Microscopic Theory of Spin Toroidization in Periodic Crystals

Yang Gao,[1] David Vanderbilt,[2] and Di Xiao[1]
[1] *Department of Physics, Carnegie Mellon University, Pittsburgh, PA 15213, USA*
[2] *Department of Physics and Astronomy, Rutgers University, Piscataway, New Jersey 08854-8019, USA*
(Dated: June 13, 2017)

Using the semiclassical theory of electron dynamics, we derive a gauge-invariant expression for the spin toroidization in a periodical crystal. We establish a direct and elengant relation between our spin toroidization and the antisymmetric magnetoelectric polarizability in insulators. By further expressing our result in the Wannier function basis, we show that the spin toroidization is comprised of two contributions: one is due to the configuration of a classical spin array, while the other comes from the coordinate shift of the electron as spin carrier in response to the inhomogeneous magnetic field. Finally, we demonstrate our theory in a tight-binding model.

Recent years have seen a surge of interest in toroidal moments in crystals [1–4], mainly motivated by their intriguing role in various magnetoelectric effects [5–11]. A toroidal moment is generally associated with a vortex-like structure of magnetic moments. Its spontaneous ordering characterizes a ferrotoroidal state that exhibits a non-vanishing magnetoelectric effect. The density of the toroidal moment, called toroidization, also constitutes an essential building block in the free energy expansion in inhomogeneous fields. However, despite its importance, a microscopic theory of the toroidization based on quantum mechanical wave functions is still missing.

In crystals the toroidization can arise from two sources, the orbital and spin moments. Here we will focus only on the contribution from spins. By treating the spins as classical vectors, it has been proposed that the spin toroidization can be written as [3, 4]

$$\boldsymbol{T}=\frac{g\mu_B}{2\hbar V}\sum_i \boldsymbol{r}_i\times\boldsymbol{s}_i\ , \tag{1}$$

where g is the gyromagnetic factor, μ_B is the Bohr magneton, $\boldsymbol{r}_i$ and $\boldsymbol{s}_i$ are the position and spin of each lattice site, and V is the volume of the sample. Later there is also an attempt to obtain a microscopic theory of the spin toroidization by treating $\boldsymbol{r}$ and $\boldsymbol{s}$ as operators and directly evaluating the expectation of Eq. (1) using Wannier functions [12]. However, the resulting expression is not gauge-invariant.

In this Letter, we develop a microscopic theory of the spin toroidization in crystals. Using the semiclassical theory of electron dynamics [13, 14], we obtain a gauge-invariant expression for the spin toroidization in terms of bulk Bloch functions, which has a remarkably similar structure to the orbital magnetization formula [15–18]. To our delight, we are able to establish a direct and elegant relation between our spin toroidization and the magnetoelectric polarizability in the case of insulators [see Eq. (14)]. Furthermore, by considering the molecular insulator limit, we find that the contributions to the spin toroidization consists of two parts with clear physical interpretations: one is due to the configuration of a classical spin array, similar to Eq. (1), while the other comes from the coordinate shift of the electron as spin carrier in response to the inhomogeneous magnetic field. Finally, we demonstrate our theory in a tight-binding model. Our formula can be easily implemented in first-principles codes.

Toroidization as a response function.—Our starting point is the free energy density $F(\boldsymbol{r})$ in an inhomogeneous magnetic field $\boldsymbol{B}(\boldsymbol{r})$. Suppose that $\boldsymbol{B}(\boldsymbol{r})$ is small and varies slowly in space. At a given point $\boldsymbol{r}$, we can perform a gradient expansion of $F(\boldsymbol{r})$ up to first order with respect to the derivatives of the magnetic field

$$\begin{aligned}F(\boldsymbol{r})=F_0(\boldsymbol{r})-\boldsymbol{M}\cdot\boldsymbol{B}(\boldsymbol{r})-\boldsymbol{T}\cdot[\nabla\times\boldsymbol{B}(\boldsymbol{r})]\\ -\frac{1}{2}Q_{ij}[\partial_i B_j(\boldsymbol{r})+\partial_j B_i(\boldsymbol{r})]+\cdots\ ,\end{aligned} \tag{2}$$

where $F_0(\boldsymbol{r})$ is the free energy density at $\boldsymbol{B}=0$ and $\boldsymbol{M}$ is the magnetization. Here and hereafter the Einstein summation convention is implied for repeated indices. In the last two terms of Eq. (2), we explicitly separate the antisymmetric and symmetric part of $\partial_i B_j(\boldsymbol{r})$. We thus define the coefficient $\boldsymbol{T}$ and Q_{ij} as the toroidization and the magnetic quadrupole moment density, respectively.

Based on Eq. (2), we can obtain a linear-response expression for $\boldsymbol{T}(\boldsymbol{r})$ by treating $\boldsymbol{B}(\boldsymbol{r})$ and $\boldsymbol{\nabla}\times\boldsymbol{B}(\boldsymbol{r})$ as independent variables, arriving at

$$\boldsymbol{T}(\boldsymbol{r})=-\lim_{\boldsymbol{B}(\boldsymbol{r})\to 0}\left.\frac{\partial F(\boldsymbol{r})}{\partial(\nabla\times\boldsymbol{B})}\right|_{\boldsymbol{B}(\boldsymbol{r})}\ . \tag{3}$$

Here the subscript $\boldsymbol{B}(\boldsymbol{r})$ in taking the derivative with respect to $\nabla\times\boldsymbol{B}$ means that the magnetic field at the point $\boldsymbol{r}$ has to be kept fixed as $\nabla\times\boldsymbol{B}(\boldsymbol{r})$ is varied.

Semiclassical theory of the spin toroidization.— With the above definition of the toroidization, we now formulate its microscopic theory. We will focus only on the spin toroidization. Therefore, we take $\boldsymbol{B}(\boldsymbol{r})$ as the Zeeman field, which couples to the spin operator $\hat{\boldsymbol{s}}$. Then the full Hamiltonian can be written as

$$\hat{H}_F=\hat{H}(i\hbar\partial_{\boldsymbol{r}},\boldsymbol{r})-\frac{g\mu_B}{\hbar}\boldsymbol{B}(\boldsymbol{r})\cdot\hat{\boldsymbol{s}}\ . \tag{4}$$

For definiteness we can consider the context to be that of a spinor implementation of density functional theory with spin-orbit interactions included. The first term, $\hat{H}(i\hbar\partial_{\boldsymbol{r}}, \boldsymbol{r})$, describes a perfect crystal in the absence of a Zeeman field, while the second term is inhomogeneous and breaks the translational symmetry, making it difficult to diagonalize the Hamiltonian (4) analytically. Here we take a different route by using the semiclassical theory of electron dynamics [13, 14], which is designed to study Bloch electrons subject to perturbations varying slowly in space.

In the spirit of the semiclassical theory, each Bloch electron responds to the external Zeeman field in the form of a wave packet, which has a specified center of mass position $\boldsymbol{r}_c$ and momentum $\boldsymbol{k}_c$. To construct the wave packet, we make a local approximation and assume that the system can be described by a set of local Hamiltonians $\hat{H}_c[\boldsymbol{B}(\boldsymbol{r}_c)] = \hat{H}(i\hbar\partial_{\boldsymbol{r}}, \boldsymbol{r}) - (g\mu_B/\hbar)\boldsymbol{B}(\boldsymbol{r}_c)\cdot\boldsymbol{s}$. Since $\hat{H}_c$ respects the lattice translational symmetry, its eigenstate has the form of a Bloch function $e^{i\boldsymbol{k}\cdot\boldsymbol{r}}|\tilde{u}_n(\boldsymbol{k}, \boldsymbol{B}(\boldsymbol{r}_c))\rangle$ with the eigenenergy $\tilde{\varepsilon}(\boldsymbol{k}_c, \boldsymbol{B}(\boldsymbol{r}_c))$, where n is the band index. In the limit $\boldsymbol{B}(\boldsymbol{r}_c) \to 0$, $|\tilde{u}_n(\boldsymbol{k}, \boldsymbol{B}(\boldsymbol{r}_c))\rangle$ reduces to $|u_n(\boldsymbol{k})\rangle$, the periodic part of the Bloch function of $\hat{H}$, and $\tilde{\varepsilon}_n(\boldsymbol{k}_c, \boldsymbol{B}(\boldsymbol{r}_c))$ reduces to $\varepsilon_n(\boldsymbol{k}_c)$, the eigenenergy of the unperturbed Hamiltonian $\hat{H}$. For simplicity, we hereafter drop the argument of $|\tilde{u}_n\rangle$, $|u_n\rangle$, $\tilde{\varepsilon}_n$ and ε_n. For illustrative purposes, we consider a single band with index 0, and the wave packet is thus the superposition of $e^{i\boldsymbol{k}\cdot\boldsymbol{r}}|\tilde{u}_0\rangle$.

The wave-packet dynamics can be properly formulated as a set of semiclassical equations of motion in the phase space spanned by $\boldsymbol{r}_c$ and $\boldsymbol{k}_c$ [13, 14]. The spatial inhomogeneity of $\boldsymbol{B}(\boldsymbol{r})$ introduces two essential ingredients for the purpose of evaluating the spin toroidization in Eq. (3). First, the phase space density of states $\mathcal{D}$ is modified. It has the form [15] (see also Sec. VI.B of Ref. [14])

$$\mathcal{D}(\boldsymbol{r}_c, \boldsymbol{k}_c) = 1 + \mathrm{Tr}(\Omega_{\boldsymbol{k},\boldsymbol{r}}) \; , \tag{5}$$

where

$$(\Omega_{\boldsymbol{k},\boldsymbol{r}})_{ij} = -2\,\mathrm{Im}\langle\partial_{k_{ci}}\tilde{u}_0|\partial_{r_{cj}}\tilde{u}_0\rangle \tag{6}$$

is the mixed Berry curvature between the real and momentum space. This modified density of states has been applied to derive the polarization in inhomogeneous crystals [19]. Secondly, the band energy $\tilde{\varepsilon}$ is also affected by the spatial inhomogeneity [13]

$$\varepsilon_0' = \tilde{\varepsilon}_0 + \mathrm{Im}\langle\partial_{k_{ci}}\tilde{u}_0|(\tilde{\varepsilon}_0 - \hat{H}_c)|\partial_{r_{ci}}\tilde{u}_0\rangle \; . \tag{7}$$

With the above two ingredients we are ready to evaluate the free energy density F. For simplicity we set $T = 0$. The free energy density is given by $F = \int \frac{d\boldsymbol{k}_c}{(2\pi)^3}\mathcal{D}(\boldsymbol{r}_c, \boldsymbol{k}_c)(\varepsilon_0' - \mu)\Theta(\mu - \varepsilon_0')$, where Θ is the Heaviside function. At first order with respect to the derivative of $\boldsymbol{B}$, the correction to the free energy density is

$$\delta F = -\int^{\mu} \frac{d\boldsymbol{k}_c}{(2\pi)^3}\,\mathrm{Im}\langle\partial_{k_{ci}}\tilde{u}_0|(\tilde{\varepsilon}_0 + \hat{H}_c - 2\mu)|\partial_{r_{ci}}\tilde{u}_0\rangle \; . \tag{8}$$

Here the upper limit μ means that the integration is taken up to $\varepsilon_0 = \mu$.

The toroidization defined in Eq. (3) can be obtained from the above free-energy correction. Since $|\tilde{u}_0\rangle$ depends on $\boldsymbol{r}_c$ through $\boldsymbol{B}$, we make the substitution $\partial_{r_{ci}}|\tilde{u}_0\rangle = \partial_{r_{ci}}B_\ell\partial_{B_\ell}|\tilde{u}_0\rangle$. We then collect terms involving the antisymmetric part of $\partial_{r_{ci}}B_\ell$ and take the derivative as in Eq. (3). The final expression is

$$\boldsymbol{T} = \frac{1}{2}\int^{\mu} \frac{d\boldsymbol{k}}{(2\pi)^3}\,\mathrm{Im}\langle\partial_{\boldsymbol{k}}\tilde{u}_0| \times (\tilde{\varepsilon}_0 + \hat{H}_c - 2\mu)|\partial_{\boldsymbol{B}}\tilde{u}_0\rangle\Big|_{\boldsymbol{B}\to 0} \; . \tag{9}$$

Here and hereafter we drop the subscript c of $\boldsymbol{k}_c$. Note that Eq. (9) can be straightforwardly generalized to the multiband case by summing over all occupied states, but we continue to focus on the single-band case here.

The similarity between Eq. (9) and the orbital magnetization formula [15–18] is striking. In fact, by making the substitution $\boldsymbol{\partial_B} \to \boldsymbol{\partial_k}$, Eq. (9) exactly coincides with the expression of the orbital magnetization. This similarity has its root in the nature of spin toroidization and orbital magnetization: they both measure the moment of some observable, which is spin for spin toroidization and velocity for orbital magnetization. To further check the validity of Eq. (9), we have also carried out a linear response calculation [20], similar to the derivation of the orbital magnetization in Ref. [18], and obtained the same result.

Equation (9) can be cast in a form involving only unperturbed Bloch states $|u_0\rangle$ instead of $|\tilde{u}_0\rangle$. Using the perturbation theory, up to the first order in the Zeeman field we have

$$|\tilde{u}_0\rangle = |u_0\rangle - \frac{g\mu_B}{\hbar}\sum_{n\neq 0}\frac{\boldsymbol{B}\cdot\boldsymbol{s}_{n0}}{\varepsilon_0 - \varepsilon_n}|u_n\rangle \; . \tag{10}$$

Then Eq. (9) can be rewritten as

$$\boldsymbol{T} = -\frac{g\mu_B}{2}\sum_{n\neq 0}\int^{\mu}\frac{d\boldsymbol{k}}{(2\pi)^3}(\varepsilon_0 + \varepsilon_n - 2\mu)\frac{\mathrm{Im}(\boldsymbol{v}_{0n}\times\boldsymbol{s}_{n0})}{(\varepsilon_0 - \varepsilon_n)^2} \; , \tag{11}$$

where $\boldsymbol{v}_{0n} = \langle u_0|\hat{\boldsymbol{v}}|u_n\rangle$ and $\boldsymbol{s}_{n0} = \langle u_n|\hat{\boldsymbol{s}}|u_0\rangle$ are the interband elements of the velocity and spin operators, respectively. Both Eq. (9) and (11) are amenable to implementation in a first-principles calculation.

It is clear that our expression (11) for the spin toroidization is gauge-invariant since neither $\boldsymbol{v}_{0n}$ nor $\boldsymbol{s}_{n0}$ changes if an arbitrary phase factor is applied to $|u_n\rangle$. As a consequence, the spin toroidization does not have any quantum of uncertainty, and it always vanishes for a system with either time-reversal or inversion symmetry. This is in sharp contrast to both the electric polarization [21, 22] and the previous theory of the spin toroidization [3, 12].

It is also worth mentioning that our toroidization cannot be used to predict a surface magnetization density, unlike the electric polarization, which has a definitive relation to the surface charge density [23]. This difference can be traced to the fact that charge is conserved but spin is not.

Connection to magnetoelectric polarizability.—The toroidization and the antisymmetric part of the magnetoelectric polarizability transform in the same way under symmetry operations [4]. However, an explicit relation between these two quantities has not previously been identified. Here we show that for an insulator, the spin toroidization admits a direct and elegant connection to the spin magnetoelectric polarizability.

According to the modern theory of polarization [21, 22], as we vary the j-th component of the Zeeman field, the change of the polarization is given by

$$\Delta P_i = e\int \frac{d\boldsymbol{k}dB_j}{(2\pi)^3}\,\mathrm{Im}\langle\partial_{k_i}\tilde{u}_0|\partial_{B_j}\tilde{u}_0\rangle\ . \tag{12}$$

Therefore, the magnetoelectric polarizability has the form [24]

$$\alpha_{ij} = \left.\frac{\partial P_i}{\partial B_j}\right|_{\boldsymbol{B}\to 0} = e\int \frac{d\boldsymbol{k}}{(2\pi)^3}\,\mathrm{Im}\langle\partial_{k_i}\tilde{u}_0|\partial_{B_j}\tilde{u}_0\rangle\Big|_{\boldsymbol{B}\to 0}\ . \tag{13}$$

On the other hand, note that for an insulator the Fermi-surface contribution to $\boldsymbol{T}$ vanishes. If we take the derivative of Eq. (9) with respect to μ, we find the desired connection

$$e\frac{\partial T_k}{\partial\mu} = -\frac{1}{2}\epsilon_{ijk}\alpha_{ij}\ , \tag{14}$$

where ϵ_{ijk} is the Levi-Civita symbol.

There is a heuristic derivation of the relation (14). Equation (2) suggests that the differential form of the free energy is $dF = -\boldsymbol{T}\cdot d(\boldsymbol{\nabla}\times\boldsymbol{B}) - \rho d\mu$, where ρ is the particle density. We can then obtain via the Maxwell relation

$$\frac{\partial T_i}{\partial\mu} = \frac{\partial\rho}{\partial(\boldsymbol{\nabla}\times\boldsymbol{B})_i}\ . \tag{15}$$

For a given point $\boldsymbol{r}$, we write $\boldsymbol{B} = (1/2)\boldsymbol{h}\times\boldsymbol{r}$ such that $\boldsymbol{\nabla}\times\boldsymbol{B} = \boldsymbol{h}$ and $\boldsymbol{B}$ vanishes exactly at $\boldsymbol{r}$. This choice ensures that $\partial_i B_j$ only has the antisymmetric component. On the other hand, the application of an inhomogeneous Zeeman field $\boldsymbol{B}(\boldsymbol{r})$ will induce an inhomogeneous polarization $\boldsymbol{P}(\boldsymbol{r})$, which in turn leads to a charge density change, i.e.,

$$e\rho = \boldsymbol{\nabla}\cdot\boldsymbol{P} = \partial_i(\alpha_{ij}B_j) = \frac{1}{2}\epsilon_{ijk}\alpha_{ij}h_k\ . \tag{16}$$

Combining Eq. (15) and (16) then yields Eq. (14).

We note that in the above argument, whether $\boldsymbol{B}$ is a Zeeman field or a magnetic field does not matter, therefore Eq. (14) should also be valid for the orbital toroidization.

Molecular insulator limit.—To shed light on the physical meaning of the spin toroidization in Eq. (9), we rewrite it for an insulator using the Wannier function representation. We label the Wannier function defined from the local Hamiltonian $\hat{H}_c$ by $|w_0(\boldsymbol{R},\boldsymbol{B})\rangle$, with 0 being the band index and $\boldsymbol{R}$ being the lattice site. In this representation Eq. (9) becomes [20]

$$\begin{aligned}\boldsymbol{T} = {}& \frac{1}{V_{\text{cell}}}\mathrm{Re}\langle w_0(\boldsymbol{B})|\boldsymbol{r}(\hat{H}_c-\mu)\times\boldsymbol{\partial_B}|w_0(\boldsymbol{B})\rangle\Big|_{\boldsymbol{B}\to 0} - \frac{g\mu_B}{2\hbar V_{\text{cell}}}\langle w_0(\boldsymbol{B})|\boldsymbol{r}\times\hat{\boldsymbol{s}}|w_0(\boldsymbol{B})\rangle\Big|_{\boldsymbol{B}\to 0}\\ &- \frac{g\mu_B}{2\hbar V_{\text{cell}}}\sum_{\boldsymbol{R}}\langle w_0(\boldsymbol{B})|\boldsymbol{r}|w_0(\boldsymbol{R},\boldsymbol{B})\rangle\Big|_{\boldsymbol{B}\to 0}\times\langle w_0(\boldsymbol{R},\boldsymbol{B})|\hat{\boldsymbol{s}}|w_0(\boldsymbol{B})\rangle\Big|_{\boldsymbol{B}\to 0}\ ,\end{aligned} \tag{17}$$

where $|w_0(\boldsymbol{B})\rangle = |w_0(\boldsymbol{R},\boldsymbol{B})\rangle$ with $\boldsymbol{R}=0$, and V_{cell} is the unit cell volume.

The meaning of Eq. (17) can be clarified further by taking the molecular insulator limit. Since the spin toroidal moment arises from a vortex-like arrangement of spins, there must be multiple atoms in a unit cell, which we call a molecule. The molecular insulator limit is then taken by letting the distance between neighboring molecules go to infinity while the relative structure of each molecule is unchanged. In this limit, $|w_0(\boldsymbol{R},\boldsymbol{B})\rangle$ is just the energy eigenstate of the molecule, translated to sit in cell $\boldsymbol{R}$. We will further assume that the system respects the combined time reversal and inversion symmetry such that $\langle w_0|\hat{\boldsymbol{s}}|w_0\rangle$ vanishes.

In the molecular insulator limit Eq. (17) consists of two parts [20]. The first part is

$$\boldsymbol{T}_1 = \frac{g\mu_B}{2\hbar V_{\text{cell}}}\langle w_0(\boldsymbol{B})|\boldsymbol{r}\times\hat{\boldsymbol{s}}|w_0(\boldsymbol{B})\rangle\Big|_{\boldsymbol{B}\to 0}\ . \tag{18}$$

It is clear that this term is due to the configuration of an array of classical spins, similar to the equation appearing as Eq. (1) in Refs. [3, 4]. The second part, coming from the modified density of states, is

$$\boldsymbol{T}_2 = -\frac{1}{2V_{\text{cell}}}(\varepsilon_0-\mu)(\partial_{\boldsymbol{B}}\times\bar{\boldsymbol{r}})\Big|_{\boldsymbol{B}\to 0}\ , \tag{19}$$

where ε_0 refers to the molecular electronic energy levels and $\bar{\boldsymbol{r}} = \langle w_0(\boldsymbol{B})|\boldsymbol{r}|w_0(\boldsymbol{B})\rangle$ is the electron position under

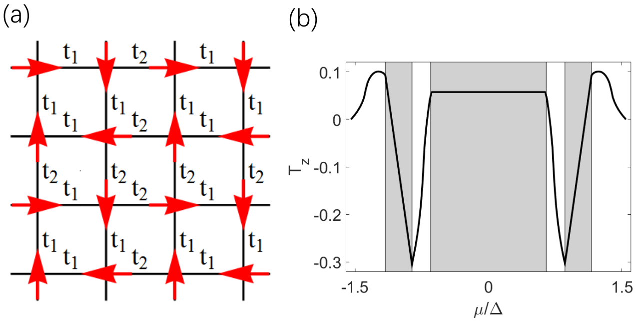

FIG. 1. Spin toroidization of a tight-binding model. Panel (a) is part of a periodic crystal. t_1 and t_2 is the nearest neighbour hopping strength. The red arrow on each lattice site indicates the direction of the local exchange field. The lattice constant is $a/2$. Panel (b) is the calculated spin toroidization (in units of $g\mu_B/4a$) as a function of the chemical potential. The shaded areas correspond to energy gaps. The parameters are chosen as follows: $t_1 = 0.3\Delta$ and $t_2 = 0.15\Delta$.

the external Zeeman field. Here $\varepsilon_0 - \mu$ is the free energy for state 0.

The $\boldsymbol{T}_2$ term can be intuitively understood as follows. In the spirit of the molecular insulator limit, if each molecule is simply a cluster of classical spins, under an inhomogeneous magnetic field the spins on each site can rotate but cannot move. However, the spins are carried by electrons, and the inhomogeneous Zeeman field will exert a spin force [25] on the electron. Therefore, the electron will shift to a new equilibrium position due to the balance between the spin force and the restoring force that binds electrons to ions. The corresponding energy change gives rise to $\boldsymbol{T}_2$. In a semiclassical picture, $\partial_{\boldsymbol{B}} \times \bar{\boldsymbol{r}}$ counts the change of the number of electronic states within a volume element located at $\boldsymbol{r}$.

Equation (19) also provides a strong hint of the relation in Eq. (14). Taking the derivative with respect to μ in Eq. (19) yields $(1/2V_{\rm cell})\boldsymbol{\partial_B} \times \bar{\boldsymbol{r}}$. Since $\bar{\boldsymbol{r}}$ is proportional to the electric polarization, its derivative with respect to the Zeeman field $\boldsymbol{B}$ is exactly the magnetoelectric polarizability.

Tight-binding model.—Next we demonstrate our theory using a tight-binding model shown in Fig. 1a. The tight-binding Hamiltonian is

$$\hat{H}_{\rm TB} = -\Delta \sum_i \boldsymbol{n}_i \cdot \boldsymbol{\sigma}_{\alpha\beta} c^\dagger_{i\alpha} c_{i\beta} + \sum_{\langle i,j \rangle} t_{ij} c^\dagger_{i\alpha} c_{j\alpha} \;, \tag{20}$$

where Δ is the local exchange field, $\boldsymbol{n}_i$ is the exchange field direction, α and β label the spin components, and t_{ij} is the spin-independent nearest neighbor hopping strength alternating between t_1 and t_2 as shown in Fig. 1a.

Since $\boldsymbol{T}$ transforms as a vector, it is useful to first analyze the symmetry of this system. The system has a 4-fold rotational symmetry about the vertical axis. Therefore, the toroidization cannot have any in-plane component. Moreover, if $t_1 = t_2$, the system also respects the combined symmetry of the mirror operation σ_h (i.e., $z \to -z$) followed by a translation across the diagonal direction. This requires that the out-of-plane component of the toroidization vanishes. Both results have been verified in our numerical calculations. We thus focus on the case $t_1 \neq t_2$ for which an out-of-plane toroidization is expected.

Figure 1b shows the toroidization calculated from Eq. (9) as a function of the chemical potential. The system has four bands with each band doubly degenerate. We can see that $\boldsymbol{T}$ decreases linearly inside the first gap due to the nonzero magnetoelectric polarizability. The curve is symmetric with respect to $\mu = 0$ because of the particle-hole symmetry of our model.

In summary, we have derived a microscopic theory of the spin toroidization in crystals. Its expression involves bulk Bloch functions and has clear physical interpretations. We have also established an explicit relation between the toroidization and the antisymmetric magnetoelectric polarizability.

This work is supported by the Department of Energy, Basic Energy Sciences, Materials Sciences and Engineering Division, Grant No. DE-SC0012509 (Y.G. and D.X.). D.V. is supported by the National Science Foundation, Grant No. DMR-1408838.

[1] V. M. Dubovik and V. V. Tugushev, Phys. Rep. **187**, 145 (1990).
[2] A. A. Gorbatsevich and Y. V. Kopaev, Ferroelectrics **161**, 321 (1994).
[3] C. Ederer and N. A. Spaldin, Phys. Rev. B **76**, 214404 (2007).
[4] N. A. Spaldin, M. Fiebig, and M. Mostovoy, J. Phys.: Condens. Matter **20**, 434203 (2008).
[5] M. Fiebig, J. Appl. Phys. D **38**, R123 (2005).
[6] T. Arima, J.-H. Jung, M. Matsubara, M. Kubota, J.-P. He, Y. Kaneko, and Y. Tokura, J. Phys. Soc. Jpn. **74**, 1419 (2005).
[7] K. Sawada and N. Nagaosa, Phys. Rev. Lett. **95**, 237402 (2005).
[8] B. B. Van Aken, J. P. Rivera, H. Schmid, and M. Fiebig, Nature **449**, 702 (2007).
[9] A. S. Zimmermann, D. Meier, and M. Fiebig, Nat. Comms. **5**, 4796 (2014).
[10] S. Hayami, H. Kusunose, and Y. Motome, Phys. Rev. B **90**, 024432 (2014).
[11] M. Fiebig, T. Lottermoser, D. Meier, and M. Trassin, Nat. Rev. Mater. **1**, 16046 (2016).
[12] F. Thöle, M. Fechner, and N. A. Spaldin, Phys. Rev. B **93**, 195167 (2016).
[13] G. Sundaram and Q. Niu, Phys. Rev. B **59**, 14915 (1999).
[14] D. Xiao, M.-C. Chang, and Q. Niu, Rev. Mod. Phys. **82**, 1959 (2010).
[15] D. Xiao, J. Shi, and Q. Niu, Phys. Rev. Lett. **95**, 137204 (2005).

[16] T. Thonhauser, D. Ceresoli, D. Vanderbilt, and R. Resta, Phys. Rev. Lett. **95**, 137205 (2005).
[17] D. Ceresoli, T. Thonhauser, D. Vanderbilt, and R. Resta, Phys. Rev. B **74**, 024408 (2006).
[18] J. Shi, G. Vignale, D. Xiao, and Q. Niu, Phys. Rev. Lett. **99**, 197202 (2007).
[19] D. Xiao, J. Shi, D. P. Clougherty, and Q. Niu, Phys. Rev. Lett. **102**, 087602 (2009).
[20] See Supplemental Materials.
[21] R. D. King-Smith and D. Vanderbilt, Phys. Rev. B **47**, 1651 (R) (1993).
[22] R. Resta, Rev. Mod. Phys. **66**, 899 (1994).
[23] D. Vanderbilt and R. D. King-Smith, Phys. Rev. B **48**, 4442 (1993).
[24] A. M. Essin, A. M. Turner, J. E. Moore, and D. Vanderbilt, Phys. Rev. B **81**, 205104 (2010).
[25] J. Shi, P. Zhang, D. Xiao, and Q. Niu, Phys. Rev. Lett. **96**, 076604 (2006)