GEOMETRICAL OBSERVABLES IN CONDENSED MATTER

ELECTRICAL POLARIZATION, ORBITAL MAGNETIZATION, AND MORE

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Dedicated to the memory of my dear friends and colleagues
Sandro Massidda (1955-2017)
and Alessandro De Vita (1965-2018)

Some intensive phenomenological observables of condensed matter evaded for many years a sound microscopic definition, and severely challenged quantum-mechanical calculations: macroscopic polarization and the orbital term in macroscopic magnetization are among them. The field has undergone a genuine revolution since the early 1990s; it is now clear that these two observables have a geometrical nature. Polarization is essentially a geometric phase (Berry phase) of the ground-state wavefunction. Orbital magnetization has a geometrical expression as well; other geometrical observables were identified over the years. Here we provide a state-of-the-art outline of the field.

1 The context

All of the present review is in the framework of band-structure theory, which is −since the 1930s− the main theoretical tool for addressing both ground-state and excitation properties of a large class of materials: crystalline solids whose electrons are well described at a mean-field level. Band-structure theory amounts to considering noninteracting electrons in a lattice-periodical one-body potential $V(\mathbf{r})$. As for the choice of the appropriate $V(\mathbf{r})$, it has been mostly semiempirical until the late 1970s [1], and mostly first-principle (either Hartree-Fock or Kohn-Sham) afterwards [2, 3].

The electronic ground state is uniquely defined in terms of the lowest one-electron orbitals, occupied according to Pauli's principle up to the Fermi level; several ground-state observables have a simple expression in terms of these orbitals. There exist, however, ground-state observables which for many years eluded solid-state theory: most notably macroscopic electrical polarization and orbital magnetization. Even the very *definition* of what these observables are −as given in the most popular texbooks [1, 4]− is flawed, not implementable in practical calculations.

A new paradigm appeared in the early 1990s, when it became clear what polarization *really is*, and how it can be computed. The modern theory of polarization is based on a geometric phase (Berry phase) [5, 6]; the geometrical nature of other ground-state observables has been elucidated over the years. The adjective "geometrical" does not refer to the geometry of the ordinary (coordinate) space; it refers instead to the quantum geometry in the Hilbert space of the state vectors, as sketched in Box 1. In the cases discussed here, the relevant state vectors are the occupied one-body orbitals.

Box 1

Quantum geometry

The funding concept in geometry is distance. Let $|\Psi_1\rangle$ and $|\Psi_2\rangle$ be two quantum states in the same Hilbert space: we adopt for their distance the expression

$$\mathcal{D}^2_{12} = -\ln|\langle\Psi_1|\Psi_2\rangle|^2 ,$$

which vanishes when the states $|\Psi_1\rangle$ and $|\Psi_2\rangle$ coincide, while it diverges when the states $|\Psi_1\rangle$ and $|\Psi_2\rangle$ are orthogonal. The states $|\Psi_1\rangle$ and $|\Psi_2\rangle$ are defined up to an arbitrary phase factor: fixing this factor amounts to a gauge choice.

The distance is clearly gauge-invariant; it can equivalently be rewritten as

$$\mathcal{D}^2_{12} = -\ln\langle\Psi_1|\Psi_2\rangle - \ln\langle\Psi_2|\Psi_1\rangle,$$

where the two terms are not separately gauge-invariant. While the distance is obviously real, each of the two terms is in general a complex number. If we write

$$\langle\Psi_1|\Psi_2\rangle = |\langle\Psi_1|\Psi_2\rangle| e^{i\varphi_{21}} ,$$

then the imaginary part of each of the two terms assumes a transparent meaning:

$$-\mathrm{Im}\ln\langle\Psi_1|\Psi_2\rangle = \varphi_{12} , \qquad \varphi_{21} = -\varphi_{12} .$$

Besides the metric, an additional geometrical concept is therefore needed: the connection, which fixes the relative phases betweeen two states in the Hilbert space.

The connection is arbitrary and cannot have any physical meaning by itself. Nonetheless, after the groundbreaking paper by Michael Berry, published in 1984, several physical observables are expressed in terms of the connection and related quantities [6].

Fundamental geometrical quantities are the quantum metric and the Berry connection, defined as the differentials of $\mathcal{D}^2_{12}$ and of φ_{12}, respectively, when $|\Psi_2\rangle$ is varied in a neighborhood of $|\Psi_1\rangle$. These two fundamental quantities are defined in terms of the state vectors solely; other geometrical quantities may involve the Hamiltonian as well (and no other operator).

2 Geometry in Bloch space

Owing to the lattice periodicity of the one-body Hamiltonian $\mathcal{H}$, the orbitals assume the Bloch form: $|\psi_{j\mathbf{k}}\rangle = e^{i\mathbf{k}\cdot\mathbf{r}}|u_{j\mathbf{k}}\rangle$, where $\mathbf{k}$ is the Bloch vector in the first Brillouin zone (BZ). The $|u_{j\mathbf{k}}\rangle$ orbitals are eigenstates of $\mathcal{H}_\mathbf{k} = \mathrm{e}^{-i\mathbf{k}\cdot\mathbf{r}}\mathcal{H}e^{i\mathbf{k}\cdot\mathbf{r}}$ with eigenvalues $\epsilon_{j\mathbf{k}}$. The $|\psi_{j\mathbf{k}}\rangle$ at different $\mathbf{k}$ values are orthogonal, hence their quantum distance is infinite. We will consider instead the geometry of the $|u_{j\mathbf{k}}\rangle$, in the Hilbert space of the lattice-periodical functions. Both the distance and the connection are thus expressed (see Box 1) in terms of the scalar products $\langle u_{j\mathbf{k}}| u_{j'\mathbf{k}'}\rangle$; the corresponding differential forms are

$$(1) \qquad D^2_{\mathbf{k},\mathbf{k}+\mathrm{d}\mathbf{k}} = g_{\alpha\beta}(\mathbf{k})\mathrm{d}k_\alpha \mathrm{d}k_\beta , \qquad \varphi_{\mathbf{k},\mathbf{k}+\mathrm{d}\mathbf{k}} = \mathcal{A}_\alpha(\mathbf{k})\mathrm{d}k_\alpha ,$$

where $g_{\alpha\beta}(\mathbf{k})$ is the quantum metric tensor and $\mathcal{A}_\alpha(\mathbf{k})$ is known as the Berry connection; summation over Cartesian indices is implicit (here and throughout).

For an insulating solid with n occupied bands the metric and the connection are a geometrical property of the occupied Bloch manifold; their explicit expressions are

$$g_{\alpha\beta}(\mathbf{k}) = \mathrm{Re} \sum_{j=1}^{n} \langle \partial_{k_\alpha} u_{j\mathbf{k}} | \partial_{k_\beta} u_{j\mathbf{k}} \rangle - \sum_{jj'=1}^{n} \langle \partial_{k_\alpha} u_{j\mathbf{k}} | u_{j'\mathbf{k}} \rangle \langle u_{j'\mathbf{k}} | \partial_{k_\beta} u_{j\mathbf{k}} \rangle \, , \tag{2}$$

$$\mathcal{A}_\alpha(\mathbf{k}) = i \sum_{j=1}^{n} \langle u_{j\mathbf{k}} | \partial_{k_\alpha} u_{j\mathbf{k}} \rangle \, . \tag{3}$$

A third important quantity in differential geometry is the curl of $\mathcal{A}(\mathbf{k})$, known as the Berry curvature:

$$\Omega_{\alpha\beta}(\mathbf{k}) = \partial_{k_\alpha} \mathcal{A}_\beta(\mathbf{k}) - \partial_{k_\beta} \mathcal{A}_\alpha(\mathbf{k}). \tag{4}$$

Since we will need the curvature even in metals, it is expedient to write its most general form as

$$\Omega_{\alpha\beta}(\mathbf{k}) = i \sum_{\epsilon_{j\mathbf{k}} \leq \mu} \left(\langle \partial_{k_\alpha} u_{j\mathbf{k}} | \partial_{k_\beta} u_{j\mathbf{k}} \rangle - \langle \partial_{k_\beta} u_{j\mathbf{k}} | \partial_{k_\alpha} u_{j\mathbf{k}} \rangle \right) , \tag{5}$$

where μ is the Fermi level. It is worth remarking that all of the above forms are real; the connection is a 1-form and is gauge-dependent, while both the metric and the curvature are 2-forms and are gauge-invariant.

The quantum distance and metric are at the root of the modern theory of the insulating state, which addresses all insulators −particularly those where band-structure theory is inadequate− and is therefore beyond the scope of the present work; to the interested reader we mention the recent review of ref. [7]. In the following we will instead address the connection, the curvature, and other related geometrical forms in band insulators and band metals.

3 Modern theory of polarization

Macroscopic electrical polarization only makes sense for insulators which are charge-neutral in average, and is comprised of an electronic (quantum) term and a nuclear (classical) term. Each of the terms separately depends on the choice of the coordinate origin, while their sum is translationally invariant. The basic tenet of the modern theory is that the electronic term is a Berry phase, expressed as a BZ integral of the Berry connection. Such integral is implemented −in its discretized version− in most electronic structure codes, and is routinely used to compute the polarization of a large class of solids [2, 3, 6].

For the sake of simplicity, we outline the theory over the simple case of a quasi-one-dimensional system (a stereoregular polymer), where the polarization P is the dipole per unit length and has the dimensions of a pure charge. The Bloch vector k is one-dimensional, and the theory yields the electronic term in P as

$$P_{\mathrm{el}} = -e \frac{\gamma_{\mathrm{el}}}{2\pi}, \qquad \gamma_{\mathrm{el}} = 2 \int_{\mathrm{BZ}} \mathrm{d}k \mathcal{A}(k) \, , \tag{6}$$

where e is the unit charge and the factor of two accounts for double orbital occupancy. We have already observed that $\mathcal{A}(k)$ is gauge-dependent; its BZ integral, instead, is gauge-invariant but is multivalued: it is only defined modulo 2π.

Even the nuclear term can be converted to a phase form; if the nuclei of charge eZ_ℓ in the unit cell sit at the positions X_ℓ along the polymer axis, it is expedient to define

$$\gamma_{\mathrm{nucl}} = \mathrm{Im} \ln e^{-i \frac{2\pi}{a} \sum_\ell Z_\ell X_\ell} , \tag{7}$$

where a is the lattice constant. The total polarization is thus

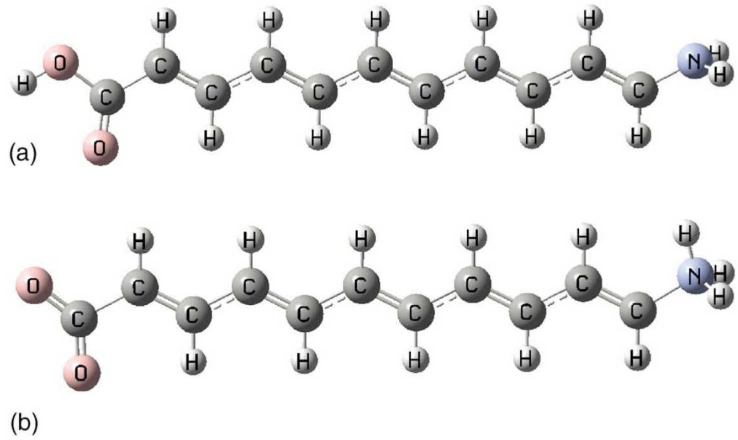

Fig. 1 A centrosymmetric polymer with two different terminations: alternant trans-polyacetylene. Here the "bulk" is five monomers long. After ref. [9].

(8) $$P = -e\frac{\gamma}{2\pi}, \qquad \gamma = \gamma_{\rm el} + \gamma_{\rm nucl}\,.$$

In the presence of inversion symmetry $P = -P$, hence γ is either zero or π (mod 2π): this has clearly a one-to-one mapping to $\mathbb{Z}_2$, the additive group of the integers modulo two. The polarization of a centrosymmetric polymer is in fact topological; arguably, it is the simplest occurrence of a $\mathbb{Z}_2$ topological invariant in condensed-matter physics. Similar arguments lead to the quantization of the soliton charge in polyacetylene, whose topological nature was discovered by Su, Schrieffer, and Heeger back in 1979 [8].

4 Multivalued nature of polarization

Macroscopic polarization **P** is phenomenologically defined by addressing bounded samples of an insulating homogenous material. It is the electrical dipole divided by the sample volume, in the large-sample limit:

(9) $$\mathbf{P} = \frac{\mathbf{d}}{V} = \frac{1}{V}\int d\mathbf{r}\, \mathbf{r}\rho(\mathbf{r})\,.$$

The integral in eq. (9) is clearly dominated by boundary contributions, and does not make any sense for an unbounded sample, where $\rho(\mathbf{r})$ is lattice periodical and extends over all space: this is the reason why the polarization problem remained unsolved until the 1990s, and wrong statements continue to appear even afterwards [4]. According to the modern theory, the bulk value of **P** is a geometric phase of the crystalline orbitals (plus the nuclear contribution). The density $\rho(\mathbf{r})$ obtains instead from the square modulus of the crystalline orbitals: therein, any phase information is obliterated.

In the simple case of a quasi-one-dimensional system the bulk polarization, eq. (8), has a modulo e ambiguity. This may appear a disturbing mathematical artefact; it is instead a key feature of the real world. Band-structure theory addresses unbounded samples, and the modulo ambiguity is fixed only after the sample termination is specified. We are going to show this in detail on the paradigmatic example of polyacetylene, where the modern theory yields $P = 0$ mod e: it is a topological $\mathbb{Z}_2$-even case.

We consider two differently terminated samples of trans-polyacetylene, as shown in fig. 1: notice that in both cases the molecule as a whole is *not* centrosymmetric, although the bulk is. The dipoles of such molecules have been computed for several lengths from the Hartree-Fock ground state, as provided by a standard quantum-chemistry code [9]. The dipoles per monomer are plotted in fig. 2:

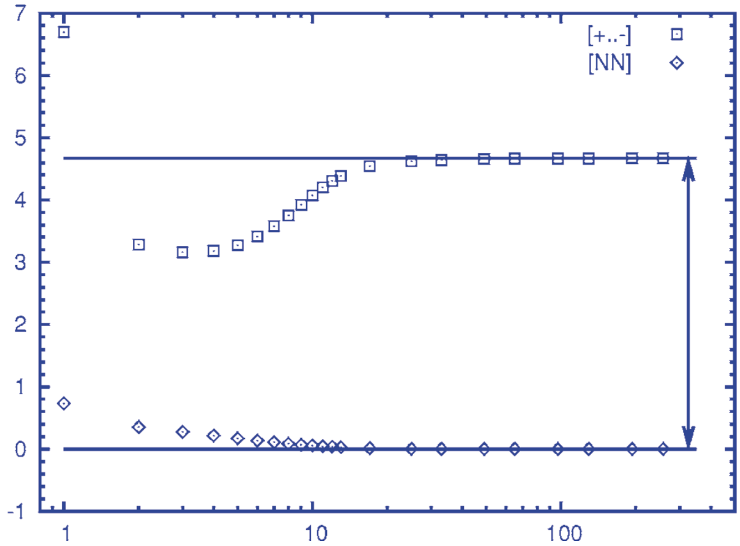

Fig. 2 Quantization of polarization in polyacetylene. Dipole per monomer (a.u.) as a function of the number of monomers in the chain, for the two different terminations. After ref. [9].

for small lengths both dipoles are nonzero, as expected, while in the large-chain limit they clearly converge to a quantized value. Since the lattice constant is $a = 4.67$ a.u., the phenomenological definition of eq. (9) yields $P = 0$ and $P = e$ for the two cases; we have obviously replaced the volume V with the length, *i.e.* the number of monomers times a.

The results in fig. 2 are in perspicuous agreement with the modern theory: in the two bounded realizations of the same quasi-one-dimensional periodic system the dipole per unit length assumes –in the large-system limit– two of the values provided by the theory. Insofar as the system is unbounded the modulo e ambiguity in the P value cannot be removed.

5 Anomalous Hall conductivity

Edwin Hall discovered the eponymous effect in 1879; two years later he discovered the anomalous Hall effect in ferromagnetic metals. The latter is, by definition, the Hall effect in the absence of a macroscopic **B** field. Nonvanishing transverse conductivity requires breaking of time-reversal symmetry: in the normal Hall effect the symmetry is broken by the applied **B** field; in the anomalous one it is spontaneously broken, for instance by the development of ferromagnetic order. The theory of anomalous Hall conductivity in metals has been controversial for many years; since the early 2000s it became clear that, besides extrinsic effects, there is also an intrinsic contribution, which can be expressed as a geometrical property of the occupied Bloch manifold in the pristine crystal. The classical review on the topic is ref. [10].

We indicate with $\sigma^{(-)}_{\alpha\beta}(0)$ the intrinsic contribution only to dc transverse conductivity: its expression is proportional to the Fermi-volume integral of the Berry curvature, *i.e.*

$$\sigma^{(-)}_{\alpha\beta}(0) = -\frac{e^2}{\hbar}\int_{\rm BZ}\frac{d\mathbf{k}}{(2\pi)^d}\,\Omega_{\alpha\beta}(\mathbf{k})\,, \tag{10}$$

where $\Omega_{\alpha\beta}(\mathbf{k})$ is given in eq. (5), and d is the dimension ($d = 2$ or 3). This formula, as well as all of the following ones, is given for single-orbital occupancy.

In 2d the integral is dimensionless, and in the insulating case the Fermi volume coincides with the whole BZ: a compact orientable manifold in mathematical speak. The celebrated Gauss-Bonnet-Chern theorem (1945) guarantees that in this case $\sigma^{(-)}_{xy}(0)$ is proportional to a topological integer, called the first Chern number $C_1 \in \mathbb{Z}$. In detail:

$$C_1 = \frac{1}{2\pi}\int_{\rm BZ} d\mathbf{k}\,\Omega_{xy}(\mathbf{k}), \qquad \sigma^{(-)}_{xy}(0) = -\frac{e^2}{h}C_1\,. \tag{11}$$

Notice that h/e^2 is the natural resistance unit: one klitzing, equal to about $2.6\cdot 10^4$ Ω.

The possible existence of $2d$ insulators with nonzero (and quantized) transverse conductivity was pointed out by Haldane in 1988 (Nobel prize 2016 [11]); actual synthesis of materials which realize the QAHE (quantum anomalous Hall effect) was first achieved in 2013.

Finally, we stress the crucially different role of the impurities in metals and in $2d$ insulators: in the former case −given that longitudinal conductivity is nondivergent− there must necessarily be extrinsic effects, while in the latter case extrinsic effects are ruled out. In insulators the dc longitudinal conductivity is zero, and, as a basic tenet of topology, impurities and disorder have no effect on transverse conductivity insofar as the system remains insulating.

6 Orbital magnetization

In analogy to anomalous Hall conductivity, even spontaneous macroscopic magnetization requires breaking of time-reversal symmetry, for instance by the development of ferromagnetic order. Magnetization is comprised of two terms: a spin and an orbital one, which can be experimentally resolved. As for the former term, in the present context it is trivial, simply proportional to the cell-averaged spin density. The latter term accounts (in common materials) for 5-10% of the total, and is a nontrivial geometrical ground-state property. We address here the orbital term only; the moment per unit volume is (in Gaussian units)

$$\mathbf{M} = \frac{\mathbf{m}}{V} = \frac{1}{2cV}\int \mathrm{d}\mathbf{r}\,\mathbf{r}\times\mathbf{j}(\mathbf{r}) \tag{12}$$

in the large-system limit, where $\mathbf{j}(\mathbf{r})$ is the microscopic orbital current. This expression has the same drawbacks as the analogous eq. (9): it does not make any sense in the framework of band-structure theory. We also observe that, while **P** is defined for insulators only, **M** is a property of both insulators and metals.

Within the modern theory of orbital magnetization [6], completed in 2006, **M** is the Fermi volume integral of a geometrical integrand, closely related to the Berry curvature:

$$M_\gamma = -\frac{ie}{2\hbar c}\varepsilon_{\gamma\alpha\beta}\sum_{\epsilon_{j\mathbf{k}}\le\mu}\int_{\mathrm{BZ}}\frac{\mathrm{d}\mathbf{k}}{(2\pi)^d}\langle\partial_{k_\alpha}u_{j\mathbf{k}}|(\mathcal{H}_\mathbf{k}+\epsilon_{j\mathbf{k}}-2\mu)|\partial_{k_\beta}u_{j\mathbf{k}}\rangle\,, \tag{13}$$

where $\varepsilon_{\gamma\alpha\beta}$ is the antisymmetric tensor. The similarity of the two expressions for **M** and for the anomalous Hall conductivity, eqs. (5) and (10), is evident. In the latter case the integrand is the Berry curvature, whose only entries are the **k**-derivatives of the orbitals; in the former case, the Hamiltonian $\mathcal{H}_\mathbf{k} = \mathrm{e}^{-i\mathbf{k}\cdot\mathbf{r}}\mathcal{H}\mathrm{e}^{i\mathbf{k}\cdot\mathbf{r}}$ and its eigenvalues also enter the formula. Both integrands are gauge-invariant 2-forms.

Given the analogy between their phenomenological expressions, eqs. (9) and (12), one would expect **P** and **M** to be expressed by similar geometrical observables; surprisingly, this is not the case. **P** is a multivalued quantity, obtained as the BZ integral of a gauge-dependent integrand, while **M** is single-valued, and obtains as a Fermi volume (BZ in insulators) integral of a gauge-invariant integrand. The profound reasons for this fundamental difference are commented below.

7 Magneto-optical sum rule

An incorrect belief, widespread in the synchrotron-physics community, holds that orbital magnetization is experimentally accessible via measurements of magnetic circular dichroism. The belief is based on a popular 1992 paper [12], which unfortunately is flawed [13]. The so-called dichroic *f*-sum rule for the integrated spectrum measures indeed a geometrical ground-state property of the solid, but this property *does not coincide* with the orbital magnetization **M**.

The difference in absorption between light with negative and positive helicities is given by twice the imaginary part of the antisymmetric optical conductivity $\sigma^{(-)}_{\alpha\beta}(\omega)$. The dichroic *f*-sum rule reads [14]

$$\text{Im} \int_0^\infty d\omega\sigma^{(-)}_{\alpha\beta}(\omega) = -\frac{i\pi e^2}{\hbar^2} \sum_{\epsilon_{j\mathbf{k}}\leq\mu} \int_{\text{BZ}} \frac{d\mathbf{k}}{(2\pi)^3} \langle \partial_{k_\alpha} u_{j\mathbf{k}} | (\mathcal{H}_\mathbf{k} - \epsilon_{j\mathbf{k}}) | \partial_{k_\beta} u_{j\mathbf{k}} \rangle ; \tag{14}$$

comparison to eq. (13) perspicuously shows the difference between the two geometrical ground-state observables.

8 Chern forms and Chern-Simons forms

We have addressed here four geometrical observables of the electronic ground state; it is clear from the above that they belong to two very different classes. **P** makes sense in insulators only, is multivalued, and is expressed as the **k**-space integral of a gauge-dependent integrand. The other three geometrical observables, instead, make sense in both insulators and metals, are single-valued, and are expressed as **k**-space integrals of gauge-invariant integrands.

The alert reader may also have noticed that the main entry of **P** is a 1-form (the Berry connection), while in all the other cases the main entries are 2-forms (the Berry curvature and related quantities). It is also worth observing that, at the bare-bone level, polarization is essentially a 1*d* phenomenon: it can be defined and understood even for 1*d* electrons. The other observables, instead, require at least dimension-two: in the magnetization case, for instance, one may address 2*d* electrons in the *xy* plane and **M** normal to it.

In order to clearly understand the profound difference between the two classes, in the following we focus only on the electronic polarization of a 1*d* system, eq. (6), and on the anomalous Hall conductivity of a 2*d* insulator, eq. (11). The former is the 1*d* BZ integral of the Berry connection, the latter is the 2*d* BZ integral of the Berry curvature. Expressions like these were well known to mathematicians well before becoming endowed with physical content.

The calculus of differential forms has a long history, related to the names of Poincaré, Cartan, Pontryagin, Weyl, and culminated with the work of Chern (since the 1940s) and Simons (1970s). The key tools are the generalized vector product (wedge product) and the generalized curl (exterior derivative). A basic tenet of differential geometry is that spaces of even and odd dimensions behave quite differently. In dimension 2*n* one may define the *n*-th Chern form, whose integral over a compact orientable manifold is quantized: eq. (11) is just a manifestation of the theorem for $n = 1$. Furthermore, the exterior derivative of a Chern form vanishes; by Poincaré's lemma, this guarantees that the Chern form is (locally) the exterior derivative of a $2n - 1$ form, called a Chern-Simons form. Clearly, in our case the Chern-Simons 1-form is the Berry connection.

In eqs. (3) and (4) we have defined the connection (Chern-Simons 1-form) and the curvature (first Chern form) starting from the scalar products $\langle u_{j\mathbf{k}} | u_{j'\mathbf{k}'} \rangle$. Using the same ingredients, the mathematical literature provides the explicit expression for the Chern-Simons 3-form: like its 1-form analogue, it is gauge-dependent but its BZ integral is gauge-invariant and multivalued. Therefore in a 3*d* crystalline insulator the Chern-Simons 3-form defines a geometrical ground-state property, which can be expressed as an angle θ_{CS}: a kind of "higher order" Berry phase. In presence of some symmetries, θ_{CS} is equal to either zero or π, mod 2π, and becomes therefore a topological $\mathbb{Z}_2$ index, in full analogy with the phase γ in centrosymmetric 1*d* systems.

Last but not least: which physical observable is defined by θ_{CS}? The answer was provided by Qi, Hughes, and Zhang in 2008: θ_{CS} yields one of the terms −called the "axion" term− in the magnetoelectric response of a crystalline insulator [6]. The bulk magnetoelectric response is multivalued, and the ambiguity is fixed only after the sample termination is specified (in analogy, again, with polarization).

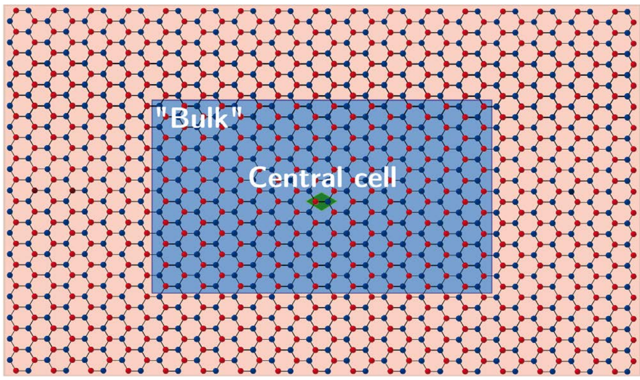

Fig. 3 A bounded flake of "Haldanium": the one shown here has 1806 sites. In the text we consider three cases: the whole flake; the "bulk" region (1/4 of the sites) and the central cell (two sites). After ref. [19].

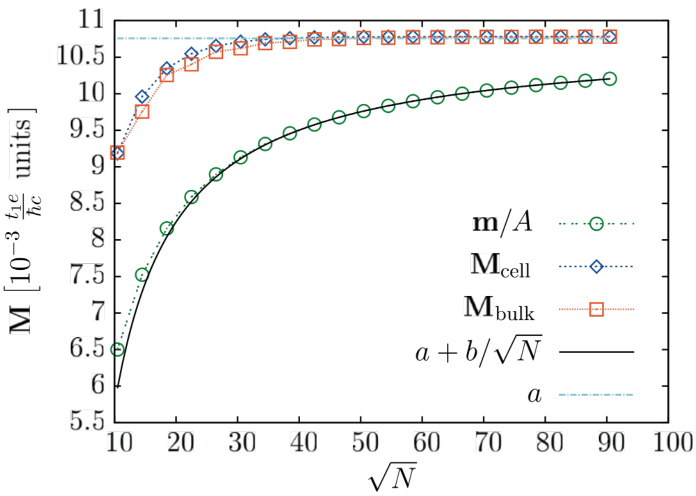

Fig. 4 Green circles: orbital magnetization, evaluated from the textbook expression **m**/*A*, as a function of the flake size, in the insulating case. The plots labeled as $\mathbf{M}_{\text{cell}}$ and $\mathbf{M}_{\text{bulk}}$ demonstrate the locality of orbital magnetization, as explained in the text. The horizontal dashed line is provided by the **k**-space formula. After ref. [16].

9 Local vs. nonlocal observables

Several bulk observables in condensed matter admit a local definition as an intensive property, which may vary over macroscopic lengths: textbook examples are temperature and pressure. In the quantum-mechanical realm, macroscopic spin-magnetization density is a local intensive property, which *e.g.* may assume different values in different homogeneous regions of a heterostructure. We may thus address the issue whether even the above geometrical observables can be defined locally in **r** space and thus admit a "density".

The case of polarization **P** is obvious after the discussion in sect. 4: "polarization density" is an ill-defined concept. Considering the two cases in fig. 1, it is clear that by accessing the central region only of the polymer the **P** value remains undetermined: it crucially depends on the sample termination. On this count, **M** and the other two observables addressed above are profoundly different: in fact their bulk value is singlevalued and *not* multivalued. We focus on **M** for the time being: when we consider a bounded sample, tinkering with its boundaries cannot alter the **M** value: this is in striking contrast with eq. (12), which would indicate a dominant role of boundary currents.

Because of the above, the possibility of defining **M** locally, or equivalently of defining an "orbital magnetization density" in **r** space, is not ruled out. But all the geometrical observables, as presented so far, have been defined as reciprocal space integrals in the framework of band-structure theory, which by definition deals with macroscopically homogenous solids and lacks spatial resolution. In recent years it has been shown that the single-valued geometrical observables can be alternatively formulated locally in **r**-space: **M** is dealt with in refs. [15, 16], and the anomalous Hall conductivity is dealt with in refs. [17, 18]. For the sake of completeness, we quote here that even the quantum metric can be made local [19].

10 Orbital magnetization as a local property

In order to illustrate the main point, we consider bounded samples (flakes) of a computational 2*d* material based on the famous Haldane's model Hamiltonian [6, 11]: it can be regarded as a model for hexagonal boron nitride −a.k.a. gapped graphene− plus "some magnetism" (needed to break time-reversal symmetry). The system is either insulating or metallic according to where the Fermi level μ is set. A typical

"Haldanium" flake is shown in fig. 3; we have addressed flakes of increasing size (at constant aspect ratio), and we have computed **M** via several different formulæ [15, 16].

The results are shown in fig. 4 for the insulating case. The circles are obtained by means of eq. (12) (where the flake area A replaces V): **M** perspicuously converges to a finite asymptotic value, which coincides with the bulk value, shown as the horizontal dashed line. The latter has been computed for the unbounded sample by means of the (discretized) **k**-space integral, eq. (13). We have not proven the locality yet: equation (12) is an **r**-space expression, but it is strongly nonlocal and dominated by boundary contributions. In refs. [15, 16] we arrived at an explicit expression for the orbital-magnetization density $\mathfrak{M}(\mathbf{r})$ (see Box 2). The identity

$$\frac{\mathbf{m}}{A} = \frac{1}{2cA}\int \mathrm{d}\mathbf{r}\; \mathbf{r} \times \mathbf{j}(\mathbf{r}) = \frac{1}{A}\int \mathrm{d}\mathbf{r}\; \mathfrak{M}(\mathbf{r}) \tag{15}$$

holds at any flake size, but the *integrands* therein are quite different. This is similar in spirit to what happens when integrating a function by parts, thus reshuffling the integrand in different space regions.

The virtue of $\mathfrak{M}(\mathbf{r})$ is that it behaves like an honest density, *i.e.* it can be integrated over an inner region of the sample (and divided by the area of that region). Figure 4 shows precisely this: diamonds and squares were obtained from integrating $\mathfrak{M}(\mathbf{r})$ over the central cell (two sites) and over the "bulk" region (1/4 of the sites), respectively, as displayed in fig. 3. The conventional formula, eq. (12), converges like the inverse linear dimension of the flake (in both the insulating and the metallic case) to the asymptotic value in the large-flake limit. Remarkably, our novel approach converges much faster; in the insulating case shown here the convergence is exponential.

Box 2

Orbital magnetization density

We consider here a bounded crystallite, or even −more generally− a bounded sample of disordered and macroscopically homogeneous material; the occupied orbitals $|\varphi_j\rangle$, with eigenvalues ϵ_j, are square-integrable. If μ is the Fermi level, the ground-state projector $\mathcal{P}$ is (for each spin channel)

$$\mathcal{P} = \sum_{\epsilon_j \le \mu} |\varphi_j\rangle\langle\varphi_j|\,;$$

it uniquely determines the many-body wavefunction, hence any ground-state observable (in the independent-electron framework). Equation (12) reads

$$\mathbf{M} = -\frac{e}{2cV}\sum_{\epsilon_j \le \mu}\langle\varphi_j|\mathbf{r}\times\mathbf{v}|\varphi_j\rangle = -\frac{e}{2cV}\int \mathrm{d}\mathbf{r}\langle\mathbf{r}|\mathbf{r}\times\mathbf{v}\mathcal{P}|\mathbf{r}\rangle,$$

where $\mathbf{v} = i\,[\mathcal{H};\mathbf{r}]/\hbar$ is the quantum-mechanical velocity.
All observables −bar the energy itself− are invariant by translation of the energy zero, ergo they are a function of $\mathcal{H}-\mu$; and in fact $\mathcal{P}$ can be formally written as $\mathcal{P} = \theta\,(\mu - \mathcal{H})$, where θ is the step function. The nasty multiplicative operator **r** is unbounded, while instead the commutator $[\mathbf{r}, \mathcal{P}]$ is bounded. The vector field $\mathfrak{M}(\mathbf{r})$, to be interpreted as the orbital magnetization density, may be cast in several equivalent forms [15, 16]. Here we display the ultimate, very elegant, formula:

$$\mathfrak{M}(\mathbf{r}) = -\frac{ie}{2\hbar c}\langle\mathbf{r}||\mathcal{H}-\mu|[\mathbf{r},\mathcal{P}]\times[\mathbf{r},\mathcal{P}]|\mathbf{r}\rangle\,;$$

therein $|\mathcal{H}-\mu| = (\mathcal{H}-\mu)(\mathcal{I}-2\mathcal{P})$, *i.e.* $|\mathcal{H}-\mu|$ acts as $\mathcal{H}-\mu$ on the unoccupied orbitals, and as $\mu-\mathcal{H}$ on the occupied ones.

11 Conclusions

We have addressed some of the known geometrical bulk observables within band-structure theory. All of them are expressed as reciprocal-space integrals of a geometrical integrand, but they can be partitioned in two very different classes. The observables of class (i) only make sense for insulators, and are defined modulo 2π (in dimensionless units), while the observables of class (ii) are defined for both insulators and metals, and are single-valued.

As for class (i), only two observables are known: electrical polarization (in dimension 1, 2, or 3), and the "axion" term in magnetoelectric response (in dimension 3) [6]. Mathematics-wise, the former is rooted in a Chern-Simons 1-form, the latter in the corresponding Chern-Simons 3-form. For both cases the modulo ambiguity of the bulk observable is fixed only after the termination of the insulating sample is specified. Notice that not only the bulk, but also the boundary must be insulating; the latter condition is always verified in a quasi-1*d* system (like the one discussed here), since its boundary is zero-dimensional. In the presence of some protecting symmetry, an observable of class (i) becomes a topological $\mathbb{Z}_2$ index: a $\mathbb{Z}_2$-even crystalline insulator cannot be "continuously deformed" into a $\mathbb{Z}_2$-odd one without closing the gap.

Several observables in class (ii) are known. Here we have addressed the time-reversal odd ones, *i.e.* those which are nonvanishing only in the absence of time-reversal symmetry. They are: intrinsic anomalous Hall conductivity; orbital magnetization; and a popular magneto-optical sum rule. We have shown that, contrary to a widespread belief, magneto-optical measurements cannot access orbital magnetization.

The geometrical observables of class (ii), when evaluated for a bounded sample, do not depend on the sample termination: this key feature owes to the fact that their **k**-space expression is single-valued. Therefore these observables admit a dual representation in **r**-space which is local in nature, *i.e.* they admit a density; the case of orbital magnetization has been discussed in some detail.

Acknowledgments

The author acknowledges very useful discussions with R. Bianco, A. Marrazzo, I. Souza, and D. Vanderbilt, over many years. Work supported by the Office of Naval Research (USA) under grant No. N00014-17-1-2803.

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