

First-principles calculation of the bulk magnetoelectric monopole density: Berry phase and Wannier function approaches

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We present a formalism to calculate the macroscopic magnetoelectric monopolization from first principles within the density-functional-theory framework. An expression for the monopolization in the case of insulating collinear magnetism is derived first in terms of spin-polarized Wannier functions, and then recast as a Berry phase. We propose an extension to the general, noncollinear case, which we implement computationally in the Wannier function form and use to calculate the magnetoelectric monopolization of LiMnPO_4 and Cr_2O_3 . We find that, while the former is well approximated by a summation over the formal local spin moments, the latter shows significant deviations from this approximation. We suggest that equating the Berry phase value with a sum over local moments provides an unambiguous route to defining the size of the local magnetic moment in magnetoelectric antiferromagnets containing only one type of magnetic ion.

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I. INTRODUCTION

The interaction energy, H_{int} , of a magnetization density $\boldsymbol{\mu}(\mathbf{r})$ with an inhomogeneous magnetic field $\mathbf{H}(\mathbf{r})$ can be written as a multipole expansion in powers of field gradients calculated at some arbitrary reference point $\mathbf{r} = \mathbf{0}$:

$$\begin{aligned} H_{\text{int}} &= -\mu_0 \int \boldsymbol{\mu}(\mathbf{r}) \cdot \mathbf{H}(\mathbf{r}) d^3\mathbf{r} \\ &= -\mu_0 \int \boldsymbol{\mu}(\mathbf{r}) \cdot \mathbf{H}(\mathbf{0}) d^3\mathbf{r} \\ &\quad - \mu_0 \int r_i \mu_j(\mathbf{r}) \partial_i H_j(\mathbf{0}) d^3\mathbf{r} - \dots, \end{aligned} \quad (1)$$

where i, j are Cartesian directions (summation over repeated indices is implied) [1].

The first term, which is sufficient for describing many magnetic phenomena, gives the usual interaction of the magnetic dipole moment, $\mathbf{m} = \int \boldsymbol{\mu}(\mathbf{r}) d^3\mathbf{r}$, with a uniform magnetic field. Well-established methods exist for calculating the magnetic dipole moment and its energy within the density-functional-theory formalism: For the case of the spin contribution to the magnetic moment, the relevant quantities are particularly straightforward to calculate, as the spin magnetic moment per unit volume (the magnetization) in collinear systems is simply the difference between the up- and down-spin charge densities, which are directly accessible from a density-functional calculation [2]. The orbital magnetization is more complicated, since it is the expectation value of the circulation operator $\mathbf{r} \times \mathbf{v}$, which is not well defined in the Bloch representation. In spite of this difficulty, however, a formalism has also been recently developed for the calculation of orbital magnetization [3] and applied, for example, to the calculation of nuclear magnetic resonance (NMR) shielding tensors [4] and the orbital contribution to the magnetoelectric response [5].

In this work, we present a formalism and initial results for the first-principles calculation of one component of the second

terms, the so-called *magnetoelectric multipoles*, in the multipole expansion. Our motivation is manifold. First, these terms are nonzero in materials that show a linear magnetoelectric response [1,6,7], and so they can be used to classify and indeed to identify new magnetoelectric materials. Second, since they break both time-reversal and space-inversion symmetries, they offer candidate order parameters for completing the group of primary ferroics. Currently ferromagnetism, ferroelectricity, and ferroelasticity break time-reversal only, space-inversion only, and neither symmetries, respectively, and a ferroic order that breaks both symmetries is sought [1,6]. Indeed, the existence of ordered domains of such magnetoelectric multipoles was recently demonstrated using second-harmonic generation and hysteretic poling in LiCoPO_4 [8,9]. In addition, since routine techniques for their direct measurement are not yet available, they represent a kind of “hidden magnetic order” beyond that of magnetic dipoles, analogous to the challenge presented by antiferromagnets 100 years ago.

Following earlier work [7], we decompose the nine-component tensor $\mathcal{M}_{ij} = \int r_i \mu_j(\mathbf{r}) d^3\mathbf{r}$ in Eq. (1) into three irreducible tensors, each of which changes sign under time-reversal and space-inversion symmetries.

(i) The trace of the tensor, which couples to the divergence of the magnetic field, and so it is often referred to as the monopole component:

$$a = \frac{1}{3} \mathcal{M}_{ii} = \frac{1}{3} \int \mathbf{r} \cdot \boldsymbol{\mu}(\mathbf{r}) d^3\mathbf{r}. \quad (2)$$

(ii) The toroidal moment vector dual to the antisymmetric part of the tensor: $t_i = \frac{1}{2} \varepsilon_{ijk} \mathcal{M}_{jk}$, which couples to the curl of the magnetic field,

$$\mathbf{t} = \frac{1}{2} \int \mathbf{r} \times \boldsymbol{\mu}(\mathbf{r}) d^3\mathbf{r}. \quad (3)$$

(iii) The traceless symmetric tensor q_{ij} describing the magnetic quadrupole moment of the system, which couples

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to the field gradient:

$$\begin{aligned} q_{ij} &= \frac{1}{2} \left(\mathcal{M}_{ij} + \mathcal{M}_{ji} - \frac{2}{3} \delta_{ij} \mathcal{M}_{kk} \right) \\ &= \frac{1}{2} \int \left[r_i \mu_j(\mathbf{r}) + r_j \mu_i(\mathbf{r}) - \frac{2}{3} \delta_{ij} \mathbf{r} \cdot \boldsymbol{\mu}(\mathbf{r}) \right] d^3 \mathbf{r}. \end{aligned} \quad (4)$$

The expansion of Eq. (1) can then be written in the form

$$\begin{aligned} \mu_0^{-1} H_{\text{int}} &= -\mathbf{m} \cdot \mathbf{H}(0) - a(\nabla \cdot \mathbf{H})_{\mathbf{r}=0} \\ &\quad - \mathbf{t} \cdot [\nabla \times \mathbf{H}]_{\mathbf{r}=0} - q_{ij}(\partial_i H_j + \partial_j H_i)_{\mathbf{r}=0} - \dots \end{aligned}$$

This decomposition transparently yields three terms that couple to the divergence, curl, and gradient of the magnetic field, respectively. We call the first the magnetoelectric monopole to avoid confusion with a true magnetic monopole, noting that, while the magnetization diverges and couples to a divergent \mathbf{H} field, there is no divergence of the \mathbf{B} field [10]. The second is referred to as the toroidal moment or anapole and the third is the magnetic quadrupole. By analogy with the bulk magnetization, their corresponding bulk quantities per unit volume are then the magnetoelectric monopolization, toroidization, and quadrupolization. In this work, we focus on the spin contribution to the magnetoelectric monopolization; for the case of the monopolization, the orbital contribution is formally zero, since $\boldsymbol{\mu}_{\text{orb}} \propto \mathbf{r} \times \mathbf{v}$, and $\mathbf{r} \cdot (\mathbf{r} \times \mathbf{v}) = 0$. We also outline the developments required to calculate the toroidization and quadrupolization, which will be the subject of future work.

The remainder of this paper is organized as follows: In Sec. II, we derive an analytical formula for the spin contribution to the macroscopic magnetoelectric monopolization in insulating collinear antiferromagnets, both in terms of Wannier functions and expressed as a Berry phase, in a form that is already accessible in most existing density-functional codes. We propose an extension of the formalism for the noncollinear case and show that, while not formally rigorous, it provides a practical route for extracting the monopolization in the case of antiferromagnets with spin canting. In Sec. III, computational details for our density-functional calculations are given. In Sec. IV, we compute the bulk magnetoelectric monopolization for two materials, LiMnPO_4 and Cr_2O_3 , and we compare our results to the previously used local-moment approximation, in which the integral in Eq. (2) is replaced by a sum over local dipole moments at atomic sites. In the final section, we argue that the magnetoelectric monopolization in magnetoelectric, antiferromagnetic insulators with only one magnetic type of atom can be used to define an effective magnetic moment. Finally, we discuss the connection between the magnetoelectric monopolization and the magnetoelectric response.

II. DERIVATION OF THE EXPRESSION FOR THE MACROSCOPIC MAGNETOELECTRIC MONOPOLIZATION

The macroscopic magnetoelectric monopolization, A , of a system of volume V is given by

$$A = \frac{1}{3V} \int \mathbf{r} \cdot \boldsymbol{\mu}(\mathbf{r}) d^3 \mathbf{r}, \quad (5)$$

where the integral is over all space [7]. In the case of a finite system, the integral can be performed directly and the magnetoelectric monopolization extracted without ambiguity. For the periodic bulk solids that we consider here, however, the nonperiodicity of the position operator poses problems analogous to those encountered in defining a ferroelectric polarization or an orbital magnetization in a bulk system. We write the magnetization density in terms of the vector of Pauli matrices, $\boldsymbol{\sigma}$, and spinors, $\Phi_n(\mathbf{r})$, summed over the band index n :

$$\boldsymbol{\mu}(\mathbf{r}) = \mu_B \sum_n \Phi_n(\mathbf{r})^\dagger \boldsymbol{\sigma} \Phi_n(\mathbf{r}). \quad (6)$$

This gives the following expression for the magnetoelectric monopolization:

$$A = \frac{\mu_B}{3V} \sum_n \int \Phi_n(\mathbf{r})^\dagger \boldsymbol{\sigma} \cdot \mathbf{r} \Phi_n(\mathbf{r}) d^3 \mathbf{r}, \quad (7)$$

which we use as the starting point for our implementation.

A. Insulating collinear systems

For collinear spin systems, Eq. (7) can be separated into two equations, one for each spin channel. Choosing the quantization axis to be along z gives

$$A = \frac{\mu_B}{3V} \left[\sum_n \int \Phi_n^\uparrow(\mathbf{r})^\dagger z \Phi_n^\uparrow(\mathbf{r}) - \sum_n \int \Phi_n^\downarrow(\mathbf{r})^\dagger z \Phi_n^\downarrow(\mathbf{r}) \right]. \quad (8)$$

One can recognize each part as the definition of the ferroelectric polarization along the z direction for the respective spin channel. By analogy to Refs. [11,12], one can then write Eq. (8) for the case of a bulk periodic system as the Berry phase expression:

$$\begin{aligned} A &= \frac{\mu_B}{3V} \left[\sum_{n_\uparrow} \int d^3 \mathbf{k} \langle \mathcal{U}_{n\mathbf{k}}^\uparrow | \nabla_{k_z} | \mathcal{U}_{n\mathbf{k}}^\uparrow \rangle \right. \\ &\quad \left. - \sum_{n_\downarrow} \int d^3 \mathbf{k} \langle \mathcal{U}_{n\mathbf{k}}^\downarrow | \nabla_{k_z} | \mathcal{U}_{n\mathbf{k}}^\downarrow \rangle \right], \end{aligned} \quad (9)$$

where $|\mathcal{U}_{n\mathbf{k}}^\sigma\rangle$ is the cell-periodic part of the Bloch functions for spin channel σ .

Alternatively, one can rewrite the Berry phase expression for the magnetoelectric monopolization using Wannier functions, which can be chosen to be exponentially localized in the case of insulators [13], and which we will see provide a particularly intuitive basis for an extension to noncollinear magnetic systems. The transformation from Bloch functions $|\psi_{n\mathbf{k}}\rangle$ to Wannier functions is in general written as [14]

$$|W_{n\mathbf{R}}\rangle = \frac{V}{(2\pi)^3} \int_{\text{BZ}} d\mathbf{k} e^{-i\mathbf{k}\cdot\mathbf{R}} \sum_m U_{mn}^k |\psi_{m\mathbf{k}}\rangle, \quad (10)$$

where U_{mn}^k is a unitary rotation matrix, and \mathbf{R} is a lattice vector (in the following, we take $\mathbf{R} = \mathbf{0}$). Also, in terms of the cell-periodic part of the Bloch functions $|\mathcal{U}_{n\mathbf{k}}\rangle$, the expectation value of the position operator, usually termed the ‘‘Wannier

center,” is given by

$$\langle W_n | \mathbf{r} | W_n \rangle = \int d^3\mathbf{k} \langle \mathcal{U}_{nk} | \nabla_{\mathbf{k}} | \mathcal{U}_{nk} \rangle. \quad (11)$$

In the case of collinear spin-polarized systems, the spin-up and spin-down manifolds can be treated separately, and therefore there is a separate set of Wannier centers for each spin channel. The expression for the magnetoelectric monopolization then reads

$$A = \frac{\mu_B}{3V} \sum_n [\langle W_n^\uparrow | r_\alpha | W_n^\uparrow \rangle - \langle W_n^\downarrow | r_\alpha | W_n^\downarrow \rangle], \quad (12)$$

where $|W_n^\uparrow\rangle$ and $|W_n^\downarrow\rangle$ are the Wannier functions for the up (down) -spin channel.

Thus, A for insulating collinear systems can be obtained using any standard first-principles code in which the Berry phase or Wannier-function calculation of the polarization is implemented simply by taking the difference between the polarization for up- and down-spin bands.

One small conceptual complication arises when extracting a collinear monopolization from a standard code, due to the fact that \mathbf{P} is a vector property while A is a scalar. In the former case, the direction of the k -space derivative is a projection of the polarization onto the respective axis. In the latter case, however, the direction of the k -space derivative corresponds to the direction in which the Pauli matrix σ is assumed to be diagonal, that is, the method assumes that the k -space derivative direction is the quantization axis of the collinear spin system, even if spin-orbit coupling is not included in the calculation. A standard density-functional code will therefore automatically provide values for the monopolization for all three orientations of the collinear spin system in a single calculation. Those values corresponding to orientations other than the actual orientation of interest should then be disregarded.

B. Extension to noncollinear systems

1. Formulation in terms of Wannier functions

The Wannier function expression provides a conceptually appealing route to extending the formalism for the case of noncollinear spin systems. In the case of periodic crystalline insulators, one can identify the spinors in Eq. (7) with spinor Wannier functions $|W_n\rangle$. Then, after a switch to bra-ket notation, Eq. (7) reads

$$A = \frac{\mu_B}{3V} \sum_n \langle W_n | \boldsymbol{\sigma} \cdot \mathbf{r} | W_n \rangle. \quad (13)$$

While the “ordinary” Wannier center $\langle W_n | \mathbf{r} | W_n \rangle$ in the multiband case is not gauge-invariant, the sum over all Wannier centers is, so that the two terms in Eq. (12) are rigorously well-defined. To provide a rigorous formal definition, the sum in Eq. (13) should also be invariant under gauge transformations among the Bloch states. Our tests indicate that the gauge invariance of the sum of the Wannier centers transfers to the sum in Eq. (13), although we do not have formal proof of this.

In the case when all Wannier functions are internally collinear, the expression can be simplified to

$$A = \frac{\mu_B}{3V} \sum_n \langle W_n | \boldsymbol{\sigma} | W_n \rangle \cdot \langle W_n | \mathbf{r} | W_n \rangle, \quad (14)$$

where $\langle W_n | \boldsymbol{\sigma} | W_n \rangle$ is the expectation value of the spin of the Wannier function, giving both its magnitude and the orientation, and $\langle W_n | \mathbf{r} | W_n \rangle$ is the Wannier center. The expression above can then be directly compared to the local moment approximation employed in Ref. [7]:

$$A = \frac{1}{3V} \sum_i \mathbf{m}_i \cdot \mathbf{R}_i, \quad (15)$$

in which the local magnetic dipole moment of the i th ion, \mathbf{m}_i , replaces the spin of the Wannier function, and the position of the i th ion, \mathbf{R}_i , replaces the Wannier center. It is clear from this comparison that in a fully ionic system, in which the magnetic moments are “point spins” located at the ionic sites, the Wannier centers will lie at the ionic sites and the two expressions will lead to identical values for the monopolization. In cases with covalency, the two values will differ, just as the ferroelectric polarization in a covalent system differs from that in a point-charge model.

We note that analogous Wannier function expressions for the toroidization T_i and quadrupolization Q_{ij} can be written as

$$T_i = \frac{\mu_B}{3V} \sum_n \epsilon_{ijk} \langle W_n | \sigma_j r_k | W_n \rangle \quad (16)$$

and

$$Q_{ij} = \frac{\mu_B}{3V} \sum_n (\langle W_n | \sigma_i r_j | W_n \rangle + \langle W_n | \sigma_j r_i | W_n \rangle - \frac{2}{3} \delta_{ij} \langle W_n | \sigma_i r_i | W_n \rangle), \quad (17)$$

respectively.

2. Formulation as a Berry phase

By using the transformation from Wannier functions to the cell-periodic part of Bloch functions, Eq. (13) can be rewritten as

$$A = \frac{\mu_B}{3V} \sum_n \langle W_n | \boldsymbol{\sigma} \cdot \mathbf{r} | W_n \rangle \quad (18)$$

$$= \frac{\mu_B}{3V} \sum_n \int d^3\mathbf{k} \langle \mathcal{U}_{nk} | \boldsymbol{\sigma} \cdot \nabla_{\mathbf{k}} | \mathcal{U}_{nk} \rangle. \quad (19)$$

Note that this expression suffers from the same ambiguity regarding the gauge dependence as we pointed out above for the Wannier-function case. Interestingly, Batista *et al.* [15] arrived earlier at a similar result, which they interpreted only for the ferrotoroidic case, although in principle their derivation is also applicable to the monopolization.

C. Multivaluedness of the magnetoelectric monopolization

It is clear from Eq. (12) that the magnetoelectric monopolization is a multivalued quantity, since the center of a Wannier function is only defined up to a lattice vector, \mathbf{R}_α . The term “monopolization increment,” ΔA , was introduced in Ref. [7] to describe the difference between branches of the associated monopolization lattice. For the case of collinear spin systems, denoting the spin quantization axis of the system by $\boldsymbol{\sigma}$, the

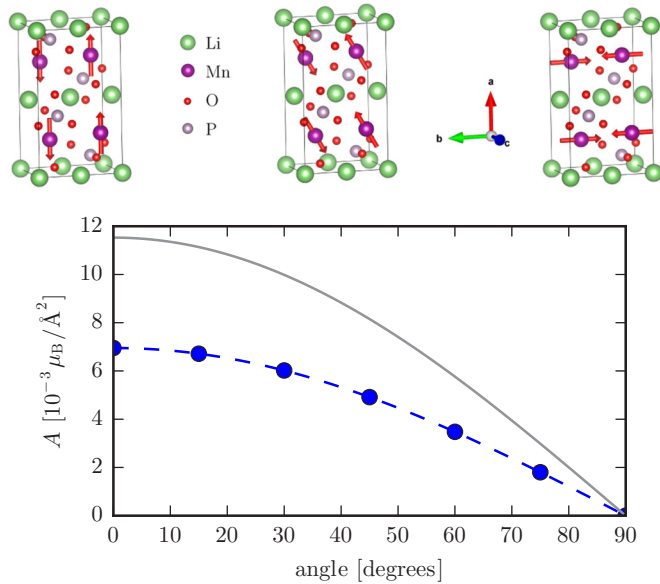


FIG. 1. Magnetoelectric monopolization in LiMnPO_4 as a function of the angle of the spins to the a axis. The monopolization has its maximum value when the spins are aligned along a , and it drops to zero as they rotate away from the a axis and their arrangement becomes toroidal. The gray line shows the monopolization increment. On top, the alignment of the spins along the crystal axis is shown for the direction that maximizes the monopolization (0°), an intermediate direction, and a direction with zero monopolization (90°).

monopolization increment is

$$\Delta A = \frac{\mu_B}{3V} \boldsymbol{\sigma} \cdot \mathbf{R}_\alpha. \quad (20)$$

For noncollinear systems the situation is more subtle, since in principle each Wannier function in Eq. (13) can have a different spin direction. Therefore, the monopolization increment can be different for each Wannier function:

$$\Delta A_n = \frac{\mu_B}{3V} \boldsymbol{\sigma}_n \cdot \mathbf{R}_\alpha, \quad (21)$$

where $\boldsymbol{\sigma}_n$ is the vector describing the spin of the n th Wannier function, and multiple monopolization increments can exist.

We see also that the monopolization increment changes as the direction of spins changes. This situation is illustrated in Fig. 1, where we show the calculated evolution of the magnetoelectric monopolization and the monopolization increment as a function of the angular rotation of the spin direction away from that which maximizes the magnetoelectric monopolization (0°). One noteworthy case occurs when $\boldsymbol{\sigma}_n$ becomes almost perpendicular to \mathbf{R}_α and the monopolization tends to zero; then the increment also becomes small, and changes between branches cannot be easily distinguished. Therefore, difficulties arise when one tries to define the monopolization difference between a nonmonopolar reference structure and a monopolar structure if the change involves only the rotation of spins and no structural change.

In this respect, the correspondence between the polarization and the monopolization is not exact. While both the electron charge and the electron spin have well-defined single values, the charge enters the expression for the polarization as a scalar quantity, whereas the spin enters as a vector, in a dot

product with its position. This means that the polarization quantum is unchanged (provided that the lattice vectors are unchanged) even if the atomic positions evolve, whereas, as we have just seen, the monopolization increment evolves with the orientation of the spin moment.

The situation is more straightforward in the case of a monopolization arising from a structural change. In this case, the monopolization increment is unchanged, in direct analogy to the polarization quantum. An example of this case is FeS , in which the transition from space group $P6_3/mmc$ to $P\bar{6}2c$ goes along with a loss of the inversion center and the occurrence of a magnetoelectric monopolization [16].

III. COMPUTATIONAL DETAILS

Calculations presented here were performed using the QUANTUM ESPRESSO code [17]. We used the PBE functional and norm-conserving pseudopotentials, with $2s$ valence states for Li, $3d$ and $4s$ for Mn and Cr, $3s$ and $3p$ for P, and $2p$ and $2s$ states for O. For both Cr_2O_3 and LiMnPO_4 , well-converged magnetoelectric monopolizations were obtained with an energy cutoff of 100 Ry for both total-energy and Berry phase calculations. The k -point grid was $3 \times 5 \times 5$ for LiMnPO_4 and $4 \times 4 \times 2$ for Cr_2O_3 in a hexagonal setting. For LiMnPO_4 , we used the Hubbard U correction [18] on the Mn sites with $U = 4$ eV and $J = 0.5$ eV. Note that the allowed antiferromagnetic A_z -type canting of the Mn spins does not lead to an energy lowering in our calculations, so our system remains collinear. (Fortunately, this allows for a direct comparison of our results with those of Ref. [7], where the canting was neglected.)

Collinear magnetoelectric monopolizations were obtained with the Berry phase implementation of QUANTUM ESPRESSO. To compare the Berry phase prescription and the Wannier function description of Eq. (14), we used the WANNIER90 code [19] to generate maximally localized Wannier functions.

IV. RESULTS

A. LiMnPO_4

We choose LiMnPO_4 , which was shown previously to have a diagonal magnetoelectric response [20,21] and a corresponding macroscopic magnetoelectric monopolization [7], as our first model system. The crystallographic space group of LiMnPO_4 is $Pnma$ and the antiferromagnetic C_x -type order of the Mn ions has the magnetic space group $Pn'm'a'$, which allows a macroscopic magnetoelectric monopolization. In Ref. [7], the size of the monopolization obtained from summing over the localized magnetic moments as in Eq. (15), using the moments obtained from projecting into the muffin-tin spheres ($4.26\mu_B$), was found to be $5.89 \times 10^{-3} \mu_B / \text{\AA}^2$. In addition, a small contribution of $0.03 \times 10^{-3} \mu_B / \text{\AA}^2$ from summing the magnetoelectric monopoles in the spheres around each atom was found. Using the lattice parameters and atomic positions from Ref. [7], we obtain a slightly smaller magnetic moment of $4.17\mu_B$ on the Mn sites, which gives a correspondingly slightly smaller local-moment magnetoelectric monopolization of $A^{\text{lm}} = 5.77 \times 10^{-3} \mu_B / \text{\AA}^2$. Note that all results from this section and the next are summarized in Table I.

TABLE I. Summary of the calculated magnetoelectric monopolarizations for LiMnPO_4 and Cr_2O_3 . The upper panel gives the formal and DFT local spin magnetic moment and corresponding local moment monopolarizations A^{lm} , whereas the bottom values give the calculated Berry phase magnetoelectric monopolarization and the derived effective moment.

	LiMnPO_4	Cr_2O_3
$m^{\text{formal}} (\mu_B)$	5	3
$m^{\text{DFT}} (\mu_B)$	4.17	2.27
$A^{\text{lm,formal}} (10^{-3} \mu_B/\text{\AA}^2)$	6.917	7.388
$A^{\text{lm,DFT}} (10^{-3} \mu_B/\text{\AA}^2)$	5.77	5.173
$A^{\text{BP}} (10^{-3} \mu_B/\text{\AA}^2)$	6.945	5.488
$m^{\text{eff}} (\mu_B)$	5.02	2.25

We begin by using the Berry phase formalism to calculate the macroscopic magnetoelectric monopolarization of LiMnPO_4 . As expected for an antiferromagnetic system in which the crystal structure contains inversion symmetry, we obtain values of equal magnitude but opposite sign for the two spin channels along the three crystal axes. Their sum gives the polarization, which is zero in all directions. Their difference is different from the monopolarization quantum in the a direction, corresponding to the case in which the Pauli matrix in this direction is diagonal, that is, the magnetic spins are aligned along a . The resulting monopolarization is $A = 6.945 \times 10^{-3} \mu_B/\text{\AA}^2 \pm n\Delta A$, where the monopolarization increment $\Delta A = 11.53 \times 10^{-3} \mu_B/\text{\AA}^2$. For spin directions along b and c , as found in the Fe, Co, and Ni analogs of LiMnPO_4 , the Berry phase magnetoelectric monopolarization is equal to zero or the monopolarization increment.

We now compare this result from the Berry phase calculation to the Wannier function formalism outlined above. Still in the collinear framework, we choose the Mn d orbitals and O p orbitals as projections and carry out the Wannier transformation in WANNIER90. The numerical result for A is almost unchanged ($A = 6.953 \times 10^{-3} \mu_B/\text{\AA}^2$). While this might seem trivial, it indicates that our choice of Wannier function projection has captured all relevant hybridizations that contribute to the monopolarization. Including spin-orbit coupling changes the monopolarization by only $10^{-6} \mu_B/\text{\AA}^2$.

We see that in the case of LiMnPO_4 , use of the local-moment approximation to calculate the magnetoelectric monopolarization makes an underestimate of $\sim 15\%$ compared to the full calculation, when the dipole moment projected into the atomic sphere is taken as the local magnetic moment. Interestingly, when we take the full formal spin-only moment of $5\mu_B$ for Mn^{2+} , we arrive at a local moment monopolarization very close to $A^{\text{lm}} = 6.917 \times 10^{-3} \mu_B/\text{\AA}^2$, and the difference between the local moment magnetoelectric monopolarization and the full Berry phase magnetoelectric monopolarization, $\Delta A = 0.03 \times 10^{-3} \mu_B/\text{\AA}^2$, corresponds precisely to the contribution of the atomic site terms obtained previously [7]. We suggest, however, that this intriguing correspondence is likely coincidental, and we wait to discuss it further until after our analysis of Cr_2O_3 , which follows.

TABLE II. Lattice parameters and Wyckoff positions for Cr_2O_3 . Values were obtained by structural relaxation using the PBE exchange-correlation functional. Experimental values are taken from Ref. [22].

	DFT		Experiment
a (\text{\AA})	4.962		4.9570
c (\text{\AA})	13.570		13.5923
Cr	12c	z	0.348
O	18e	x	0.306

B. Cr_2O_3

Next, we turn our attention to chromium dioxide, Cr_2O_3 , which is the prototypical magnetoelectric material [23]. It crystallizes in the corundum structure (space group $R\bar{3}c$) with a collinear antiferromagnetic structure consisting of antiferromagnetic chains along the hexagonal c axis with the moments aligned along c . This leads to the magnetic space group $R\bar{3}'c'$, which allows a macroscopic monopolarization but no spin canting. First, we fully relaxed the structure; the resulting coordinates are given in Table II alongside experimental values with which they compare favorably.

The collinear Berry phase calculation along z yields $A = 5.488 \times 10^{-3} \mu_B/\text{\AA}^2$; using the Wannier-function formalism with Cr t_{2g} and O p orbitals as projections, we again obtain an almost unchanged result ($A = 5.469 \times 10^{-3} \mu_B/\text{\AA}^2$). Including spin-orbit coupling, one obtains $A = 5.496 \times 10^{-3} \mu_B/\text{\AA}^2$. While this change is not huge, the effect that spin-orbit coupling has on the monopolarization is larger than in LiMnPO_4 .

In our first-principles calculations, we obtain a magnetic moment of $2.27\mu_B$ on the Cr sites, which gives a local moment magnetoelectric monopolarization of $A = 5.173 \times 10^{-3} \mu_B/\text{\AA}^2$. As in the case of LiMnPO_4 , this is an underestimate of the full Berry phase value, but this time by only $\sim 6\%$. The correction from the atomic site monopoles is $0.69 \times 10^{-3} \mu_B/\text{\AA}^2$; adding this contribution to the local moment approximation leads to an overestimation of the Berry phase value by $\sim 7\%$. Taking the formal spin-only moment of $3\mu_B$ for Cr^{3+} , however, one obtains $A = 7.388 \times 10^{-3} \mu_B/\text{\AA}^2$, which is a substantial overestimate of the Berry phase value. To recover the Berry phase result in a local-moment picture, one has to take an effective magnetic moment of $2.253\mu_B$ on the Cr sites.

V. DISCUSSION

The origin of the differences between LiMnPO_4 and Cr_2O_3 , in terms of the size of the local magnetic moment that must be used to bring the monopolarization calculated within the local moment approximation into agreement with the full Berry phase value, is unclear. In both cases, the local magnetic moments differ substantially from the formal ionic values (by 17% in the case of LiMnPO_4 and by 24% for Cr_2O_3), indicating significant hybridization between oxygen $2p$ and transition-metal $3d$ electrons, and consequent deviation from the ionic limit. It is therefore particularly surprising that in LiMnPO_4 , the local moment approximation is almost exact

for the formal spin-only Mn moment of $5\mu_B$. In both cases, the contribution from the local monopolizations within the spheres around the atomic sites is small compared to the local moment monopolization. In LiMnPO_4 , it is negligible ($A^{\text{as}} = 0.03 \times 10^{-3} \mu_B/\text{\AA}^2$), due largely to a cancellation of the contributions from different oxygen sites [7]. It is larger in Cr_2O_3 ($A^{\text{as}} = 0.69 \times 10^{-3} \mu_B/\text{\AA}^2$), since while the magnitudes of the atomic site oxygen contribution ($9.3 \times 10^{-3} \mu_B \text{\AA}$) and Cr contribution ($2.6 \times 10^{-3} \mu_B \text{\AA}$) are comparable to the analogous values in LiMnPO_4 , all contributions have the same sign and therefore do not cancel each other.

Definition of the local magnetic moment associated with an ion is of course ambiguous in a covalently bonded solid, and the differences likely reflect as much the details of the projection of the Bloch states into the atomic sphere as real physics. We suggest that the value of the local magnetic moment that brings the local-moment approximation to the magnetoelectric monopolization into equality with the full Berry phase value can be used as a way of unambiguously defining the local magnetic moment in magnetoelectric antiferromagnets containing only one kind of magnetic ion, and it is certainly a relevant definition in the discussion of magnetoelectric monopolizations. Note that the local magnetic moment defined in this way is distinct from the magnetic charge of Ref. [24], which gives the change in magnetization with atomic displacement.

Next, we turn our attention to the relation between the magnetoelectric coefficients and the magnetoelectric monopolization. In Ref. [7], a relation between these two quantities was derived from the following free-energy expression:

$$U = \frac{1}{2\epsilon} P^2 - \mathbf{P} \cdot \mathbf{E} + \frac{\mu_0}{2\chi} M^2 - \mu_0 \mathbf{M} \cdot \mathbf{H} + \frac{1}{2} \beta A^2 + \frac{1}{4} \gamma A^4 + c \mathbf{A} \mathbf{P} \cdot \mathbf{M}, \quad (22)$$

where ϵ and χ are the electric and magnetic susceptibilities, β and γ are temperature-dependent coupling coefficients, and c determines the strength of the magnetoelectric coupling. Minimizing this expression leads to a relationship between the magnetoelectric coefficient and the monopolization with the electric and magnetic susceptibilities as proportionality constants:

$$\alpha = c\epsilon\chi A. \quad (23)$$

The coupling strength c , however, is unknown. Indeed it was argued in Ref. [1] that c is not of physical relevance, since the magnetoelectric tensor describes the second-order correction to the free energy in external electric and magnetic fields, while magnetic multipoles are generated by the expansion of the first-order correction to the free energy in powers of magnetic-field gradients.

Here, we estimate the value of c for Cr_2O_3 using literature values for the various quantities appearing in Eq. (23), and then make a comparison to calculated values in the high- and low-frequency limits. The results are summarized in Table III. The dielectric susceptibility is around 10 at low temperature, with only a small anisotropy between parallel and perpendicular (to z) orientation [25,26]. The low-temperature magnetic susceptibility in perpendicular orientation has the value 1.5×10^{-3} (dimensionless SI) [27]. From Ref. [10], we take the monopolar part of the magnetoelectric tensor as

$\tilde{\alpha} = \frac{1}{3} \text{Tr}(\alpha) = 0.7 \text{ps/m}$. Putting together these experimental results and our calculated magnetoelectric monopolization, we estimate the coupling strength as $c = 1 \times 10^{-5} \text{s}/(\text{A m})$.

First-principles-based investigations are able to distinguish between electronic and lattice contributions to the various susceptibilities. In the following, we take the results from Ref. [2] (note that a range of slightly different values for the spin-only response has been obtained [2,28,29], with all values overestimating the experimental values) and augment them with new calculations of the static and high-frequency dielectric susceptibility. By employing density-functional perturbation theory, we obtain the lattice contribution $\epsilon^{\text{latt}} = 3.5$ and the electronic contribution $\epsilon^{\text{el}} = 5.8$. The two contributions agree reasonably well with the experimental values [26]. The lattice contribution to the spin magnetic susceptibility has been previously shown to be negligible [24].

Since A is a thermodynamic quantity, that is, it is not frequency-dependent and χ is almost frequency-independent, we see immediately that the proportionality factor

$$c = \frac{\alpha}{\epsilon\chi A} \quad (24)$$

is only constant if the frequency dependence of ϵ and α is the same. The spin-electronic magnetoelectric response leads to a high-frequency (electronic only) coupling strength of $c^\infty = 4 \times 10^{-6} \text{s}/(\text{A m})$, while the total spin magnetoelectric response leads to a low-frequency (electronic plus lattice) coupling strength $c^{\text{tot}} = 1 \times 10^{-5} \text{s}/(\text{A m})$. The latter value is consistent with the estimates extracted from the experimental range of susceptibilities, and the difference between c^{tot} and c^∞ confirms the assertion of Ref. [1] that the proportionality constant does not represent a fundamental, physically universal parameter. Indeed, we expect the behavior of c to be especially interesting close to magnetoelectric phase transitions, where it is known that ϵ , χ , and α can all diverge [30,31].

VI. SUMMARY

In summary, we have derived the Berry phase theory for macroscopic magnetoelectric monopolization for insulating collinear antiferromagnets, we proposed a generalization to the noncollinear phase, and we implemented it in its Wannier function form within the density-functional formalism. We applied the method to two prototypical magnetoelectric materials, LiMnPO_4 and Cr_2O_3 . Our results highlight two different behaviors: In LiMnPO_4 , the bulk monopolization is close to

TABLE III. Summary of the calculated coupling strengths c . Here, $\tilde{\alpha} = \frac{1}{3} \text{Tr}(\alpha)$, and ϵ and χ are the electronic and magnetic susceptibility. Experimental values are taken from Refs. [10,25–27], and the DFT results for $\tilde{\alpha}$ and χ are taken from Ref. [2].

	$\tilde{\alpha}$ (ps/m)	ϵ	χ	c [s/(A m)]
Experimental	0.7	10	1.5×10^{-3}	1×10^{-5}
DFT electronic	0.23	5.8	1.9×10^{-3}	4×10^{-6}
DFT total	0.97	9.3	1.9×10^{-3}	1×10^{-5}

the value obtained by a simple local moment formalism using the formal ionic magnetic moment. In contrast, in Cr_2O_3 , use of the projected atomic-site local moment yields a better agreement. We proposed a comparison of the local-moment approximation and full Berry phase values of the monopolization as an unambiguous way to define the local magnetic moment in magnetoelectric antiferromagnets. Finally, we discussed the quantitative connection between the magnetoelectric response and the monopolization via the dielectric and magnetic susceptibilities.

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- [1] N. A. Spaldin, M. Fiebig, and M. Mostovoy, *J. Phys.: Condens. Matter* **20**, 434203 (2008).
- [2] E. Bousquet, N. A. Spaldin, and K. T. Delaney, *Phys. Rev. Lett.* **106**, 107202 (2011).
- [3] T. Thonhauser, D. Ceresoli, D. Vanderbilt, and R. Resta, *Phys. Rev. Lett.* **95**, 137205 (2005).
- [4] T. Thonhauser, D. Ceresoli, A. A. Mostofi, N. Marzari, R. Resta, and D. Vanderbilt, *J. Chem. Phys.* **131**, 101101 (2009).
- [5] A. Malashevich, I. Souza, S. Coh, and D. Vanderbilt, *New J. Phys.* **12**, 053032 (2010).
- [6] C. Ederer and N. A. Spaldin, *Phys. Rev. B* **76**, 214404 (2007).
- [7] N. A. Spaldin, M. Fechner, E. Bousquet, A. Balatsky, and L. Nordström, *Phys. Rev. B* **88**, 094429 (2013).
- [8] A. S. Zimmermann, D. Meier, and M. Fiebig, *Nat. Commun.* **5**, 4796 (2014).
- [9] B. B. Van Aken, J.-P. Rivera, H. Schmid, and M. Fiebig, *Nature (London)* **449**, 702 (2007).
- [10] F. W. Hehl, Y. N. Obukhov, J.-P. Rivera, and H. Schmid, *Phys. Rev. A* **77**, 022106 (2008).
- [11] R. Resta, *Ferroelectrics* **136**, 51 (1992).
- [12] R. D. King-Smith and D. Vanderbilt, *Phys. Rev. B* **47**, 1651(R) (1993).
- [13] C. Brouder, G. Panati, M. Calandra, C. Mourougane, and N. Marzari, *Phys. Rev. Lett.* **98**, 046402 (2007).
- [14] N. Marzari, A. A. Mostofi, J. R. Yates, I. Souza, and D. Vanderbilt, *Rev. Mod. Phys.* **84**, 1419 (2012).
- [15] C. D. Batista, G. Ortiz, and A. A. Aligia, *Phys. Rev. Lett.* **101**, 077203 (2008).
- [16] F. Ricci and E. Bousquet, [arXiv:1511.01327](https://arxiv.org/abs/1511.01327).
- [17] P. Giannozzi, S. Baroni, N. Bonini, M. Calandra, R. Car, C. Cavazzoni, D. Ceresoli, G. L. Chiarotti, M. Cococcioni, I. Dabo, A. Dal Corso, S. de Gironcoli, S. Fabris, G. Fratesi, R. Gebauer, U. Gerstmann, C. Gougoussis, A. Kokalj, M. Lazzeri, L. Martin-Samos, N. Marzari, F. Mauri, R. Mazzarello, S. Paolini, A. Pasquarello, L. Paulatto, C. Sbraccia, S. Scandolo, G. Sclauzero, A. P. Seitsonen, A. Smogunov, P. Umari, and R. M. Wentzcovitch, *J. Phys.: Condens. Matter* **21**, 395502 (2009).
- [18] A. I. Liechtenstein, V. I. Anisimov, and J. Zaanen, *Phys. Rev. B* **52**, R5467 (1995).
- [19] A. A. Mostofi, J. R. Yates, G. Pizzi, Y.-S. Lee, I. Souza, D. Vanderbilt, and N. Marzari, *Comput. Phys. Commun.* **185**, 2309 (2014).
- [20] M. Mercier, E. F. Bertaut, G. Quézel, and P. Bauer, *Solid State Commun.* **7**, 149 (1969).
- [21] R. Toft-Petersen, N. H. Andersen, H. Li, J. Li, W. Tian, S. L. Bud'ko, T. B. S. Jensen, C. Niedermayer, M. Laver, O. Zaharko, J. W. Lynn, and D. Vaknin, *Phys. Rev. B* **85**, 224415 (2012).
- [22] H. Sawada, *Mater. Res. Bull.* **29**, 239 (1994).
- [23] I. E. Dzyaloshinskii, *J. Exp. Theor. Phys.* **37**, 881 (1959) [*Sov. Phys. JETP* **10**, 628 (1960)].
- [24] M. Ye and D. Vanderbilt, *Phys. Rev. B* **89**, 064301 (2014).
- [25] P. H. Fang and W. S. Brower, *Phys. Rev.* **129**, 1561 (1963).
- [26] G. Lucovsky, R. J. Sladek, and J. W. Allen, *Phys. Rev. B* **16**, 4716 (1977).
- [27] S. Foner, *Phys. Rev.* **130**, 183 (1963).
- [28] A. Malashevich, S. Coh, I. Souza, and D. Vanderbilt, *Phys. Rev. B* **86**, 094430 (2012).
- [29] J. Iñiguez, *Phys. Rev. Lett.* **101**, 117201 (2008).
- [30] I. Dzyaloshinskii, *Europhys. Lett.* **96**, 17001 (2011).
- [31] E. Bousquet and N. A. Spaldin, *Phys. Rev. Lett.* **107**, 197603 (2011).