tot} = \delta\mathcal{H}/\delta\Phi$, where $\boldsymbol{A}$ and Φ are vector and scalar potentials [22,23]. Based on the spin dependence, the total current and charge can be uniquely separated into two parts: $\boldsymbol{j}_{\rm tot} = \boldsymbol{j} + c\boldsymbol{\nabla}\times\boldsymbol{M}_S$ and $\rho_{\rm tot} = \rho - \boldsymbol{\nabla}\cdot\boldsymbol{P}_S$. The current density $\boldsymbol{j}$ and magnetization $\boldsymbol{M}_S$ have already been defined above. The charge density and electric polarization are given by

$$\rho = \left(1 + \frac{\hbar^2}{8m^2c^2}\boldsymbol{\nabla}^2\right)e\psi^\dagger\psi \simeq e\psi^\dagger\psi = \rho_0, \qquad (4)$$

$$\boldsymbol{P}_S = \frac{\hbar e}{8m^2c^2}\psi^\dagger\overleftrightarrow{\boldsymbol{p}}\times\boldsymbol{\sigma}\psi. \qquad (5)$$

The second term in ρ originates from the uncertainty of the position in relativistic quantum mechanics. However, this second term has only a minor correction on the charge distribution since it originates from the second derivative of the large first term (ρ_0), and the spin degrees of freedom are not directly involved. This correction term has the same origin as the Darwin term in the Hamiltonian [28], which only affects the s electron ($\ell = 0$) and vanishes for $\ell > 0$.

Here we make a few comments on the spin-derived electric polarization $\boldsymbol{P}_S$. The Gordon decomposition of the charge and current also introduces the microscopic magnetization and electric polarization [28,29]. We also note that the presence of the microscopic electric polarization has the same physical origin as the Aharonov-Casher effect [30], in which the particles with magnetization are affected by the electric field.

The present spin-derived electric polarization $\boldsymbol{P}_S$ is exactly related to microscopic spin current. The connection between the spin current and electric polarization has been discussed for the noncollinear magnets [31] and the electron gas model in the context of the spintronics [22]. The spin-derived electric polarization $\boldsymbol{P}_S$ can be further rewritten as

$$P_{S\mu} = \frac{\hbar^2 e}{8m^2c^2}\epsilon_{\mu\nu\lambda} j_{S\nu\lambda}, \tag{6}$$

where the spin current $j_{S\mu\nu} = -\mathrm{i}\psi^\dagger \overleftrightarrow{\partial}_\mu \sigma^\nu \psi$ and the antisymmetric tensor $\epsilon_{\mu\nu\lambda}$ are introduced $(\mu, \nu, \lambda = x, y, z)$ [22]. Furthermore, the spin current tensor $j_{S\mu\nu}$ may be classified into the components with rank 0 (pseudoscalar), 1, and 2 [12]. We find that the rank-0 pseudoscalar component is related to the chirality degrees of freedom in the Dirac equation. The chirality density in the second-quantized form is defined by the annihilation operators for right- and left-handed chiral fermions, $\psi_{R,L}$, in the Weyl basis as follows:

$$\tau^Z = \psi_R^\dagger \psi_R - \psi_L^\dagger \psi_L, \tag{7}$$

where the subscript R and L denote the chirality degrees of freedom. The chirality density is evaluated in the nonrelativistic limit as follows [23,24]:

$$\tau^Z \simeq \frac{1}{2mc}\psi^\dagger \overleftrightarrow{\boldsymbol{p}} \cdot \boldsymbol{\sigma}\psi = \frac{\hbar}{2mc} j_{S\mu\mu}. \tag{8}$$

Namely, the pseudoscalar part of the spin current tensor represents the chirality density operator in the nonrelativistic limit. Equation (8) has a structure like the helicity, i.e., how much the moving direction of the electron is aligned along the direction of its spinning axis. In condensed matter physics, the chiral magnetic anisotropy effect is expected, if the chirality density integrated over the bulk has a finite expectation value [32,33].

The chirality operator is further supplemented by another operator related to the chirality degrees of freedom R, L:

$$\tau^X = \psi_R^\dagger \psi_L + \psi_L^\dagger \psi_R \simeq \frac{1}{e}\rho_0, \tag{9}$$

$$\tau^Y = -\mathrm{i}(\psi_R^\dagger \psi_L - \psi_L^\dagger \psi_R) \simeq \frac{1}{e}\boldsymbol{\nabla}\cdot \boldsymbol{M}_S, \tag{10}$$

which correspond to the Lorentz scalar and pseudoscalar [23,24], respectively, and the rightmost sides in Eqs. (9) and (10) express nonrelativistic limits. Equations (7), (9), (10) are represented by a pseudospin in the "chirality space." In the nonrelativistic limit, the R and L components almost equally exist, leading to the dominant $\langle \tau^X \rangle$ component.

All of the multipole distribution functions now represent the microscopic physical quantities, i.e., $\rho, \boldsymbol{M}_S, \boldsymbol{j}, \boldsymbol{P}_S, \tau^{X,Y,Z}$. They are summarized in Table I with their signs from parity for spatial inversion and time-reversal transformations. As shown in Table I, the electric toroidal moment $G(2q+1) \equiv X[(2q+1)_d]$ appears only with the chirality density operator τ^Z and electric polarization $\boldsymbol{P}_S$. It is also notable that the divergence $\boldsymbol{\nabla}\cdot\boldsymbol{P}_S$ is absent, which implies the rotating nature. In this context, it is interesting to compare it with the magnetic toroidal moment $T(2q) \equiv X((2q)_d)$, which is not accompanied by $\tau^Y \sim \boldsymbol{\nabla}\cdot\boldsymbol{M}_S$.

Analysis of the $\ell = 1$ model.—To gain more insight, let us consider a mean-field Hamiltonian in the simple $\ell = 1$ localized model, given by $\mathcal{H}_{\mathrm{MF}} = \sum_i [\lambda(\boldsymbol{\ell}\cdot\boldsymbol{s})_i - \boldsymbol{h}_i \cdot \boldsymbol{G}_i]$ where i is a site index. λ is the spin-orbit coupling, $\boldsymbol{G}_i \equiv (\boldsymbol{\ell}\times\boldsymbol{s})_i = \sqrt{2}\boldsymbol{X}_i(1_d)$ is an electric toroidal multipole, and $\boldsymbol{h}_i = \sum_j J_{ij}\langle \boldsymbol{G}_j \rangle$ is the local mean-field generated by the spontaneous symmetry breaking with the exchange interaction J_{ij} [34].

Hereafter we clarify the physical consequence of the electric toroidal moment. For simplicity, the site index i is omitted. Without loss of generality, we can choose $\boldsymbol{h} = h\hat{\boldsymbol{z}}$ $(h \geq 0)$. The ground-state wave function is written as $|\psi_\pm\rangle = \mathrm{i}\alpha|\frac{3}{2}, \pm\frac{1}{2}\rangle + |\frac{1}{2}, \pm\frac{1}{2}\rangle$, where $\alpha = (3\lambda - \sqrt{9\lambda^2 + 8h^2})/2\sqrt{2}h \simeq -(2\sqrt{2}h/3\lambda)$ $(|\alpha| \ll 1)$ and the ground-state energy is $E = -\frac{1}{4}(\lambda + \sqrt{9\lambda^2 + 8h^2})$. The single electron state is written as $|jj_z\rangle = \sum_{m\sigma}\langle 1m\frac{1}{2}\sigma|jj_z\rangle c_{m\sigma}^\dagger|0\rangle$. The ground-state degeneracy is protected by the time-reversal symmetry. In the ordered state, any physical quantities can be calculated with the density matrix $\hat{\rho} = |\psi_+\rangle\langle\psi_+| + |\psi_-\rangle\langle\psi_-|$.

Through the calculation of spin current [23], we can explicitly evaluate the expectation value of the electric polarization as

$$\frac{\langle \boldsymbol{P}_S(\boldsymbol{r})\rangle}{R^2(r)} = \frac{\hbar^2 e}{8m^2c^2}\frac{(-2 + \frac{\alpha^2}{2})\hat{\boldsymbol{r}} - \frac{3\alpha}{\sqrt{2}}\boldsymbol{C}_z + \frac{3\alpha^2}{2r}z\hat{\boldsymbol{z}}}{2\pi r(1+\alpha^2)}, \tag{11}$$

where $r^2 = x^2 + y^2 + z^2$ and $R(r)$ is a radial wave function. We have defined $\boldsymbol{C}_z(\boldsymbol{r}) = (x\hat{\boldsymbol{y}} - y\hat{\boldsymbol{x}})/r$, which is circularly rotating around the z axis. This vector field is schematically plotted on a unit sphere in Fig. 1. It can be expanded by the order of α. The $O(1)$ contribution enters from the spin-orbit coupling λ, which is proportional to $\hat{\boldsymbol{r}}$. The contribution of $O(\alpha^1)$ is a leading-order contribution from $\langle G^z \rangle$, which is rotating around the z axis. There is also the small $O(\alpha^2)$ contribution pointing the z direction.

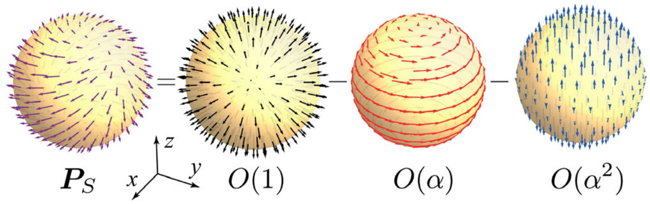

FIG. 1. Schematic picture for the spatial distribution of the electric polarization $\boldsymbol{P}_S(\boldsymbol{r})$ on a unit sphere. In the right-hand side, the contributions from $O(1)$, $O(\alpha)$, $O(\alpha^2)$ [see Eq. (11)] in the $\alpha \to 0$ limit are separately plotted.

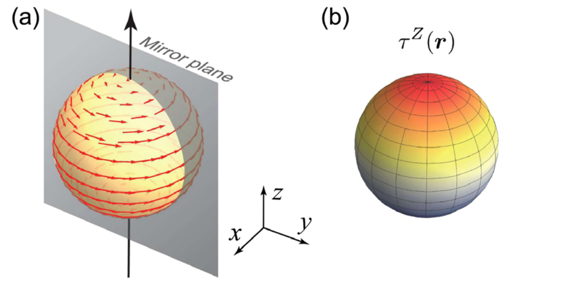

FIG. 2. (a) Schematic for the mirror symmetry breaking of $\langle \boldsymbol{P}_S(\boldsymbol{r})\rangle$, where the mirror is located parallel to the z axis. (b) Spatial distribution of the chirality density $\langle \tau^Z(\boldsymbol{r})\rangle$ on a unit sphere where red (around north pole) and blue (south pole) parts indicate right-chirality-rich and left-chirality-rich regions, respectively.

Based on the Landau theory, we expect the temperature dependence $\alpha \sim (h/\lambda) \propto \sqrt{T_c - T}$ near the transition temperature. Hence the $O(\alpha^1)$ contribution proportional to $\boldsymbol{C}_z$ in $\boldsymbol{P}_S$ reflects the presence of the primary order parameter $\langle \boldsymbol{G}\rangle$. However, the $O(\alpha)$ contribution vanishes in the total charge $\rho_{\mathrm{tot}} = \rho - \boldsymbol{\nabla}\cdot\boldsymbol{P}_S$, which behaves as $\propto (T_c - T)$ (not square root). The primary order parameter would be thus veiled.

As shown in the $O(\alpha)$ contribution of Fig. 1, the $\langle G^z\rangle$-ordered state breaks the mirror symmetry along the z axis [see Fig. 2(a)]. The characteristics also appear in the chirality density. Indeed, its expectation value shows the leading-order $O(\alpha)$ contribution as follows,

$$\frac{\langle \tau^Z(\boldsymbol{r})\rangle}{R^2(r)} = \frac{\hbar}{2mc}\frac{3\sqrt{2}\alpha z}{2\pi r^2(1+\alpha^2)}. \tag{12}$$

Figure 2(b) shows the spatial distribution of $\langle \tau^Z(\boldsymbol{r})\rangle$ on a unit sphere, which clearly shows the emergence of the chirality dipole distribution. The red region around the north pole indicates the right-handed electron rich region, while the south pole is the left-handed rich region. The dipole distribution of $\langle \tau^Z(\boldsymbol{r})\rangle$ may also be understood in analogy with the electric dipole distribution. Namely, the assembly of the local dipoles in $\langle \rho\rangle$ in solids forms a polar crystal. Similarly, the assembly of the local chirality dipole in $\langle \tau^Z\rangle$ will induce an electric toroidal state in solids characterized by the circulating electric polarization.

Furthermore, using Eqs. (11) and (12), we arrive at the relation

$$\langle \tau^Z\rangle = \frac{4mc}{i\hbar^2 e}\boldsymbol{L}\cdot\langle \boldsymbol{P}_S\rangle = -\frac{4mc}{\hbar e}\boldsymbol{r}\cdot(\boldsymbol{\nabla}\times\langle \boldsymbol{P}_S\rangle), \tag{13}$$

where only the fundamental physical constants appear as the proportional coefficient. The right-hand side is often used as the definition of the electric toroidal multipoles [35]. We note that the right-hand side of Eq. (13) directly includes $\boldsymbol{r}$ and hence depends on the choice of the origin, while the chirality in the left-hand side does not. Thus the $\boldsymbol{G} = \boldsymbol{\ell}\times\boldsymbol{s}$ order parameter is closely related to the microscopic chirality operator τ^Z, which derives from the fundamental Dirac theory and is relevant to the electric toroidal moment. Chirality is an indispensable degree of freedom to unambiguously describe electronic states.

Coupling to external fields.—In the preceding discussion, we addressed the significance of the spin-derived electric polarization and chirality density of matter. We now proceed to examine their coupling with external fields. Once the magnetization and electric polarization are given, the coupling to the external electromagnetic fields in the Hamiltonian is written as

$$\mathcal{H}_{\mathrm{ext}} = \int \mathrm{d}\boldsymbol{r}\left(\rho\Phi - \frac{1}{c}\boldsymbol{j}\cdot\boldsymbol{A} - \boldsymbol{M}_S\cdot\boldsymbol{B} - \boldsymbol{P}_S\cdot\boldsymbol{E}\right) \tag{14}$$

in the linear response. Here the external magnetic field $\boldsymbol{B} = \boldsymbol{\nabla}\times\boldsymbol{A}$ and the electric field $\boldsymbol{E} = -\boldsymbol{\nabla}\Phi$ are introduced. In the atomic limit model with fixed ℓ, the uniform electric field does not couple with the electric polarization directly since $\int \mathrm{d}\boldsymbol{r}\boldsymbol{P}_S(\boldsymbol{r}) = 0$. We need the electric field modulating on an atomic scale for the finite coupling to the electric polarization in the present setup.

The spatially uniform fields lead to the familiar form of the contribution to magnetization and electric polarization. It is natural (but not unique) to define the potentials as $\Phi(\boldsymbol{r}) = -\boldsymbol{E}_0\cdot\boldsymbol{r}$ and $\boldsymbol{A}(\boldsymbol{r}) = \frac{1}{2}\boldsymbol{B}_0\times\boldsymbol{r}$. We then have another expression $\mathcal{H}_{\mathrm{ext}} = -\int \mathrm{d}\boldsymbol{r}, \quad (\boldsymbol{M}\cdot\boldsymbol{B}_0 + \boldsymbol{P}\cdot\boldsymbol{E}_0)$ where the magnetization and electric polarization are $\boldsymbol{M} = (e/4mc)\psi^\dagger\overleftrightarrow{\boldsymbol{L}}\psi + \boldsymbol{M}_S$ and $\boldsymbol{P} = \boldsymbol{r}\rho + \boldsymbol{P}_S$ with $\boldsymbol{L} = \boldsymbol{r}\times\boldsymbol{p}$. This expression provides an intuitive understanding of magnetization and polarization.

Equation of continuity.—Finally, we discuss how the source and/or sink of the material chirality appears using the equation of continuity. We begin with the axial current which satisfies $\partial_\mu j^{\mu 5} = 2mP + (e^2/16\pi^2)\epsilon^{\mu\nu\lambda\rho}F_{\mu\nu}F_{\lambda\rho}$, where $j^{\mu 5}$ is the axial current, P the Lorentz pseudoscalar, and F the electromagnetic field with the antisymmetric tensor ϵ [25,36]. When we take its nonrelativistic limit, the leading-order contributions are of $O(c^0)$, but they are exactly canceled [37]. Here we further consider the

$O(c^{-2})$ contributions which describe the dynamics of chirality as [23]

$$\frac{\partial\langle\tau^Z\rangle}{\partial t}+\nabla\cdot\langle\boldsymbol{j}^Z\rangle=\frac{2}{\hbar}\boldsymbol{E}\cdot\left(\langle\boldsymbol{M}_S\rangle+\frac{e^2}{4\pi^2\hbar c}\boldsymbol{B}\right), \quad (15)$$

where τ^Z is defined in Eq. (7) and the chirality current is given by [23]

$$\boldsymbol{j}^Z=\frac{1}{4m^2c}\left(\psi^\dagger\overleftrightarrow{\boldsymbol{p}}(\overleftrightarrow{\boldsymbol{p}}\cdot\boldsymbol{\sigma})\psi+\frac{\hbar}{2}\nabla\times\psi^\dagger\overleftrightarrow{\boldsymbol{p}}\psi\right), \quad (16)$$

where the second term is divergence-free. The last term in Eq. (15) proportional to $\boldsymbol{B}$ represents the chiral anomaly inherent in the quantum field theory of fermions [25,36]. Thus, the coupling between magnetization and electric field are the source of the chirality of matter.

The above chirality of matter is analogous to the chirality of electromagnetic field, $C=\boldsymbol{E}\cdot(\nabla\times\boldsymbol{E})+\boldsymbol{B}\cdot(\nabla\times\boldsymbol{B})$, which is known as the Lipkin's zilch [38]. This quantity is shown to be useful in determining the asymmetry of the optical absorption rate between left- and right-handed systems [39–41]. Its equation of continuity defines also the corresponding current and source of the zilch, which are contrasted against those in the Poynting theorem for the energy density $U=(\boldsymbol{E}^2+\boldsymbol{B}^2)/8\pi$ [39].

We recognize that the relation between the chirality density τ^Z and the charge density ρ is analogous to that between C and U. Hence, the apparent similarity between the material chirality and the optical chirality suggests the relevance of τ^Z to characterization of the asymmetry between left- and right-handed materials. It is also interesting to point out that the magnetic helicity $H=\int d\boldsymbol{r}\boldsymbol{A}\cdot(\nabla\times\boldsymbol{A})$, which has been rarely discussed in condensed matter physics, is closely related to the chiral anomaly of fermions [42].

Summary and discussion.—We have investigated the electronic degrees of freedom in the localized electron orbitals using the knowledge of relativistic quantum mechanics. We clarified that electric toroidal multipoles are microscopically characterized by spin-derived electric polarization and chirality in the Dirac theory, which are closely related to the spin current tensor. In particular, the chirality intrinsic to elementary particles is the essence of electric toroidal multipoles.

When considering the ordered state of such electric toroidal multipoles, the corresponding components of the spin current tensor are modulating on an atomic scale. It would be hard to detect the primary order parameter by conventional spectroscopies. In this context, it is interesting to study some exotic phase transitions, such as URu_2Si_2 [43] and CeCoSi [44,45].

Thus, the spin-derived electric polarization and the chirality are fundamental quantities characterizing the quantum states of materials. Recently, the importance of the electric toroidal monopole in chiral crystals and molecules has been noted [16,17]. The microscopic quantities discussed in this Letter are relevant to any materials with the spin-orbit coupling. Mapping out the spin-derived electric polarization and the chirality distributions in these materials is an interesting future challenge.

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