Orbital Magnetization in Solids: Boundary contributions as a non-Hermitian effect

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The theory of orbital magnetization is reconsidered by defining additional quantities that incorporate a non-Hermitian effect due to anomalous operators that break the domain of definition of the Hermitian Hamiltonian. As a result, boundary contributions to the observable are rigorously and analytically taken into account. In this framework, we extend the standard velocity operator definition in order to incorporate an anomaly of the position operator that is inherent in band theory, which results in an explicit boundary velocity contribution. Using the extended velocity, we define the electrons’ intrinsic orbital circulation and we argue that this is the main quantity that captures the orbital magnetization phenomenon. As evidence of this assertion, we demonstrate the explicit relation between the nth band electrons’ collective intrinsic circulation and the approximated, evaluated with respect to Wannier states, local and itinerant circulation contributions that are frequently used in the modern theory of orbital magnetization. A quantum mechanical formalism for the orbital magnetization of extended and periodic topological solids (insulators or metals) is re-developed without any Wannier-localization approximation or heuristic extension [Caresoli, Thonhauser, Vanderbilt and Resta, Phys. Rev. B 74, 024408 (2006)]. It is rigorously shown that, as a result of the non-Hermitian effect, an emerging covariant derivative enters the one-band (adiabatically deformed) approximation k-space expression for the orbital magnetization. In the corresponding many-band (unrestricted) k-space formula, the non-Hermitian effect contributes an additional boundary quantity which is expected to give locally (in momentum space) significant contributions whenever band crossings occur along with Hall voltage due to imbalance of electron accumulation at the opposite boundaries of the material.

I. INTRODUCTION

Boundary effects are ubiquitous in condensed matter systems. However, how these effects influence bulk quantities such as the bulk orbital magnetization $M$ seems to be still unclear. Circular dichroism measurements have confirmed the existence of surface states with non-trivial orbital moment textures in k-space due to Orbital Rashba Effect, while gigantic orbital magnetization values are predicted to occur in the vicinity of band crossings at the surfaces of sp alloys. A simple and direct method to link boundary properties with bulk quantities, if found, would conceptually give a direct realization of a bulk-boundary correspondence in a general sense. Hints of such a link have appeared but they have not yet been combined in a single theoretical framework for condensed matter systems. In the chemists’ community the link between boundary effects and “bulk” quantities seems to have been studied in detail and is formalized as surface integrals (fluxes) of certain generalized currents in the so-called atomic theorems that determine atom properties viewed as parts (fragments) of a molecule; for example, the atomic dielectric polarization and atomic magnetic susceptibility have been determined within that method. In the mathematical physics community the connection between boundary effects and bulk quantities can be attributed to anomalous operators that break the domain of definition of the Hamiltonian operator, thereby leaving residues either in the Ehrenfest theorem or in the Hellmann-Feynman theorem; these can be converted into space coordinate surface integrals (for 3D systems) over the system’s boundaries. In this paper we rigorously take into account these boundary residues as non-Hermitian effects in order to model the boundary contributions to the orbital magnetization of non-interacting electrons.

In general, anomalous operators act on states that belong within a given Hilbert space, where the Hamiltonian is assumed Hermitian and the system is closed, and they produce states that are outside this given Hilbert space; this leads to emergent non-Hermiticity in the Hamiltonian which is precisely the above mentioned boundary residue.

One of the most common examples of such an anomalous operator (that leaves a boundary residue in the Ehrenfest theorem) is the position operator whenever periodic boundary conditions at the ends of the system are adopted for the wavefunctions. In Solid State Physics one usually bypasses this kind of anomaly as in Ref. by redefining a proper (periodic) operator for the electrons’ position that does not leave any boundary residue and by working with its expectation value. In this way we deal with this problem in a direct way, that is we maintain the standard electrons’ expectation value as defined within the Schrödinger picture (despite the fact that the electrons’ position expectation value becomes undefined within the Bloch representation in the thermodynamic limit, its displacement $\Delta(r)$ after a finite time interval is always a well-defined quantity as shown in Appendix A) and simply extend the standard velocity operator by adding to it an extra operator term that takes into account the non-Hermitian effect of the Hamiltonian operator. The expectation value of the added operator term is determined entirely from the boundaries of the system and it rigorously gives a boundary velocity contribution for the electron (although formalized in a
Orbital magnetization can be larger than spin magnetization, in materials with topological behaviors, as well as relevant consequences with respect to transport properties that are carried by the system’s boundaries. However, although the boundary velocity expectation value $\langle v_b \rangle$ is well defined and not zero within Bloch representation in the thermodynamic limit, the expectation value of certain observable operators involved in orbital magnetization calculations in the literature, can be undefined, e.g., the position operator expectation value $\langle r \rangle$ and the circulation operator expectation value $\langle r \times v \rangle$. Such subtle behaviors, as well as relevant consequences with respect to the modern theory of orbital magnetization, are presented in Sec.[] and summarized in Table[].

Orbital magnetization is the quantity to be crucially affected by the above non-Hermitian effect and it is this observable that is the focus of our treatment. Before we start, let us note that, although in conventional materials the orbital magnetization is only of the order of a few percent of the total magnetization, in materials with topologically nontrivial band structures the electrons’ collective orbital magnetization can be larger than spin magnetization which has been confirmed in experiments, owing to large orbital magnetization contribution arising from the effective reciprocal space monopoles near the band crossings.

Nowadays, the so-called modern theory of orbital magnetization $M$ has been argued to have come to a mature stage. Three main methods for deriving the bulk orbital magnetization formula in the context of modern theory are currently widespread: a quantum mechanical method with direct calculation of circulating currents for trivial band insulators in the presence of boundaries, a semiclassical wave packet approximation method, and one that takes the derivative of free energy with respect to magnetic fields under periodic boundary conditions. In the first of the above methods two incompatible features had to be overcome in order for the magnetization to be a genuine bulk property, namely adoption of periodic boundary conditions (PBCs) and usage of the circulation operator $r \times v$ in the Bloch representation. This was done with the aid of the Wannier representation which can be rigorously employed in normal insulators with zero Chern number.

Furthermore, it has been argued that bulk behavior of observables in crystalline materials is ensured when computing within PBCs. In spite of this belief, and contrary to what has been stated in the literature, the system by construction has a “terminated” boundary surface (assuming a 3D material), the one on which PBCs are imposed; boundary contributions due to non-Hermitian effects are therefore generally not ruled out, especially whenever observables incorporate anomalous operators, such as the position operator that enters the expressions for the electron’s magnetic and electric dipolar moments.

In the spirit of re-examining the orbital magnetization formula within a quantum mechanical theoretical framework that takes into account boundary effects and at the same time relaxes the Wannier-localization approximation, we were motivated to define a circulation operator that contains the extended velocity operator in the form $1/2 (r \times v_{ext} - v_{ext} \times r)$, in order to analytically determine the orbital magnetization of a system of effectively non-interacting electrons (i.e., in a density functional theoretical framework). Although this circulation operator takes into account boundary contributions as a consequence of the extended velocity operator $v_{ext}$, its expectation value is still problematic in the Bloch representation within PBCs and it becomes undefined for extended systems in the thermodynamic limit (see Appendix A).

In spite of the undefined expectation value of the latter circulation operator in periodic and extended systems, and to our surprise, we found out that it can always be decomposed into two distinct parts, namely, an intrinsic one that has a definite value and an extrinsic one that carries the undefined value. The intrinsic one has an intensive and bulk behavior that properly counts the local and circulating probability micro-currents embodied in the (generally) extended wavefunction’s structure with boundary contributions being explicitly taken into account due to the non-Hermitian effect.

Specifically, the expectation value of the intrinsic orbital circulation is found to have the following properties: (i) it does not depend on the system’s size and has a finite value within PBCs in the Bloch representation in the thermodynamic limit, (ii) it carries information about the electrons’ orbital circulating probability micro-currents which are encoded as structured wavefunction in real space (for free electrons and plane waves it becomes zero), (iii) its value does not depend on the position origin (as long as the shift of the origin can be attributed to a unitary transformation of the wavefunction) and (iv) it takes into account boundary contributions as a consequence of the non-Hermitian effect.

Although we do not use any Wannier states in this work, we nevertheless demonstrate how an explicit relation between the electrons’ $n$th band collective intrinsic circulation (evaluated with respect to Bloch eigenstates)
and a starting point formula of the modern theory of orbital magnetization (namely, the electrons’ collective circulation evaluated with respect to Wannier states) can be established. This is accomplished by using the standard velocity, the newly defined boundary velocity and the intrinsic circulation and by assuming that each Bloch eigenstate satisfies the periodic gauge. In this respect, we expand each Bloch eigenstate into the basis of localized bulk Wannier states and localized surface orbitals, and as a result the n-th band electrons’ collective intrinsic circulation (initially evaluated with respect to Bloch eigenstates) acquires two distinct contributions which are the same as the ones given in Ref. that is, the collective local circulation contribution (LC) plus the collective itinerant circulation contribution (IC), the latter being, in our formulation, explicitly attributed to the new boundary velocity. It is important to re-emphasize that, using the relation between the boundary and the standard velocity, the IC can be recast in a form that can be evaluated as a bulk property.

In this framework we propose that the intrinsic circulation is the proper quantity that encodes the electrons’ intrinsic orbital behavior in periodic (or moderately disordered) and extended systems, without the need of any approximation, and as such it must be employed in a rigorous quantum mechanical theoretical framework for calculating the orbital magnetization.

In the fashion described above, we exploit the intrinsic orbital circulation in order to model the orbital magnetization of non-interacting electrons and as such we use it to derive two quantum mechanical formulas, one as an \( \mathbf{r} \)-space and another one as a “reciprocal” \( \mathbf{k} \)-space formula, both being relaxed from any Wannier-localization approximation.

The \( \mathbf{r} \)-space formula is derived for an extended system within PBCs over the terminated boundaries, giving therefore the bulk orbital magnetization.

In the derivation of the \( \mathbf{k} \)-space expression we relax the PBCs constraint, and as a consequence, certain interesting features emerge. Namely, a covariant derivative appears in the one-band (adiabatically deformed) approximation formula for the orbital magnetization as an emerging operator, and survives due to the non-Hermitian effect that is attributed to the anomalous momentum gradient operator \( \partial_{\mathbf{r}} \) that enters the static (off-diagonal) Hellmann-Feynman theorem that we derive in Appendix. In the many-band (unrestricted) formula the non-Hermitian effect contributes an additional boundary quantity which explicitly depends on the off-diagonal matrix elements of the boundary velocity operator \( \mathbf{v}_b \) as well as on a new boundary momentum gradient operator \( \mathbf{k}_b \) (defined in Eq. ). The latter additional boundary quantity, is expected to give locally (in momentum space) giant orbital magnetization contributions (due to its structure) whenever band crossings occur along with Hall voltage as a consequence of boundary conditions that may generally break the standard Born-von Kármán periodicity.

The theoretical method that we propose can be employed either for calculating the built-in orbital magnetization of solids in the absence of external fields or for calculating the induced orbital magnetization as a response to external fields, e.g. to an electric field. In this work we determine the built-in magnetization in solids when time reversal symmetry is assumed to be broken, either from a staggered magnetic field that averages to zero over the unit cell, or through spin-orbit coupling to a background of ordered local moments.

We have organized the paper as follows. In Sec. we define the electrons’ boundary velocity and then the extended velocity operators, as well as the electrons’ intrinsic and extrinsic orbital circulations with the aid of the extended velocity operator. In Sec. the electrons’ intrinsic circulation we derive two quantum expressions for the bulk orbital magnetization of non-interacting electrons, one as an \( \mathbf{r} \)-space and the other as a “reciprocal” \( \mathbf{k} \)-space formula. We summarize and conclude in Sec. Some details concerning analytical manipulations and derivations are given in three Appendices.

II. DEFINITIONS

A. Extended velocity operator

By taking into account the evolution of the state under consideration, and by demanding that the velocity operator expectation value must always be equal with the rate of change of the electrons’ expectation value \( \frac{d}{dt} \langle \mathbf{r} \rangle \), it is necessary to define the velocity operator in an extended theoretical framework as,

\[
\mathbf{v}_{\text{ext}} = \mathbf{v} + \mathbf{v}_b
\]

(1)

where,

\[
\mathbf{v} = \frac{i}{\hbar} [H(\mathbf{r}, t), \mathbf{r}]
\]

(2)

is the standard velocity operator and

\[
\mathbf{v}_b = \frac{i}{\hbar} \left( H(\mathbf{r}, t)^+ - H(\mathbf{r}, t) \right) \mathbf{r}
\]

(3)

is the boundary velocity operator.

The introduction of this new operator \( \mathbf{v}_b \) is rather naturally motivated by Ref. and its expectation value is not zero only whenever the position operator becomes anomalous due to the non-Hermitian effect, in which case there are paradoxes first noted in Ref.

For closed systems \( \langle \Psi(t) | \Psi(t) \rangle = 1 \), the Hamiltonian is Hermitian \( H(\mathbf{r}, t)^+ = H(\mathbf{r}, t) \) with respect to the states that belong within the domain of its definition and these states form the given Hilbert space. The non-Hermitian effect emerges whenever the state \( \mathbf{r} \Psi(\mathbf{r}, t) \) does not belong within the given Hilbert space, that is...
The boundary velocity operator can also be useful in the study of materials with strong spin-orbit coupling interaction if a modification of its expectation value form is made, that is, by taking into account the spin dependence of the standard velocity operator (as an outcome of the non-relativistic limit of the Dirac equation)

$$\mathbf{v} = \frac{1}{m} \mathbf{\Pi} + \frac{\hbar}{4mc^2} \sigma \times \nabla \mathbf{r}$$

that enters the local probability current density $J_{pr}(\mathbf{r}, t) = \text{Real}[\Psi(\mathbf{r}, t)^* \mathbf{v} \Psi(\mathbf{r}, t)]$ which now must be evaluated with respect to spinors.

With the aid of Eq. (1) – (3), the extended velocity operator can be recast in the form

$$\mathbf{v}_{ext} = \frac{i}{\hbar}(\mathbf{H}(\mathbf{r}, t)^+ \mathbf{r} - \mathbf{rH}(\mathbf{r}, t)),$$

and the equality $⟨\mathbf{v}_{ext}⟩ = \frac{d}{dt}(\mathbf{r})$ holds irrespectively of the position operator behavior (hence irrespective of the boundary conditions). By the definition as given in Eq. (5) and by working in the position representation $\mathbf{r}^+ = \mathbf{r}$, we can easily deduce that the extended velocity operator is always a Hermitian operator $\mathbf{v}_{ext}$ and its expectation value is always real, in agreement with a discussion below.

A simple and intuitive criterion to demonstrate the necessity of introducing the extended velocity operator is as follows: Consider a stationary and extended plane wave state of a free electron of mass $m$ with well defined momentum $\hbar \mathbf{k}$ in a finite volume $V$. The system is assumed to be closed, that is the electrons’ wavefunction is normalized to unity at every instant $t$ within the volume $V$, $\langle \Psi(t) | \Psi(t) \rangle = 1$. In this fashion, the electrons’ displacement $\Delta(\mathbf{r})$ must always be smaller than (or equal to) the systems’ size. Using the standard velocity definition $\mathbf{v} = \frac{i}{\hbar} [\mathbf{H}(\mathbf{r}, t), \mathbf{r}]$ the electrons’ displacement acquires the value $\Delta(\mathbf{r}) = \frac{\hbar \kappa}{m} t$ which will eventually lead the electron out of the system. This paradox is bypassed within the extended velocity operator definition, as it turns out that the boundary velocity contributes an equal magnitude and opposite sign than the bulk electrons’ velocity $\langle \mathbf{v} \rangle$ resulting in zero displacement $\Delta(\mathbf{r}) = 0$ at every instant $t$ for the assumed stationary state. In fact, the extended velocity operator guarantees that every stationary state (irrespective of the static potentials) will always produce zero displacement for the electron, that is $\frac{d}{dt}⟨\mathbf{r}⟩ = ⟨\mathbf{v}_{ext}⟩ = ⟨\mathbf{v}⟩ + ⟨\mathbf{v}_b⟩ = 0$, as expected from the trivial fact that the position operator expectation value is a static quantity with respect to any stationary state.

In this fashion, we can develop a simple and direct method to link boundary effects with bulk properties as a form of a bulk-boundary correspondence in a general sense for every stationary state, namely $⟨\mathbf{v}⟩_n = -⟨\mathbf{v}_b⟩_n$ where $n$ indexes the Hamiltonian eigenstate; this is an
example, therefore, of a bulk formulation that properly takes into account boundary currents that are rigorously related to the bulk band structure.

There are two important features of the extended velocity operator $v_{\text{ext}}$ that can be deduced from its off-diagonal matrix elements with respect to the (generally time-dependent) Hamiltonian instantaneous eigenstates $|n(t)\rangle$. These are derived by direct application of Eq. (9) and Eq. (11) and are given by

$$\langle m(t)|v|n(t)\rangle + \langle m(t)|v_{\text{b}}|n(t)\rangle = \frac{i}{\hbar} (E_{m}(t) - E_{n}(t)) \langle m(t)|r|n(t)\rangle \quad (10)$$

where, the off-diagonal matrix elements of the boundary velocity operator are explicitly calculated (after a straightforward integration by parts) as

$$\langle m(t)|v_{\text{b}}|n(t)\rangle = -\frac{1}{2} \iint_{S} \mathbf{r} \cdot \left( (\psi_{m})_{\dagger} \psi_{n} + (\psi_{n})_{\dagger} \psi_{m} \v v \right) \cdot dS$$

$$+ \frac{i}{2m} \iint_{S} (\psi_{m})_{\dagger} \psi_{n} dS, \quad (11)$$

$\psi_{n} = \psi_{n}(\mathbf{r}, t) = (\mathbf{r}|n(t)\rangle$ are the Hamiltonian’s instantaneous eigenfunctions and $\mathbf{v}$ is the velocity operator given by Eq. (2). Eq. (11) can be viewed as the off-diagonal counterpart of Eq. (5).

The two important features then follow. First, the off-diagonal position matrix elements in Eq. (10) will explicitly be involved in the many-band (unrestricted) formula of the orbital magnetization that we will derive in this article; therefore, boundary contributions due to the off-diagonal boundary velocity matrix elements will explicitly be taken into account. Second, the off-diagonal position matrix elements in Eq. (10) are proportional to the electrons’ transition dipole moment, therefore the emission and absorption of photons can be rigorously related with boundary properties owing to the off-diagonal boundary velocity matrix elements.

Generalizing the results of this subsection we point out that, whenever one defines an operator in an extended way $O_{\text{ext}}$ so that its expectation value $\langle O_{\text{ext}} \rangle$ is equal with the rate of change of the expectation value of a given Hermitian operator $\mathbf{G}$, that is $\langle O_{\text{ext}} \rangle = \frac{d}{dt} \langle \mathbf{G} \rangle$, the definition of $O_{\text{ext}}$ can be consistently given by the Ehrenfest theorem, as long as a corresponding boundary operator $O_{b}$ is taken into account. The expectation value of the boundary operator $\langle O_{b} \rangle$ is extremely sensitive to the boundary conditions of the wavefunction and takes a nonzero value only whenever the given Hermitian operator $\mathbf{G}$ (entering the theorem) becomes anomalous due to the non-Hermitian effect. Specifically, by working in position representation, due to symmetry of the integrand, after a straightforward integration by parts, the expectation value $\langle O_{b} \rangle$ is always cast in the form of a boundary integral (assuming real scalar and vector potentials) of a generalized current $\mathbf{J}_{\text{G}}$ flux as

$$\langle O_{b} \rangle = \frac{i}{\hbar} \langle \Psi(t) | (H(\mathbf{r}, t) + H(\mathbf{r}, t)) \mathbf{G} | \Psi(t) \rangle$$

$$= \iint_{S} \mathbf{J}_{\text{G}} dS \quad (12)$$

where the generalized current density $\mathbf{J}_{\text{G}}$ is given by

$$\mathbf{J}_{\text{G}} = -\frac{1}{2} \mathbf{n} \cdot (\mathbf{v}\psi(\mathbf{r}, t))^{\dagger} + (\mathbf{v}(\mathbf{r}, t))^{\dagger} \psi(\mathbf{r}, t) \mathbf{G} \psi(\mathbf{r}, t). \quad (13)$$

The wavefunction $\psi(\mathbf{r}, t)$ entering Eq. (13) can be either the electrons’ two component spinor wavefunction for spinfull electron (and this will be nontrivially useful in solids with strong spin-orbit interaction) or the scalar wavefunction for spinless electron motion (where the generalized current has the same structure but with the dagger operation $\dagger$ being replaced by the complex conjugation * operation only) and $\mathbf{n}$ is the unit vector locally normal to the surface $S$. For the special case of $\mathbf{G} = \mathbf{r}$ and either spinfull or spinless electron motion, by analytically calculating the directional velocity operator $\mathbf{n} \cdot \mathbf{v}$ action on $\mathbf{G} \psi(\mathbf{r}, t)$ within Eq. (13) and Eq. (12), we recover Eq. (5). Alternatively, if we choose $\mathbf{G}$ to be the identity operator $I$, then $\mathbf{J}_{\text{G}}$ becomes the usual probability current $\mathbf{J}_{\text{p}}$ and for a closed system Eq. (12) becomes zero, which is consistent with the conservation of total probability (valid for states belonging within the Hilbert space of closed systems).

**B. Intrinsic and extrinsic orbital circulation**

In order to define the electrons’ intrinsic and extrinsic orbital circulation for an extended and periodic system, we first choose to define a Hermitian circulation operator as

$$\mathbf{C} = \frac{1}{2} (\mathbf{r} \times \mathbf{v}_{\text{ext}} - \mathbf{v}_{\text{ext}} \times \mathbf{r}) \quad (14)$$

namely the electrons’ orbital circulation operator that employs the extended velocity operator; it is therefore designed to take into account the inherited anomaly of the position operator when computing circulating currents in periodic systems. The circulation operator always behaves as a Hermitian operator $\mathbf{C}^{\text{+}} = \mathbf{C}$ irrespectively of the wavefunctions’ boundary conditions as evidenced from Eq. (14) and Eq. (11). With the aid of Eq. (11) and $\mathbf{r} \times \mathbf{r} = 0$, the circulation operator can be recast in the forms $\mathbf{C} = \frac{i}{2\hbar} \mathbf{r} \times (H(\mathbf{r}, t)^{\dagger} + H(\mathbf{r}, t)) \mathbf{r}$ and $\mathbf{C} = \mathbf{r} \times \mathbf{v} + \frac{1}{2} \mathbf{r} \times \mathbf{v}_{b}$. It is interesting to note that in the latter form of $\mathbf{C}$ the $\frac{1}{2} \mathbf{r} \times \mathbf{v}_{b}$ term is an anti-Hermitian operator that has imaginary expectation value which exactly cancels any remnant imaginary part of the $\mathbf{r} \times \mathbf{v}$ term expectation value. Direct calculation gives the
orbital circulation operator $C$ expectation value form, which is found to be
\[
\langle \Psi(t) | C | \Psi(t) \rangle = \text{Im} \left[ i \langle \Psi(t) | (\mathbf{r} \times \mathbf{v}) | \Psi(t) \rangle \right] = \iiint_V \mathbf{r} \times \mathbf{J}_{pr}(\mathbf{r}, t) d\mathbf{V} \quad (15)
\]
where the quantum state under consideration $|\Psi(t)\rangle$ is normalized within the volume $V$ of the system. In spite of the cautious definition of the circulation operator in order to take into account the possible anomaly of the position operator for periodic systems, it is shown in Appendix A that its expectation value $\langle C \rangle$ with respect to a Bloch eigenstate does not quite lead to any theoretical progress as it becomes undefined for an extended system in the thermodynamic limit.

Motivated, however, by classical mechanics, either by rigid body dynamics or by continuous medium (hydrodynamical) theories, we find out that the expectation value of the circulation operator $\langle C \rangle$ can always be decomposed into two distinct parts. Namely, an intrinsic circulation part $\langle C_{\text{intr}} \rangle$ that always has an intensive and bulk behavior (with well defined value within Bloch representation in the thermodynamic limit) and an extrinsic circulation part $\langle C_{\text{extr}} \rangle$ that has an extensive and position origin-dependent behavior (with undefined value within Bloch representation in the thermodynamic limit). The definitions of the intrinsic and extrinsic circulations are given by
\[
\langle \Psi(t) | C_{\text{intr}} | \Psi(t) \rangle = \text{Im} \left[ i \langle \Psi(t) | (\mathbf{r} - \langle \mathbf{r} \rangle) \times \mathbf{v} | \Psi(t) \rangle \right] = \iiint_V (\mathbf{r} - \langle \mathbf{r} \rangle) \times \mathbf{J}_{pr}(\mathbf{r}, t) d\mathbf{V} \quad (16)
\]
and
\[
\langle \Psi(t) | C_{\text{extr}} | \Psi(t) \rangle = \text{Im} \left[ i \langle \Psi(t) | \langle \mathbf{r} \rangle \times \mathbf{v} | \Psi(t) \rangle \right] = \iiint_V \langle \mathbf{r} \rangle \times \mathbf{J}_{pr}(\mathbf{r}, t) d\mathbf{V} \quad (17)
\]
respectively, where $V$ is the volume of the system and $\langle \mathbf{r} \rangle = \iiint_V \mathbf{r} |\Psi(\mathbf{r}, t)\rangle^2 d\mathbf{V}$ is the position operator expectation value that takes an undefined value within Bloch representation in the thermodynamic limit (as shown in Appendix A).

The intrinsic circulation $\langle C_{\text{intr}} \rangle$ has no ambiguity and is a position origin-independent quantity whenever the shift of the position origin causes a $U(1)$ transformation for the scalar wavefunction (assuming a spinless electron). The origin-independence is a consequence of the combined transformation (under a shift of the position origin) of the operator $(\mathbf{r} - \langle \mathbf{r} \rangle) \times \mathbf{v}$ and the $U(1)$ transformation of the wavefunction that compensates each other. For spinfull electrons the velocity operator acquires spin-dependence and, as long as the shift of the position origin can be described by an $SU(2)$ transformation of the spinor wavefunction, the intrinsic circulation remains a position origin-independent quantity without any ambiguity.

The electrons’ intrinsic orbital circulation as given by Eq. (16) has an inherited boundary contribution which is revealed when taking into account Eqs. (11) and (13) – 8. In the special case of a stationary state $|\Psi_n(t)\rangle$ the electrons’ intrinsic orbital circulation has the explicit boundary dependence given in
\[
\langle \Psi_n(t) | C_{\text{intr}} | \Psi_n(t) \rangle = \iiint_V \mathbf{r} \times \mathbf{J}_{pr(n)}(\mathbf{r}) d\mathbf{V} - \langle r \rangle_n \times \iiint_S r (\mathbf{J}_{pr(n)}(\mathbf{r}), d\mathbf{S}), \quad (18)
\]
Assuming an extended Bloch eigenstate $\Psi_n(\mathbf{r}, t, \mathbf{k})$ that obeys PBCs over the boundaries of the system (and is normalized within its volume $V$), and in spite of the position operator (undefined) expectation value $(\mathbf{r})$ that explicitly enters Eq. (10), we find after a straightforward calculation shown in Appendix A that the electrons’ intrinsic orbital circulation takes a well-defined value at the infinite volume limit $V \to \infty$, given by
\[
\langle \Psi_n(t, \mathbf{k}) | C_{\text{intr}} | \Psi_n(t, \mathbf{k}) \rangle = \iiint_{V_{\text{cell}}} (\mathbf{r} - \langle u_n(\mathbf{k}) | u_n(\mathbf{k}) \rangle_{\text{cell}}) \times \mathbf{J}_{pr(n)}(\mathbf{r}, \mathbf{k}) d\mathbf{V} \quad (19)
\]
with $u_n(\mathbf{r}, \mathbf{k})$ the cell periodic eigenstates, where all space integrals have been truncated (due to symmetry of the integrands) and evaluated within a unit cell of volume $V_{\text{cell}}$, the local probability current density being determined with respect to a Bloch eigenstate. It is evident from Eq. (19) that the intrinsic circulation is a bulk and intensive quantity of a periodic and extended system. On the contrary, the extrinsic circulation as given from Eq. (17), takes an undefined value for a periodic and extended system (owing to the position operator expectation value); it is therefore not a proper quantity to model any bulk or boundary property of such a periodic and extended system. We note that, in deriving Eq. (19) we have assumed the normalization convention $\langle \Psi_n(\mathbf{k}) | \Psi_n(\mathbf{k}) \rangle = < u_n(\mathbf{k}) | u_n(\mathbf{k}) >_{\text{cell}} = 1$, that is we have assumed a Bloch state in the form $|\Psi_n(\mathbf{k})\rangle = \frac{1}{\sqrt{N}} e^{i \mathbf{k} \cdot \mathbf{r}} | u_n(\mathbf{k}) \rangle$, where $N$ is the total number of the unit cells enclosed within the volume $V$ of the system.

Summarizing, and with Eq. (10) as well as Eq. (19) in mind, we can conclude that the quantity $(\mathbf{r} - \langle \mathbf{r} \rangle) \times \mathbf{J}_{pr}(\mathbf{r}, t)$ is a well defined local intrinsic circulation density, even if it is computed with respect to an extended Bloch state in the thermodynamic limit where the electrons’ position expectation value acquires an undefined value.

1. **Physical meaning of the intrinsic orbital circulation**

A physically and intuitively important feature of the intrinsic orbital circulation is that it is a quantity
that properly counts the circulating probability micro-currents embodied in the wavefunction’s structure. In order to clarify this feature in a simple manner let us consider two spinless and free electron motions in 3D space: one electron with well defined linear momentum vector $\hbar \mathbf{k}$ and another one with partially well defined linear momentum vector, e.g., only its $z$ component $\hbar k_z \mathbf{e}_z$ (with $k_x$ and $k_y$ being undetermined). We assume that each electron is in an extended state motion that is normalized within a volume $V$. The free electron motion with well defined linear momentum vector $\hbar \mathbf{k}$, hence with a plane wave form for the wavefunction, has a local probability current density that is a homogeneous vectorial quantity proportional to $\hbar \mathbf{k}/m$. On the contrary, the free electron motion with partially well defined linear momentum $\hbar k_z \mathbf{e}_z$ has a local probability current density that is an inhomogeneous vectorial quantity with a constant $z$ component proportional to $\hbar k_z/m$. Using Eq. (16), we can easily find that the intrinsic orbital circulation of the free electron motion with well defined linear momentum $\hbar \mathbf{k}$ is zero (due to the homogeneous local probability current density), while the intrinsic orbital circulation of the free electron with partially well defined linear momentum $\hbar k_z \mathbf{e}_z$ is non-vanishing (due to the inhomogeneous local probability current density) and takes contributions only from the $x$ and $y$ non-constant components of the local probability current density that may constitute a vortex circulating probability micro-current field on the planes normal to $\mathbf{e}_z$ (with free electron vortex state being an example, see below).

Considering such a structured wavefunction, its phase is indeterminate on the dislocation lines (in 3D space) where the modulus of the wavefunction becomes zero. The intrinsic orbital circulation of the electron as given by Eq. (16) becomes zero, namely, 

$$
\iint_V \mathbf{r} \times \mathbf{J}_{pr}(\mathbf{r}, t) dV - \langle \mathbf{r} \rangle \times \iint_V \mathbf{J}_{pr}(\mathbf{r}, t) dV = 0
$$

whenever, in the simplest scenario, the local probability current density is zero (the gradient of the wavefunction’s phase is zero) or whenever the local probability current density is a homogeneous quantity (the gradient of the wavefunction’s phase has a constant and well-defined value), therefore the wavefunction is structureless. On the contrary, in structured wavefunctions the electrons’ intrinsic orbital circulation is generally not zero and has two competing contributions as given in Eq. (16), which are explicitly dependent on the local probability current density field. The bigger the difference of these two competing contributions the bigger the electrons’ intrinsic orbital circulation, which occurs for example whenever the internal structure of the wavefunction has such a symmetry that makes some of the components of 

$$
\iint_V \mathbf{J}_{pr}(\mathbf{r}, t) dV
$$

become zero. The latter symmetry feature is found in the free electron motion that are described by vortex states\textsuperscript{22,33} where the electron has well defined linear momentum $\hbar k_z \mathbf{e}_z$ only in the $z$ direction and at the same time has a well defined canonical orbital angular momentum along the same direction (characterized by the azimuthal index $l$). Due to the rotational (azimuthal) symmetry of the wavefunction, the azimuthal component of 

$$
\iint_V \mathbf{J}_{pr}(\mathbf{r}, t) dV
$$

becomes zero.

Structured wavefunctions appear naturally in motions under external potentials, e.g. in atomic orbitals with nonzero mechanical angular momentum or in Landau states in a magnetic field. In this respect, we generally expect that the ionic environment will in principle produce structured and extended cell periodic electronic wavefunctions $u_n(\mathbf{r}, \mathbf{k})$, with the dislocation lines being periodically ordered in the bulk owing to the periodicity of $u_n(\mathbf{r}, \mathbf{k})$, while spiraling probability micro-currents around those lines can be taken into account by Eq. (16) and Eq. (19). Intrinsic orbital circulation is the starting point quantity for the microscopic understanding of the orbital magnetization origin and as such will be used in the following to model the orbital magnetization in band theory without the need of any Wannier-localization approximation.

2. Physical meaning of the extrinsic orbital circulation

The extrinsic orbital circulation $\langle C_{extr} \rangle = \text{Im} \{ i \langle \mathbf{r} \times \langle \mathbf{v} \rangle \rangle \}$ is an extensive quantity that counts the circulation of the global probability current $\langle \mathbf{v} \rangle$ with respect to a specific position origin. It does not carry any tractable information about the structure of the wavefunction or the circulating probability micro-currents (due to being a position origin dependent quantity), and has an undefined value within Bloch representation in the thermodynamic limit (owing to the position operator expectation value being undefined).

C. Subtle behaviors and relevant consequences within Bloch representation

The scope of this subsection is ultimately to facilitate a comparison of our results (derived in later sections) with the literature, and more specifically (i) to point out the behavior of operators (with respect to their expectation values and position origin dependence) that are commonly used in the modern theory of orbital magnetization, and (ii) to show some subtle consequences that emerge due to implicit Hermiticity assumptions that were silently made during calculations in recent theoretical works\textsuperscript{2,3,30}.

The expectation value of the position operator with respect to a Bloch eigenstate $\langle \psi_n(\mathbf{k}) | \mathbf{r} | \psi_m(\mathbf{k}) \rangle$ turns out to be an undefined value in the thermodynamic limit, as shown by Eq. (A5) derived in Appendix A. On the other hand, the corresponding off-diagonal matrix elements $\langle \psi_n(\mathbf{k}) | \mathbf{r} | \psi_m(\mathbf{k}) \rangle$ given by Eq. (A6) (also derived in Appendix A) remain well defined quantities.
In this respect we also note that the matrix elements of the operator $(r - \langle \psi_n(k)|r|\psi_n(k)\rangle)$, evaluated with respect to any Bloch state, have a well defined value in the thermodynamic limit. This can be shown by taking the expectation value with respect to $|\psi_n(k)\rangle$, that is, $\langle \psi_n(k)|r|\psi_n(k)\rangle - \langle \psi_n(k)|r|\psi_n(k)\rangle$, which by using the 3D analogue of Eq. (A14), shows that the undefined terms cancel each other and, as a result, the expectation has a well defined value. The same pattern, that is, the undefined terms canceling each other, is what makes the intrinsic circulation $\text{Im}[i \langle \psi_n(k)|r|\psi_n(k)\rangle] \times v |\psi_n(k)\rangle$ have a well defined value in the thermodynamic limit. On the other hand, the real part of the circulation operator expectation value $\text{Im}[i \langle \psi_n(k)|r|\psi_n(k)\rangle]$, is an undefined quantity as shown by Eq. (A12). For what follows it is worth pointing out that, in all the above mentioned calculations, no constraint is assumed with respect to the boundary velocity expectation value.

By then using the Bloch form of the considered state as well as $v = \frac{i}{\hbar}[H(r), r]$ and $r \times r = 0$, the circulation operator takes the form $\frac{1}{\hbar} \text{Im} \left[ \langle u_m(k)|r \times H_b(r, k) r|u_n(k)\rangle \right]$ where $H_b(r, k) = e^{-ikr}H(r)e^{ikr}$. Assuming then that the state $r|u_n(k)\rangle$ can be expanded in the complete orthonormal basis of the cell periodic eigenstates $|u_m(k)\rangle$, that is, using the closure relation $I = \sum_m \langle u_m(k)|u_m(k)\rangle$ and acting from the left on the above state $r|u_n(k)\rangle$, the circulation operator becomes

$$\frac{1}{\hbar} \sum_m \text{Im} \left[ \langle u_n(k)|rH_b(r, k)u_m(k)\rangle \times \langle u_m(k)|r|u_n(k)\rangle \right]$$

which has far reaching consequences. Firstly, the latter operator is now transformed into a well defined quantity due to taking the form $-\frac{1}{\hbar} \sum_m \text{Im} \left[ \langle u_n(k)|r|u_m(k)\rangle E_m(k) \times \langle u_m(k)|r|u_n(k)\rangle \right]$, where we have used $\langle u_n(k)|r|u_m(k)\rangle \times \langle u_m(k)|r|u_n(k)\rangle = 0$. This is the basic idea behind the theoretical work made in Refs 2, 3, and 30 which, however, was performed in a slightly different way. Specifically, these works used a spectral resolution of the Hamiltonian $H(r) = IH(r)I$, where the closure is given by $I = \sum_n \langle \phi_m|\phi_m\rangle$ and $|\phi_m\rangle$ are the orbitals.

As a result of this spectral resolution, the (undefined) diagonal matrix elements of the position operator are excluded from their circulation operator formula.

The subtle consequence of the above two calculations, is that one unintentionally assumes that the state $r|\phi_n\rangle$ belongs within the domain of $H(r)$, that is, certain boundary conditions for $\phi_n(r)$ are assumed which guarantee that the wavefunction $r\phi_n(r)$ also belongs within the domain of definition of the Hamiltonian, and as a result the non-Hermitian boundary velocity Eq. (4) becomes zero. Specifically, the identification $r|\phi_n\rangle = \sum_m C_m|\phi_m\rangle$ is the one that enforces the state $r|\phi_n\rangle$ to belong within the domain of the Hamiltonian and the boundary velocity expectation value to become zero. This is evident when one (i) takes the inner product of $r|\phi_n\rangle$ with $\frac{i}{\hbar}\langle \phi_m|H(r)^+ - H(r)\rangle$, (ii) uses Eq. (4) for the definition of the boundary velocity operator $v_b$, and (iii) exploits the fact that the states $|\phi_n\rangle$ belong within the domain of definition of $H(r)$ which finally gives

$$\langle \phi_n|v_b|\phi_n\rangle = \frac{i}{\hbar}\langle \phi_m|H(r)^+ - H(r)\rangle r|\phi_n\rangle$$

$$= \frac{i}{\hbar} \sum_m C_m \langle \phi_n|(H(r)^+ - H(r))|\phi_m\rangle = 0.$$

In this framework, the method of calculation used by

| Operator | Matrix element | Value | Origin | Boundary velocity is |
|----------|----------------|-------|--------|---------------------|
| r | $\langle \psi_n|r|\psi_n\rangle$ | undefined | dependent | well defined |
| r | $\langle \psi_n|r|\psi_m\rangle$ if $n \neq m$ | well defined | independent | well defined |
| $r \times v$ | $\langle \psi_n|r \times v|\psi_n\rangle$ | undefined | dependent | well defined |
| $\frac{i}{\hbar} r \times H_b \sum_m |u_m\rangle \langle u_m|r$ | $\langle \psi_n|r \times v|\psi_n\rangle$ | well defined | independent | zero |
| $r - \langle \psi_n|r|\psi_n\rangle$ | $\langle \psi_m| (r - \langle \psi_n|r|\psi_n\rangle)|\psi_m\rangle$ | well defined | independent | well defined |
| $(r - \langle \psi_n|r|\psi_n\rangle) \times v$ | $\langle \psi_m| (r - \langle \psi_n|r|\psi_n\rangle) \times v|\psi_n\rangle$ | well defined | independent | well defined |
| $\langle \psi_n|r|\psi_n\rangle \times v$ | $\langle \psi_m| (r - \langle \psi_n|r|\psi_n\rangle \times v|\psi_n\rangle$ | undefined | dependent | well defined |
Ref 2, 3 and 30 enforced on one hand the circulation operator to have a well defined value, but, on the other hand, unwillingly, they induced Hermiticity which sweeps away boundary contributions to the orbital magnetization; in this respect, the conclusion about the irrelevance of the boundary on the orbital magnetization of metals that was made by Ref 2, although reasonable, is rather unjustified. We also point out that, due to the above mentioned spectral resolution of the Hamiltonian (performed within the circulation operator) the orbitals $|\phi_n\rangle$ that were assumed in Refs 2, 3 and 30 must have zero standard (bulk) velocity expectation value $\langle \phi_n | v | \phi_n \rangle = 0$ owing to the relation $\langle \phi_n | v | \phi_n \rangle = - \langle \phi_n | v_b | \phi_n \rangle$ that holds for any stationary eigenstate of the Hamiltonian.

To demonstrate at a glance the various subtleties hidden in the literature, in Table I we summarize the behaviors of certain operators that are related to the modern theory of orbital magnetization: we summarize their values, their position origin dependence, as well as relevant boundary constraints. The presented values are results of calculations performed with respect to Bloch eigenstates in the thermodynamic limit.

### D. Decomposition of the intrinsic orbital circulation into local (LC) and itinerant circulation (IC) contributions

At this point it is useful to make a connection between the one electron’s intrinsic circulation as given by Eq. (16) and the decomposition of the nth band collective electrons’ circulation that was made in a rather ambiguous way, namely, to local circulation (LC) and itinerant circulation (IC) in the seminal work of Ref 22 in order to model the orbital magnetization of normal insulators within a quantum mechanical method. Therein, they started from the assumption that each electron’s eigenstate can be represented by an exponentially localized Wannier function (thus the Bloch states that they used satisfy the periodic gauge $|\Psi_n(k+G)\rangle = |\Psi_n(k)\rangle$ and have zero Chern invariant) and they began their calculation with a collective circulation computed with respect to these Wannier functions, turning at the end of their calculation to the Bloch eigenstates. In the present work we follow an opposite route, that is we start our calculation from the one electron’s intrinsic circulation Eq. (16) without any gauge assumptions (restrictions) with respect to the Bloch eigenstates, and using those states as building blocks in the many-body Slater determinant wavefunction we determine analytically the electrons’ (ground state) collective orbital magnetization. By then taking into account the above mentioned relation between the standard and the boundary velocity for stationary states $\langle v \rangle_n = - \langle v_b \rangle_n$, the electrons’ intrinsic circulation with respect to a Bloch eigenstate $\Psi_n(r,t,k)$ is given by

\[
\langle \Psi_n(k) | C_{intr} | \Psi_n(k) \rangle = \text{Im} \left[ i \langle \Psi_n(k) | r \times v | \Psi_n(k) \rangle \right] + \text{Im} \left[ i \langle r \rangle_n \times \langle \Psi_n(k) | v_b | \Psi_n(k) \rangle \right].
\]  

(20)

In order to establish the connection with Ref 22 method we assume that the Bloch eigenstates $\Psi_n(r,t,k)$ entering Eq. (20) satisfy the periodic gauge and we expand it as

\[
\langle \Psi_n(k) | v_b | \Psi_n(k) \rangle = \frac{1}{\sqrt{N}} \sum_{R} e^{i k \cdot R} |n,R\rangle
\]  

\[
= \frac{1}{\sqrt{N}} \sum_{R_j} e^{i k \cdot R_j} |n,R_j\rangle + \frac{1}{\sqrt{N}} \sum_{R_s} e^{i k \cdot R_s} |n,R_s\rangle
\]  

(21)

where $N$ is the number of primitive cells of the system, $|n,R_i\rangle$ is the nth band Wannier function in the bulk cell $R$ and $|n,R_s\rangle$ is the nth surface localized orbital on the surface cell $R_s$. By then taking into account that the expectation value of the boundary velocity $\langle \Psi_n(k) | v_b | \Psi_n(k) \rangle$ is determined by a boundary integral, that is, only the boundary localized orbitals $|n,R_s\rangle$ enter into the expansion of the expectation value

\[
\langle \Psi_n(k) | v_b | \Psi_n(k) \rangle = \frac{1}{N} \sum_{R_j} \sum_{R_s} e^{i k \cdot (R_s-R_j')} \langle n,R_s' | v_b | n,R_s \rangle,
\]  

(22)

we calculate the nth band collective electrons’ intrinsic circulation given by

\[
C_{(coll)} = \frac{V}{(2\pi)^3} \int_{BZ} \langle \Psi_n(k) | C_{intr} | \Psi_n(k) \rangle d^3k,
\]

which takes the form

\[
C_{(coll)} = \sum_{R} \langle n,R | r \times v | n,R \rangle
\]  

\[
+ \sum_{R_j} \sum_{R_s} \sum_{R_s'} \delta_{R_j'-R_s} \delta_{R_j+R_s-R_s'} \langle n,R_j' | r | n,R_j \rangle
\]  

\[
\times \langle n,R_s' | v_b | n,R_s \rangle.
\]  

(23)

Assuming then that the crystal has inversion symmetry in the bulk $\langle n,-R_j | r | n,-R_j \rangle = \langle n,R_j | r | n,R_j \rangle$, that is $\sum_{R_j} \langle n,R_j | r | n,R_j \rangle = 0$, as well as that for $R_s' \neq R_s$ the matrix elements $\langle n,R+R_s-R_s' | r | n,R_s \rangle$ can be taken as zero, the nth band electrons’ collective intrinsic circulation takes the approximate form

\[
C_{(coll)} = \sum_{R} \langle n,R | r \times v | n,R \rangle
\]  

\[
+ \sum_{R_s} \langle n,R_s | r | n,R_s \rangle \times \langle n,R_s | v_b | n,R_s \rangle
\]  

(24)

where the first term on the right hand side of Eq. (24) gives the electrons’ nth band collective local circulation.
contribution (LC) and the second term the collective itinerant circulation contribution (IC), as given respectively in Ref.\textsuperscript{22}.

In Ref.\textsuperscript{22} and \textsuperscript{23} they notice that the itinerant circulation (IC) contribution that involves only the surface WFs can always be calculated as a bulk quantity that involves the bulk WFs, and they emphasize that this is quite remarkable and one of their central results. Their finding is explained whenever in the starting Eq. (20) we use the bulk expression Eq. (11) for the boundary velocity expectation value and at the same time replace \( \langle H(r)\Psi_n(k) | r\Psi_n(k) \rangle \) with its equal \( \langle \Psi_n(k) | r H(r)\Psi_n(k) \rangle \), which is true for all stationary states according to Eq. (9) (and the vanishing of its expectation value). Therefore, with the aid of the extended velocity operator and the intrinsic circulation definitions, we can elucidate and rigorously explain the origin of the heuristic partitioning of the orbital magnetization that was made in Ref.\textsuperscript{22} and \textsuperscript{23}.

### III. ORBITAL MAGNETIZATION QUANTUM FORMULAS

In this section we use the electrons' intrinsic orbital circulation presented in Sec. II in order to derive quantum mechanical formulas for the orbital magnetization of non-interacting electrons by accounting for the circulating probability micro-currents. The formulas that we derive are applicable either to conventional or to topological crystalline materials, under periodic or realistic boundary conditions for the electrons' wavefunctions, while any localization assumptions are absent.

In a system of non-interacting electrons we can define the (single-eigenstate) orbital magnetization \( M_n(k) \) per electron as

\[
M_n(k) = \frac{m_n(k)}{V} = \frac{e}{2eV} \langle \Psi_n(t,k) | C_{\text{inter}} | \Psi_n(t,k) \rangle
\]

(25)

where \( m_n(k) \) is the electrons' orbital magnetic moment, \( \Psi_n(r,t,k) \) is a Bloch eigenstate, \( V \) is the volume of the system, \( c \) is the speed of light and \( e < 0 \) is the electron charge.

#### A. r-space orbital magnetization quantum formula

In the derivation of the r-space formula we do not take into account the realistic boundary contributions to the orbital magnetization due to the realistic wavefunctions' boundary conditions; rather we provide a formula that has a bulk character. Namely, we calculate the orbital magnetization within PBCs which are imposed on the wavefunction over a “terminated” boundary surface of the (3D) material in the thermodynamic limit.

Using Eq. (19) for the electrons' intrinsic orbital circulation and Eq. (25) for the orbital magnetization per electron, as well as the collective electrons' ground state magnetization (assumed to be evaluated with respect to a many-body Slater determinant wavefunction) given by

\[
M = \frac{1}{(2\pi)^3} \int_{E_\mu \leq \mu} \iint_{BZ} f_n(k,\mu) m_n(k) \, d^3k,
\]

where \( \mu \) is the Fermi energy and \( f_n(k,\mu) \) is the occupation function, the bulk orbital magnetization of spinless and non-interacting electrons is given by

\[
M = \frac{e}{2e(2\pi)^3} \sum_{E_n \leq \mu} \iint_{BZ} f_n(k,\mu) \, \left( \iint_{V_{cell}} (r - (u_n(k)|r|u_n(k))_{cell}) \times J_{pr(n)}(r,k) \, dV \right) \, d^3k
\]

(26)

where all expectation value position-integrals are truncated (due to symmetry) and carried out within a primitive cell of volume \( V_{cell} \) as shown in Appendix A. The orbital magnetization r-space formula is the first major result in this work and the integrand of Eq. (20) can be seen as a local orbital magnetization density with respect to real space.

We re-emphasize that, although the position operator that enters Eq. (16) has by itself an undefined expectation value \( \langle r \rangle \) within Bloch representation, its problematic behavior does not show up and it effectively behaves as a well defined operator when it appears within Eq. (10) and subsequently within Eq. (20). Therefore, the position operator does not have to be “sandwiched” between the ground-state projector and its complement as done in Ref.\textsuperscript{23} in order to get a well defined local expression for the electrons' orbital magnetization with respect to periodic and extended states, but this can be realized in a straightforward manner with Eq. (20).

As evidenced from Eq. (20), the orbital magnetization acquires significant value whenever the difference between the two competing contributions gets as large as possible. We therefore expect that the orbital magnetization will have significant contributions from those states that possess some kind of rotational symmetry within the unit cell that results in

\[
\iint_{V_{cell}} J_{pr(n)}(r,k) \, dV \rightarrow 0.
\]

Although we considered spinless electrons, the orbital magnetization as given by Eq. (20) is a property that silently car-
ries an explicit spin dependence. In crystals with strong spin-orbit interaction the velocity operator acquires spin dependence \( v = \frac{1}{m} + \frac{\hbar}{2 m^2 c^2} \sigma \times \nabla V_{xy}(r) \) which is inherited in the local probability current density \( J_{yz}(r, k) = \text{Real}[\langle \Psi_n(r, k) | v \Psi_n^*(r, k) \rangle] \) that enters Eq. \((20)\). Therefore, in materials with strong spin-orbit interaction the spin degree of freedom is essential, the orbital magnetization is directly influenced (apart from the wavefunctions) by the crystal force field that interacts with the electron.

B. k-space orbital magnetization quantum formula

In this subsection we derive an orbital magnetization formula that is valid for general boundary conditions for the electrons’ wavefunction. Boundary contributions are explicitly taken into account as a consequence of the emergent non-Hermitian effect.

In order to derive the k-space formula we assume that, each electrons’ motion is described from a (generalized extended and stationary form eigenstate (normalized within the volume of the material) in the form

\[
\langle \Psi_n(t, k) | e^{-iE_n/k} | u_n(k) \rangle = e^{-iE_n/k} e^{i\Theta_n(t, k)} \langle \Psi_n(t, k) | u_n(k) \rangle
\]

and no Wannier-localization approximation is involved. The bulk values of each (position representation) wavefunction \( u_n(r, k) \) are assumed to be periodic (with respect to any direct lattice vector translation \( \mathbf{R} \)), while we relax this property near the boundaries of the material in order to take into account the realistic boundary contributions. We derive below a k-space orbital magnetic formula \( m_n(k) \) for each electron, starting from

\[
m_n(k) = \frac{e}{2c} \text{Im} \left[ i \langle \Psi_n(t, k) | (r - \langle r \rangle_n) \times | \Psi_n(t, k) \rangle \right]
\]

(cf. Eqs \((16)\) and \((25)\)), and by straightforward generalization we provide the collective orbital magnetization formula for non-interacting electrons calculated with respect to a many-body Slater determinant wavefunction. The formula we derive will explicitly incorporate \( k \) derivatives (with the thermodynamic limit assumed), thus we are cautious from the very beginning against possible \( k \)-dependent ambiguities of our final result. For this reason we consider the dynamical phase as well as an arbitrary \( k \)-dependent phase (due to gauge freedom) for the wavefunctions from the very beginning of our derivation. Therefore, the Bloch type quantum eigenstates that we consider (for each electron) have the form \( | \Psi_n(t, k) \rangle = e^{iH(r, k)} e^{i\Theta_n(t, k)} | u_n(k) \rangle \), where \( \Theta_n(t, k) \) is the dynamical phase augmented by an additional \( k \)-dependent gauge phase. The \( \Theta_n(t, k) \) phase has explicit form, for a static \( H \), given by \( \Theta_n(t, k) = -\frac{1}{\hbar} E_n(k) t + \Lambda(k) \).

By taking into account the above Bloch type eigenstate for each electron, the standard velocity operator as given by Eq. \((2)\), and the Schrödinger equation that evolves for each electron, starting from \( \langle \Psi_n(t, k) | r \rangle_{\text{EF}} \) and no Wannier-momentum \( \hbar \mathbf{R} \) will be made at the end of this subsection after Eq. \((19)\). In virtue of Eq. \((27)\) and Eq. \((19)\), the orbital magnetic moment is always a well defined quantity even if the wavefunction is an extended one and the volume \( V \) of the system infinite. It is a quantity that emerges due to the circulating probability micro-currents embodied in the wavefunction’s (bulk as well as boundary) structure. For free electron and plane wavefunction, namely, a wavefunction with a well defined crystal momentum \( \hbar \mathbf{k} \), the electron’s orbital magnetic moment Eq. \((27)\) becomes zero. In virtue now of Eq. \((29)\), where Eq. \((28)\) has been used, although the orbital magnetic moment holds its above mentioned physical origin, is now also explicitly dependent on the remnant non-Hermitian boundary term \( (H_k(r, k) - E_n(k)) \partial_k u_n(k) \) of the Hellmann-Feynman theorem, a fact first noticed in Ref. \((16)\). Specifically, by taking the inner product of Eq. \((28)\), with \( \langle \Psi_n(t, k) \rangle \), the electrons standard velocity expectation value is found to be

\[
\langle \Psi_n(k) | v u_n(k) \rangle = \frac{1}{\hbar} \langle \partial_k E_n(k) \rangle
\]

\[
- \frac{1}{\hbar} \langle u_n(k) | (H_k(r, k) - E_n(k)) | \partial_k u_n(k) \rangle,
\]

where the second term on the right side of Eq. \((30)\) is precisely the non-Hermitian boundary term of Ref. \((16)\).
which emerges due to the momentum gradient operator $\partial_k$ that becomes anomalous. In this respect, despite the fact that the electron’s orbital magnetic moment Eq. (27) is an intensive quantity, when we transform it into a k-derivative formula, Eq. (28), this is dominated by the remnant boundary term $(H_k(r, k) - E_n(k))\partial_k u_n(k)$.

We then express the action of the operator $r - \langle r \rangle_n$ on the eigenstate $|u_n(k)\rangle$ as a k-derivative formula, and then substitute the result in Eq. (29). This is done by taking into account that the time-independent eigenstate $|u_n(k)\rangle$ can be recast in the form $|u_n(k)\rangle = e^{-i k \cdot r} e^{-i \Lambda(k)} |\Psi_n(k)\rangle$, where the time-dependence has been eliminated. In this manner, the action of the position operator on the eigenstate $|u_n(k)\rangle$ is expressed as a k-derivative given by

$$ r |u_n(k)\rangle = i [\partial_k u_n(k)] - \partial_k \Lambda(k) |u_n(k)\rangle $$

$$ - i e^{-i k \cdot r} e^{-i \Lambda(k)} [\partial_k \Psi_n(k)] . \quad (31) $$

Accordingly, the expectation value of the position operator $r$ with respect to the eigenstate $|u_n(k)\rangle$ takes the form

$$ \langle u_n(k) | r | u_n(k)\rangle = A_{n, n}(k) - \partial_k \Lambda(k) - i \langle \Psi_n(k) | \partial_k \Psi_n(k) \rangle , \quad (32) $$

where $A_{n, n}(k) = i \langle u_n(k) | \partial_k u_n(k) \rangle$ is the Abelian Berry connection. By acting with Eq. (32) on $|u_n(k)\rangle$ and then subtracting the product from Eq. (31) we obtain the identity

$$ (r - \langle r \rangle_n) |u_n(k)\rangle = (i \partial_k - A_{n, n}(k)) |u_n(k)\rangle $$

$$ - i e^{-i k \cdot r} e^{-i \Lambda(k)} [\partial_k \Psi_n(k)] $$

$$ + i e^{-i k \cdot r} e^{-i \Lambda(k)} \langle \Psi_n(k) | \partial_k \Psi_n(k) \rangle |\Psi_n(k)\rangle . \quad (33) $$

The first two terms on the right hand side of Eq. (33) can be recast in the form,

$$ (i \partial_k - A_{n, n}(k)) |u_n(k)\rangle = i \tilde{\partial}_k |u_n(k)\rangle \quad (34) $$

where

$$ \tilde{\partial}_k = \partial_k + i A_{n, n}(k) \quad (35) $$

is the one-band covariant derivative (of the $n$th band) that will explicitly enter the final many-body orbital magnetization formula as an emerging operator, and as such has never shown up in the literature of modern theory of orbital magnetization. On the contrary, in the orbital magnetization modern theory, they implement by heuristic argument covariant derivatives in order to make their final orbital magnetization formulas gauge invariant.

In this fashion, Eq. (33) takes the form

$$ (r - \langle r \rangle_n) |u_n(k)\rangle = i \tilde{\partial}_k |u_n(k)\rangle $$

$$ - i e^{-i k \cdot r} e^{-i \Lambda(k)} [\partial_k \Psi_n(k)] $$

$$ + i e^{-i k \cdot r} e^{-i \Lambda(k)} \langle \Psi_n(k) | \partial_k \Psi_n(k) \rangle |\Psi_n(k)\rangle . \quad (36) $$

We then expand the state $|\partial_k \Psi_n(k)\rangle$ of Eq. (36) on the complete basis of the Bloch eigenstates $|\psi_m(k')\rangle$ by using the identity operator

$$ I = \sum_{m, k'} |\psi_m(k')\rangle \langle \psi_m(k')| , \quad (37) $$

that is, we substitute

$$ |\partial_k \Psi_n(k)\rangle = \sum_{m, k'} \langle \psi_m(k') | \partial_k \psi_n(k) \rangle |\psi_m(k')\rangle . \quad (38) $$

By then taking into account that the operator $(r - \langle r \rangle_n)$ is by definition Hermitian (without the need of any specific boundary conditions to be imposed) owing to the position representation that we are working in $(r^+ = r)$ and to the reality of the position operator expectation value $\langle r \rangle_n$, we let it act on the left to the eigenstate $\langle u_n(k) |$ in Eq. (29), which is carried out by taking the Hermitian conjugate of Eq. (36) and then plugging it into Eq. (29). In this respect and as analytically shown in Appendix B 2, Eq. (29) takes the form (B17), namely

$$ m_n(k) = - \frac{e}{2 c \hbar} \text{Im} \left[ \langle \tilde{\partial}_k u_n(k) | \chi (H_k(r, k) - E_n(k)) |\partial_k u_n(k)\rangle \right] $$

$$ - \frac{e}{2 c \hbar} \sum_{m \neq n} \text{Im} \left[ \langle \Psi_n(k) | \partial_k \Psi_m(k) \rangle \times |u_m(k)\rangle H_k(r, k) - E_n(k) |\partial_k u_n(k)\rangle \right] , \quad (39) $$

which, by using the identity $(H_k(r, k) - E_n(k)) |\partial_k u_n(k)\rangle = (H_k(r, k) - E_n(k)) |\tilde{\partial}_k u_n(k)\rangle$, takes the form

$$ m_n(k) = - \frac{e}{2 c \hbar} \text{Im} \left[ \langle \tilde{\partial}_k u_n(k) | \chi (H_k(r, k) - E_n(k)) |\tilde{\partial}_k u_n(k)\rangle \right] $$

$$ - \frac{e}{2 c \hbar} \sum_{m \neq n} \text{Im} \left[ \langle \Psi_n(k) | \partial_k \Psi_m(k) \rangle \times |u_m(k)\rangle H_k(r, k) - E_n(k) |\partial_k u_n\rangle \right] . \quad (40) $$

Now, some further analysis is in order concerning the off-diagonal elements in Eq. (40). As rigor-
ously shown in Appendix C by deriving an off-diagonal Hellmann-Feynman theorem that takes into account non-Hermitian corrections, the off-diagonal matrix elements \( \langle \psi_n(k)|\partial_k \psi_m(k) \rangle \) are found to be emergent non-Hermitian boundary quantities, that are given by

\[
\langle \psi_n(k)|\partial_k \psi_m(k) \rangle = \frac{S_{nm}(k)}{(E_n(k) - E_m(k))} \quad (39)
\]

where the matrix elements of the non-Hermitian term \( S_{nm}(k) \) are always transformed after an integration by parts (due to symmetry of the integrands) into a boundary quantity that is given by

\[
S_{nm}(k) = \frac{i\hbar}{2} \iint_S \mathbf{n} \cdot (\mathbf{v} \psi_n)^* + \psi_n^* \mathbf{v}) \partial_k \psi_m dS, \quad (40)
\]

where \( S_{nm}(k) \) is defined as

\[
S_{nm}(k) = \langle H(r) \psi_n(k)|\partial_k \psi_m(k) \rangle - \langle \psi_n(k)|H(r)\partial_k \psi_m(k) \rangle
\]

\[
= \langle \psi_n(k)| (H(r)^+ - H(r)) \partial_k \psi_m(k) \rangle. \quad (41)
\]

By then using the considered Bloch eigenstate \( |\psi_n(k)\rangle = e^{i\mathbf{k} \cdot \mathbf{r}} e^{i\Lambda} |\psi_n(r)\rangle \) in the non-Hermitian boundary term expression \( S_{nm}(k) \), we transform the non-Hermitian boundary term and express it in a form that is evaluated only by the use of the cell periodic eigenstates. Straightforward calculation shows that

\[
S_{nm}(k) = \hbar \langle u_n(k) | v_b | u_m(k) \rangle + \langle u_n(k) | k_b | u_m(k) \rangle, \quad (42)
\]

where,

\[
\langle u_n(k) | v_b | u_m(k) \rangle = \frac{i}{\hbar} \left( \langle H_k(r, k)^+ - H_k(r, k) \rangle r u_m(k) \right)
\]

\[
- \langle u_n(k) | H_k(r, k) r u_m(k) \rangle \quad (43)
\]

are the off-diagonal matrix elements of the boundary velocity operator \( v_b \) defined as

\[
v_b = \frac{i}{\hbar} \left( H_k(r, k)^+ - H_k(r, k) \right) r, \quad (44)
\]

while

\[
\langle u_n(k) | k_b | u_m(k) \rangle = \langle H_k(r, k) u_n(k) | \partial_k u_m(k) \rangle
\]

\[
- \langle u_n(k) | H_k(r, k) \partial_k u_m(k) \rangle \quad (45)
\]

are the off-diagonal matrix elements of the boundary momentum gradient “operator” defined as

\[
k_b = (H_k(r, k)^+ - H_k(r, k)) \partial_k, \quad (46)
\]

where the Hamiltonian \( H_k(r, k) \) is the standard Hamiltonian \( H_k(r, k) = e^{-i\mathbf{k} \cdot \mathbf{r}} H(r) e^{i\mathbf{k} \cdot \mathbf{r}} \) and \( u_m = u_m(r, k) \) are the cell-periodic eigenfunctions.

In position representation and after an integration by parts, both the above off-diagonal matrix elements are always transformed (due to symmetry of the integrands) to boundary quantities given by

\[
\langle u_n(k) | v_b | u_m(k) \rangle = -\frac{1}{2} \iint_S \mathbf{n} \cdot \left( (\mathbf{v} u_n)^* + u_n^* \mathbf{v} \right) r u_m dS
\]

\[
= -\frac{1}{2} \iint_S (\mathbf{v} u_n)^* u_m + u_n^* \mathbf{v} u_m) \cdot dS
\]

\[
+ \frac{i\hbar}{2m} \iint_S u_n^* u_m dS \quad (47)
\]

which comes out from Eq. (41), and

\[
\langle u_n(k) | k_b | u_m(k) \rangle = \frac{i\hbar}{2} \iint_S \mathbf{n} \cdot \left( (\mathbf{v} u_n)^* + u_n^* \mathbf{v} \right) \partial_k u_m dS \quad (48)
\]

respectively, where \( u_m = u_m(r, k) \) are cell-periodic in the bulk. We note that Eq. (47) and Eq. (48) are not zero only whenever the position operator \( r \) and the momentum gradient operator \( \partial_k \) become anomalous respectively. For example, for bulk localized states (defined as the ones that the wavefunction \( u_m(r, k) \) and all of its derivatives are zero over the materials boundaries) both operators behave as normal operators and have zero matrix elements, \( \langle u_n(k) | v_b | u_m(k) \rangle = 0 \) and \( \langle u_n(k) | k_b | u_m(k) \rangle = 0 \) respectively. On the other hand, for extended states that satisfy PBSs over the material boundaries \( \langle u_n(k) | v_b | u_m(k) \rangle \neq 0 \) while \( \langle u_n(k) | k_b | u_m(k) \rangle = 0 \). We also point out that the matrix elements \( \langle u_n(k) | v_b | u_m(k) \rangle \) and \( \langle u_n(k) | k_b | u_m(k) \rangle \), thus also their sum \( S_{nm}(k) \), can equally be computed as bulk quantities whenever the integrations by parts are not performed.

Using Eq. (38) and Eq. (39) we find the second major result in this work, namely the k-space orbital magnetic moment of each electron \( \mathbf{m}_n(k) \) that is given by

\[
\mathbf{m}_n(k) = -\frac{e}{2\hbar} \text{Im} \left[ \left( \partial_k \langle u_n(k) | \mathbf{H}_k(r, k) - E_n(k) \rangle \right) \langle u_n(k) | \partial_k \right]
\]

\[
-\frac{e}{2\hbar} \sum_{n \neq m} \text{Im} \left[ \frac{1}{(E_n(k) - E_m(k))} S_{nm}(k) \times \langle u_m(k) | \mathbf{H}_k(r, k) - E_n(k) \rangle \partial_k u_n(k) \right]. \quad (49)
\]

It is worth noticing that, due to the off-diagonal Hellmann-Feynman theorem Eq. (C6),
the combination of the off-diagonal matrix elements \((A_{nm}(k) - \langle u_n(k)|r|u_m(k)\rangle)\), where \(A_{nm}(k) = i \langle u_m(k)|\partial_k u_n(k)\rangle\) is the non-Abelian Berry connection, turns out to be a boundary-dependent quantity that emerges due to the non-Hermitian effect and is given by

\[
i \langle \psi_n(k) | \partial_k \psi_m(k) \rangle = (A_{nm}(k) - \langle u_n(k)|r|u_m(k)\rangle) = i \langle S_{nm}(k)|\quad(E_n(k) - E_m(k))\rangle, \tag{50}
\]

which can be viewed as a new result in the Berry phase literature showing the role of the non-Hermitian effect on Berry curvatures.

By using Eq. \((49)\) we can now make a comparison with the semi-classical electron’s orbital magnetic moment given by Ref. \(25\). In that framework, the electron’s state \(|W_\alpha\rangle\), is a localized wave packet state, composed of one band Bloch states. The wave packet is sharply centered in \(k\)-space around the wave vector \(k_\alpha\) and its center of mass is well defined and given by \(\langle W_\alpha|r|W_\alpha\rangle = r_\alpha\).

Due to the self rotation of the wave packet around its center of mass, they found that the electron acquires an intrinsic orbital magnetic moment given by \(m_n(k_\alpha) = \frac{ie}{2\hbar c} \partial_{k_\alpha} u_n(k_\alpha) \times (H_{k_\alpha}(k_\alpha) - E_n(k_\alpha)) |\partial_k u_n(k_\alpha)\rangle\) where they have used the convention \(e > 0\). If we assume that the electron’s state is a bulk state, as well as that the electron completely avoids the boundaries of the system where it is enclosed, hence the wavefunction \(u_n(r, k)\) and all of its derivatives are zero over the boundaries, then all non-Hermitian boundary terms become zero. In this respect, letting \(S_{nm}(k) = 0\) in Eq. \((49)\) we find \(m_n(k) = -\frac{e}{2\hbar c} \text{Im} \left[ (\partial_k u_n(k)|\times (H(k, r) - E_n(k))|\partial_k u_n(k)\rangle \right]\).

The term \(\langle u_n(k)|(H_k(r, k) - E_n(k))|\partial_k u_n(k)\rangle\) in the above equation, is also a non-Hermitian boundary term, which by assumption is also zero (due to the wavefunction \(u_n(r, k)\) and of its derivatives being zero over the boundaries). In this respect, for the assumed bulk states, defined as the ones that the electron completely avoids the boundaries, the electron’s magnetic moment is given by

\[
m_n(k)|_{\text{Localized State}} = -\frac{e}{2\hbar c} \text{Im} \left[ (\partial_k u_n(k)|\times (H_k(r, k) - E_n(k))|\partial_k u_n(k)\rangle \right]\tag{51}
\]

which is a form that has the same structure as the real part of semi-classical electron’s orbital magnetic moment \(\text{Re}[m_n(k_\alpha)]\) of Ref. \(25\).

It is evident that, the semi-classical electron’s orbital magnetic moment \(m_n(k_\alpha)\) does not explicitly take into account contributions from the realistic boundaries of a material, and as a consequence, the electrons’ magnetization formulas that are derived by semi-classical means do not take into account such boundary contributions. We expect that our more general result Eq. \((49)\) will be able to provide such contributions.

Moreover, our own result for the electron’s orbital magnetic moment formula Eq. \((49)\) satisfies the two basic invariant properties, namely it is invariant with respect to gauge transformations of the form \(u_n(k) \rightarrow e^{if_n(k)}u_n(k)\) and with respect to a shift of the zero of the Hamiltonian \(H_k(r, k) \rightarrow H_k(r, k) + \epsilon\); we expect therefore that the many body orbital magnetization formula that we derive further below will share the same invariant properties. Also, as will be explicitly shown in the next subsection, a boundary contribution that is encoded by the one-band covariant derivative is hidden within the first term of the right hand side of our Eq. \((49)\) and it is attributed to the emerging momentum gradient operator \(\partial_k\) anomaly.

Finally, let us in what follows use our Eq. \((49)\) (or Eq. \((35)\)) to provide a general result for the total orbital magnetization and apply it to particular cases, by always keeping an eye on corresponding results in the literature. (Our total final result is Eq. \((58)\) below.) Let us, however, first start with the simplest one-band case.

1. One-band formula

In the one-band formula we assume that each combination of the off-diagonal matrix elements
\[(A_{nm}(k) - \langle u_n(k) | r | u_m(k) \rangle)\] can be neglected, due to
\[
\frac{S_{nm}(k)}{(E_n(k) - E_m(k))} \to 0
\]
which is a good approximation for conventional insulators with large band gap and negligible boundary contributions as evidenced from Eq. (48) and Eq. (42). If we assume that in Eq. (49) each of the non-Hermitian effect terms \(S_{nm}(k)\) is zero, then \(\hbar \langle u_n(k) | v_b | u_m(k) \rangle = - \langle u_n(k) | k_0 | u_m(k) \rangle\) must be satisfied, which in the simplest scenario is fulfilled whenever the electrons completely avoid the boundaries of the material and at the same time no band-crossings exist in the Brillouin zone.

In a different point of view, the assumption of zero value for the off-diagonal matrix elements, namely, \((A_{nm}(k) - \langle u_n(k) | r | u_m(k) \rangle) = 0\) (cf. Eq. (50)) can be attributed to adiabatically deformed Bloch eigenstates \(|\Psi_n(k)\rangle\) with respect to crystal momentum differentiation, that is, \(|\partial_k \Psi_n(k)\rangle = (\Psi_n(k) | \partial_k \Psi_m(k) \rangle |\Psi_m(k)\rangle\). The latter equality is satisfied whenever each one of the off-diagonal amplitudes \((\Psi_n(k) | \partial_k \Psi_m(k) \rangle)\) is zero which defines the restriction \(|\Psi_n(k)\rangle |\partial_k \Psi_m(k)\rangle = 0\) for \(n \neq m\).

Substituting \(\Psi_n(r, k) = e^{ik \cdot r} u_n(r, k)\) in the latter adiabatically deformed restriction we find the former assumption of zero value for each one of the off-diagonal matrix elements \((A_{nm}(k) - \langle u_n(k) | r | u_m(k) \rangle)\).

In this respect and within the one-band (adiabatically deformed) approximation, the many-body electron orbital magnetization (Eq. (49)) is given by

\[
M = -\frac{e}{2\hbar c(2\pi)^3} \sum_{E_n \leq \mu} \iiint_{BZ} f_n(k, \mu) \text{Im} \left[ \langle \partial_k u_n(k) | \times (H(k, r, k) - E_n(k)) | \partial_k u_n(k) \rangle \right] d^3k \tag{52}
\]

which satisfies the two basic invariant properties, namely, it is gauge invariant and invariant with respect to a shift of the zero of the Hamiltonian.

Although we have apparently dropped out any boundary contributions of the orbital magnetization by approximating the off-diagonal matrix elements \(S_{nm}(k)\) values as zero, there still exists an explicit boundary contribution within Eq. (52) which is attributed to the one-band covariant derivative. Specifically, if we use the definition of the one-band covariant derivative as given by Eq. (35) we can recast the integrand of Eq. (52) in the following form

\[
\langle \partial_k u_n(k) | \times (H(k, r, k) - E_n(k)) | \partial_k u_n(k) \rangle
\]

\[= \langle \partial_k u_n(k) | \times (H(k, r, k) - E_n(k)) | \partial_k u_n(k) \rangle
\]

\[= -i A_{nn}(k) \times \langle u_n(k) | H(k, r, k) - E_n(k) | \partial_k u_n(k) \rangle.
\]

The second term on the right hand side of Eq. (53) gives a non-zero boundary contribution to the orbital magnetization only whenever the non-Hermitian effect with respect to the momentum gradient operator emerges, that is

\[
\langle u_n(k) | H(k, r, k) - E_n(k) | \partial_k u_n(k) \rangle =
\]

\[= - \langle u_n(k) | H(k, r, k)^\dagger - H(k, r, k) | \partial_k u_n(k) \rangle
\]

\[= \frac{i\hbar}{2} \iiint_{S} n \cdot (v u_n)^* + u_n^* v \cdot \partial_k u_n \, dS \neq 0
\]

where \(u_n = u_n(r, k)\) are the cell-periodic eigenfunctions. If we further assume within a stricter approximation that the position operator \(r\) and the momentum gradient operator \(\partial_k\) are separately normal operators, that is the expectation value of the boundary momentum gradient operator \(\langle u_n(k) | k_0 | u_n(k) \rangle\) is zero, \(\langle u_n(k) | H(k, r, k) - E_n(k) | \partial_k u_n(k) \rangle = 0\), we can replace the covariant derivative entering Eq. (52) with the normal derivative that yields the orbital magnetization formula that was derived in Ref. (22) but with the correct opposite sign between the Hamiltonian operator and the energy. Alternatively, if one assumes from the beginning a solid with one band denoted by \(n\) then, the sum in the second term on the right side of Eq. (53) will not be present due to the one band closure relation \(I = \iiint_{BZ} d^3k' |\psi_n(k')\rangle \langle \psi_n(k')|\), that must be used in Eq. (121) and subsequently in Eq. (124) leading to Eq. (67).

2. Many-band formula

In the many-band formula we don’t a priori make any assumption with respect to the behavior of the position operator \(r\) and the momentum gradient operator \(\partial_k\), thus no restrictions for the wavefunctions’ boundary conditions are made; the goal is to derive a general formula applicable to non-interacting electrons within topological materials, insulators or semimetals. In this respect, and because of Eq. (19), the many-band orbital magnetization formula of non-interacting electrons within a periodic solid is given by
which is valid for arbitrary boundary conditions on the wavefunctions $u_m(r, k)$. Orbital magnetization many-band formula Eq. (55) is the major result of this work; it rigorously provides within a quantum mechanical theoretical framework, and without any Wannier-localization approximation or heuristic extension, the manner in which one could generally model the orbital magnetization of periodic topological solids.

The energy differences in the denominator of the second term on the right hand side of Eq. (55) captures the possible local (in momentum space) gigantic orbital magnetization contributions in the vicinity of band crossings. These gigantic orbital magnetization contributions are predicted to occur only whenever band crossings exist along with an imbalance of electron accumulation at the opposite boundary surfaces of the material that creates a Hall voltage.

In order to verify the need of the presence of a Hall voltage, we will show that within PBSs for the wavefunctions (thus with no electron accumulation occurring) no gigantic local contribution of the orbital magnetization is possible even if the material is topological. Within PBCs the momentum gradient operator $\partial_k$ does not break the domain of definition of the Hamiltonian, that is the wavefunctions $u_n(r, k)$ and $\partial_k u_n(r, k)$ both satisfy periodic boundary conditions in $r$-space. Indeed, the latter periodicity of $\partial_k u_n(r, k)$ can be deduced from the periodicity $u_n(r + L, k) = u_n(r, k)$, where $L$ is the length of the material, by differentiating both sides with respect to the momentum $k$ (which is treated as an independent parameter in the assumed thermodynamic limit) that gives $\partial_k u_n(r + L, k) = \partial_k u_n(r, k)$. In this fashion, each one of the matrix elements $\langle u_n(k)|k_\mu|u_m(k)\rangle$ is zero due to symmetry, and any emergence of the non-Hermitian effect owing to the momentum gradient operator $\partial_k$ anomaly is prohibited. We point out that the absence of this non-Hermitian effect is invariant with respect to twisted boundary conditions of the form $u_n(r + L, k) = e^{iL E_n(k)} u_n(r, k)$ as long as the system is closed.

By recasting the $\langle u_m(k)|H_k(r, k) - E_n(k)\rangle \partial_k u_n(k)$ term entering the right hand side of Eq. (55) in the form

$$\langle u_m(k)|H_k(r, k) - E_n(k)\rangle \partial_k u_n(k) = (E_m(k) - E_n(k)) \langle u_m(k)|\partial_k u_n(k)\rangle - \langle u_m(k)|k_\mu|u_n(k)\rangle,$$

(56)

as well as by taking into account the non-Hermitian boundary term as given by Eq. (12)

$$S_{nm} = \hbar \langle u_n(k)|v_b|u_m(k)\rangle + \langle u_n(k)|k_\mu|u_m(k)\rangle,$$

then, under periodic boundary conditions the boundary momentum gradient “operator” $k_\mu$ matrix elements given by Eq. (13) are zero $\langle u_n(k)|k_\mu|u_n(k)\rangle = 0$, and the multi-band and unrestricted orbital magnetization formula Eq. (55) takes the form

$$M = -\frac{e}{2\hbar(2\pi)^3} \sum_{E_n \leq \mu} \iiint_{BZ} f_n(k, \mu) \text{Im} \left[ \langle \partial_k u_n(k) | (H_k(r, k) - E_n(k)) | \partial_k u_n(k) \rangle \right] d^3k$$

$$+ \frac{e}{2\hbar(2\pi)^3} \sum_{E_n \leq \mu} \sum_{m \neq n} \iiint_{BZ} f_n(k, \mu) \text{Im} \left[ \langle u_n(k) | v_b | u_m(k) \rangle \times \langle u_m(k) | \partial_k u_n(k) \rangle \right] d^3k$$

(57)

where we have also replaced the one-band covariant derivative with the normal one

$$\langle \partial_k u_n(k) | (H_k(r, k) - E_n(k)) | \partial_k u_n(k) \rangle$$

$$= \langle \partial_k u_n(k) | (H_k(r, k) - E_n(k)) | \partial_k u_n(k) \rangle$$

due to $\langle u_n(k)|k_\mu|u_n(k)\rangle = 0$ in accordance with Eq. (53) and Eq. (54).

It is now clear from Eq. (57) that, whenever a Hall voltage is zero owing to periodic boundary conditions, the orbital magnetization cannot acquire local gigantic values, even if the material is topological with non-trivial band structure crossings, while whenever imbalance of electron charge is formed, local gigantic orbital magnetization contributions near the band crossings are generically expected to occur.

It is also interesting to point out that, whenever the material’s realistic boundary conditions are periodic,
by expanding the cell periodic functions in a Fourier series over all reciprocal lattice vectors $\mathbf{G}$, namely, 

$$u_n(r, \mathbf{k}) = \sum_{\mathbf{G}} C_n(\mathbf{k}, \mathbf{G}) e^{-i \mathbf{G} \cdot \mathbf{r}}$$

it is evident that $\partial_k u_n(r, \mathbf{k})$ is periodic in space (as well as $u_n(r, \mathbf{k})$ and the Hamiltonian $H_n(r, \mathbf{k})$). By then using the normalization convention $\langle \Psi_n(t, \mathbf{k}) | \Psi_n(t, \mathbf{k}) \rangle = (u_n(\mathbf{k})|u_n(\mathbf{k})\rangle_{cell} = 1$, that is, assume a Bloch state in the form $|\Psi_n(t, \mathbf{k})\rangle = \frac{1}{\sqrt{N}} e^{-i E_n(\mathbf{k}) t} e^{i \mathbf{k} \cdot \mathbf{r}} |u_n(\mathbf{k})\rangle$, we replace $|u_n(\mathbf{k})\rangle \rightarrow \frac{1}{\sqrt{N}} |u_n(\mathbf{k})\rangle$ in all terms in Eq. (57) (the initially assumed eigenstate was normalized over the volume $V$ without taking into account the cell normalization convention, therefore it defers by a factor $1/\sqrt{N}$) and exploiting the symmetry of the integrands, the orbital magnetization formula it truncates into the form

\[
M = -\frac{e}{2\hbar c (2\pi)^3} \sum_{E_n \leq \mu} \iiint_{BZ} f_n(\mathbf{k}, \mu) \text{Im} \left[ \langle \partial_k u_n(\mathbf{k}) | (H_n(\mathbf{r}, \mathbf{k}) - E_n(\mathbf{k})) | \partial_k u_n(\mathbf{k}) \rangle_{cell} \right] d^3k 
+ \frac{e}{2\hbar c (2\pi)^3} \sum_{E_n \leq \mu} \sum_{m \neq n} \iiint_{BZ} f_n(\mathbf{k}, \mu) \text{Im} \left[ \langle u_n(\mathbf{k}) | v_b | u_m(\mathbf{k}) \rangle_{cell} \right] \times \langle u_m(\mathbf{k}) | \partial_k u_n(\mathbf{k}) \rangle_{cell} \right] d^3k
\]

where all space integrals are performed within one primitive cell, and the off-diagonal matrix elements of the boundary velocity are given by

\[
\langle u_n(\mathbf{k}) | v_b | u_m(\mathbf{k}) \rangle = -\frac{1}{2} \iiint_{cell} \mathbf{r} \left( \mathbf{v} u_n \right)^* u_m + u_n^* \mathbf{v} u_m \right) \cdot dS
\]

in accordance with Eq. (47), where we have taken into account that $u_n(r, \mathbf{k})$ are periodic over the unit cell boundaries. Eq. (59) can be thought as the $\mathbf{k}$-space analog of Eq. (26).

It is worth comparing (i) the orbital magnetization formula of periodic solids that is given by Eq. (57) with the one that was proposed in Ref. 23 by a heuristic argument, as well as, (ii) compare the general orbital magnetization formula Eq. (59) with the one derived in Ref. 2, where they propose a theoretical approach to discriminate the separate contributions of the total magnetization, that is, the one contribution coming from the bulk states and the other coming from the surface states.

(i) Orbital magnetization formula Eq. (57), is relaxed from any Wannier localization approximation as well as from the periodic gauge approximation, and it is therefore valid for topological materials as long as the electrons’ wavefunctions satisfy periodic boundary conditions (zero Hall voltage) over the materials boundaries. The heuristic extension of the orbital magnetization formula by an additional term, assumed to be proportional to the chemical potential, that was made in Ref. 23 in order to model the orbital magnetization of Chern insulators and metals, is rigorously given by the second term of the right hand side of Eq. (57). This term has explicit boundary contributions due to the off-diagonal matrix elements of the boundary velocity operator $v_b$ which are not zero due to the emerging non-Hermitian effect of the position operator $\mathbf{r}$ that becomes anomalous within periodic boundary conditions, as should be expected.

(ii) In Ref. 2 they use the standard circulation operator together with the spectral resolution of the Hamiltonian, and as a result of this spectral resolution, the (undefined) diagonal matrix elements of the position operator are excluded from the circulation operator formula; one can therefore evaluate the standard circulation operator expectation value (even in the thermodynamic limit within PBCs), hence one can calculate the orbital magnetization. Due to the spectral resolution within the circulation operator, the assumed orbitals must satisfy $\langle \phi_n | \mathbf{v} \phi_n \rangle = -\langle \phi_n | v_b | \phi_n \rangle = 0$ owing to $\langle \phi_n | \mathbf{v} \phi_n \rangle = 0$, therefore, the orbitals that are taken into account indeed describe bulk states. Then, Ref. 2 extracted their result from the semi-classical orbital magnetization formula given in Ref. 24 and they stated that the remaining part gives the boundary contribution of the orbital magnetization. The theoretical method that they use rests on the argument that the semi-classical orbital magnetization formula given in Ref. 24 correctly gives the total (bulk and boundary) orbital magnetization of non interacting electrons. We argue that this may not be entirely true due to the approximations that are made during the derivation of the Ref. 24 orbital magnetization formula. First, as we have shown in the derivation of Eq. (51), the structure of the semi-classical electron’s orbital magnetic moment can be attained by the unrestricted quantum formula Eq. (49) whenever the electron’s state is a localized bulk state, that is, when the electron completely avoids the boundaries of the system where it is enclosed. Therefore, the orbital magnetization that is evaluated only by taking into account the electron’s semi-classical orbital magnetic moment, does not account for magnetization contributions.
coming from all possible states, i.e. does not take into account topologically non trivial extended states. On the other hand, the semi-classical orbital magnetization formula given in Ref. 24, namely as the derivative of the electrons’ total energy with respect to the magnetic field (at zero magnetic field), besides the contribution coming from the electrons’ intrinsic orbital moment, it also acquires two extra terms that come up due to the modified density of states. One is attributed to the explicit magnetic field dependence of the density of states and the other is due to the resulting change in the Fermi volume. The two extra terms cannot carry any topologically non trivial information, on one hand due to the localized wavepacket employed, and on the other hand due to the explicit assumption \( \nabla_k \cdot \Omega_n(k) = 0 \), where \( \Omega_n(k) \) is the Berry curvature, that was made in Ref. 24 for deriving the modified density of states (hence Berry type of monopoles, crucial for the non trivial topology, were ignored). In this framework, these two extra terms most probably represent corrections to the semi-classical orbital magnetization formula and do not carry any topologically non trivial information. We argue therefore that, although the method followed in Ref. 2 is reasonable, the findings do not represent the orbital magnetization of topologically non trivial surface states, but they instead provide trivial corrections to the orbital magnetization for non localized states. This discussion here is given so that our results Eq. (55) or Eq. (57) can be directly compared with the state of the art results.

IV. CONCLUSIONS

We have reconsidered the modern theory of orbital magnetization through careful definition of additional quantities that rigorously and analytically take into account the boundary contributions to the observable. These contributions are shown to originate from non-Hermitian effects that emerge whenever the position operator \( \mathbf{r} \) and the momentum gradient operator \( \partial_k \) (that enter the Ehrenfest and the Hellmann-Feynman theorems respectively) become anomalous, in the sense that they break the domain of definition of the Hamiltonian operator. In this theoretical framework, we have first extended the standard velocity operator definition in order to incorporate the anomaly of the position operator that is inherited in band theory, which results to an explicit boundary velocity contribution.

Using the extended velocity, we have defined the electrons’ intrinsic orbital circulation within Bloch representation which we have shown that is an intensive and well defined quantity of periodic solids that properly counts the circulating micro-currents embodied in the wavefunctions’ bulk and boundary structure. Using the defined electrons’ intrinsic circulation, we have made a rigorous connection between the nth band electrons’ collective intrinsic circulation and the local (LC) and itinerant circulation (IC) contributions, that are used within Wannier-localization and periodic gauge approximation in the modern theory of orbital magnetization\(^{21–23}\).

With these concepts in hand, we have been able to rigorously reconsider the modern theory of orbital magnetization and derive quantum mechanical expressions for the orbital magnetization of non-interacting electrons that move within extended and topological solids (insulators or semimetals), without any Wannier-localization approximation\(^{21,22,35}\) or heuristic extension\(^{23}\) been made.

We have rigorously shown that, in the one-band approximation \( k \)-space formula, a one-band covariant derivative enters the magnetization formula as an emerging operator due to the non-Hermitian effect that is attributed to the anomaly of the momentum gradient operator \( \partial_k \); the one-band covariant derivative can be replaced by the normal derivative only whenever PBCs are satisfied.

In the many-band and unrestricted \( k \)-space formula of the orbital magnetization, the non-Hermitian effect has been shown to contribute an additional boundary term that originates from the anomalies of the position operator \( \mathbf{r} \) and the momentum gradient operator \( \partial_k \). This additional boundary term, is expected to give local gigantic orbital magnetization contributions in the vicinity of band crossings in topological materials (insulators or semimetals) whenever band crossings exist along with Hall voltage due to imbalance of electron accumulation at the opposite boundaries of the materials. These local gigantic orbital magnetization contributions are encoded by the emerging non-Hermitian effect of the momentum gradient operator \( \partial_k \) that becomes anomalous whenever PBCs for the electrons’ wavefunctions are broken. On the contrary, whenever Hall voltage is zero and the electrons’ wavefunctions satisfy PBCs, the momentum gradient operator \( \partial_k \) has a well defined behavior and, as a consequence, gigantic boundary contributions are not possible. By making a comparison between our derived formula and the one that had heuristically been given (in order to model the orbital magnetization of Chern insulators and metals) in Ref.\(^{24}\) we have shown the (previously unnoticed) property that, within periodic boundary conditions, the orbital magnetization has explicit boundary contributions encoded by the off-diagonal matrix elements of the boundary velocity operator (which are not zero due to the emerging non-Hermitian effect of the position operator that becomes anomalous within PBCs). Finally, we point out that, all boundary contributions that emerge due to non-Hermitian effects can equally be calculated as bulk properties whenever the integrations by parts are not performed.
Appendix A: Position expectation value \( \langle r \rangle \), displacement \( \Delta \langle r \rangle \), orbital circulation \( \langle C \rangle \), and intrinsic orbital circulation \( \langle C_{\text{intr}} \rangle \)

In the following all calculations are performed for one electron states within Bloch representation.

1. Explicit calculation of \( \langle r \rangle \)

For simplicity and without loss of generality we assume 1D configuration (while the generalization to 3D is straightforward). We assume a closed system \( \langle \Psi(t) | \Psi(t) \rangle = 1 \) of length \( L_x \) with PBSs for the wavefunction over the edges. We calculate the electrons position expectation value \( \langle \Psi(t) | x | \Psi(t) \rangle \) with respect to a Bloch eigenstate \( \hat{\Psi}(t,k) = \frac{1}{\sqrt{N_x}} e^{ikx} \langle u_n(k) \rangle \). The length \( L_x \) of the system is equal to \( L_x = N_x \alpha_x \), where \( \alpha_x \)

\[
\langle \psi_n(k) | x | \psi_n(k) \rangle = \int_0^{\alpha_x} |u_n(x,k)|^2 \, dx + \frac{1}{N_x} \alpha_x \left( 1 + 2 + 3 + \cdots + (N_x - 1) \right) \int_0^{\alpha_x} |u_n(x,k)|^2 \, dx
\]

\[
= \langle u_n(k) | x | u_n(k) \rangle_{\text{cell}} + \frac{1}{N_x} \alpha_x N_x \frac{(N_x - 1)}{2} \langle u_n(k) | u_n(k) \rangle_{\text{cell}}
\]

where the cell subscript denotes that the space integrals are evaluated within the primitive cell located at the system’s edge. Using the normalization condition Eq. (A2) takes the form

\[
\langle \psi_n(k) | x | \psi_n(k) \rangle = \frac{\alpha_x N_x}{2} + \left( \langle u_n(k) | x | u_n(k) \rangle_{\text{cell}} - \frac{\alpha_x}{2} \right).
\]

Performing analogous calculation as that in Eq. (A2), we evaluate the off-diagonal matrix elements of the position operator for \( n \neq m \) which gives

\[
\langle \psi_n(k) | x | \psi_m(k) \rangle = \langle u_n(k) | x | u_m(k) \rangle_{\text{cell}} + \alpha_x \frac{(N_x - 1)}{2} \langle u_n(k) | u_m(k) \rangle_{\text{cell}},
\]

where using \( \langle \psi_n(k) | \psi_m(k) \rangle = \langle u_n(k) | u_m(k) \rangle_{\text{cell}} = \delta_{nm} \), we finally find that the off-diagonal matrix elements are given by

\[
\langle \psi_n(k) | x | \psi_m(k) \rangle = \langle u_n(k) | x | u_m(k) \rangle_{\text{cell}}.
\]

Therefore, in the system’s infinite length limit \( L_x \rightarrow \infty \), the number of primitive cells enclosed within the system also becomes infinite \( N_x \rightarrow \infty \), and as a result, the electrons’ position expectation value Eq. (A3) takes an undefined value (due to the first term of the right hand side), in contrast to the off-diagonal position matrix elements Eq. (A5) which they return a well defined value.

2. Explicit calculation of \( \Delta \langle r \rangle \)

We assume a position periodic and closed system of length \( L_x \). We will calculate the electrons’ displacement after a finite time interval \( T \) in the limit of infinite length \( L_x \rightarrow \infty \) and show that is a well-defined quantity. We assume that the electron is in an extended and time-dependent Bloch type state at every instant, that is, \( \langle \Psi(t,k(t)) \rangle = \frac{1}{\sqrt{N_x}} e^{ik(t)x} |u(t,k(t))\rangle \), where the state \( |u(t,k(t))\rangle \) has arbitrary time-dependence and is cell-periodic at every instant, as well as \( \langle \Psi(t,k(t)) | \Psi(k,k(t)) \rangle = \langle u(t,k(t)) | u(t,k(t)) \rangle_{\text{cell}} = 1 \).

Using similar reasoning as in Eq. (A3) we find that the electrons’ displacement is given by
\[
\Delta \langle x \rangle = \Delta \langle \Psi(t, k(t)) | x | \Psi(t, k(t)) \rangle = \frac{1}{N_x} \langle u(t + T, k(t + T)) | x | u(t + T, k(t + T)) \rangle - \frac{1}{N_x} \langle u(t, k) | x | u(t, k) \rangle
\]

\[
= \langle u(t + T, k(t + T)) | x | u(t + T, k(t + T)) \rangle_{\text{cell}} - \langle u(t, k) | x | u(t, k) \rangle_{\text{cell}}
\]

(A6)

where the undefined terms \( \frac{\alpha_x N_x}{2} \) canceled each one another. In this fashion, Eq. (A6) takes the form

\[
\Delta \langle x \rangle = \int_t^{t+T} \frac{d}{dt} \langle u(t', k(t')) | x | u(t', k(t')) \rangle_{\text{cell}} dt',
\]

where, by using the extended velocity operator \( v_{\text{ext}} \) defined in Eq. (9) in the main text, it turns out that the electron displacement in a position periodic system has the form

\[
\alpha \langle C | \Psi_n(k) \rangle = \frac{1}{N_x N_y} \int_0^{N_x \alpha_x} \int_0^{N_y \alpha_y} r \times J_{\text{pr}(n)}(x, y, k) dx dy
\]

(A9)

where the local probability current density, is evaluated with respect to the cell periodic eigenstate \( u_n(r, k) \) and is a cell-periodic quantity. We first carry out the integral \( \int_0^{N_x \alpha_x} \int_0^{N_y \alpha_y} r \times J_{\text{pr}(n)}(x, y, k) dy \), where we exploit the periodicity of the local probability current density and “transfer” \((N_y - 1)\) primitives cells along the \( y \) direction on the \( y = 0 \) line which gives

\[
\frac{1}{N_y} \int_0^{N_y \alpha_y} r \times J_{\text{pr}(n)}(x, y, k) dy = \int_0^{\alpha_y} r \times J_{\text{pr}(n)}(x, y, k) dy + \frac{1}{N_y} \left( 1 + 2 + \ldots + (N_y - 1) \right) \alpha_y \times \int_0^{\alpha_y} J_{\text{pr}(n)}(x, y, k) dy
\]

\[
= \int_0^{\alpha_y} r \times J_{\text{pr}(n)}(x, y, k) dy + \frac{1}{N_y} N_y \left( N_y - 1 \right) \frac{1}{2} \alpha_y \times \int_0^{\alpha_y} J_{\text{pr}(n)}(x, y, k) dy.
\]

(A10)

Exploiting the periodicity of the local probability current, we perform analogous calculation for the integral along the \( x \) direction which gives

\[
\frac{1}{N_x N_y} \int_0^{N_x \alpha_x} dx \left( \int_0^{N_y \alpha_y} r \times J_{\text{pr}(n)}(x, y, k) dy \right) = \int_0^{\alpha_x} \int_0^{\alpha_y} r \times J_{\text{pr}(n)}(x, y, k) dx dy
\]

\[
+ \left( \frac{N_x - 1}{2} \alpha_x + \frac{N_y - 1}{2} \alpha_y \right) \times \int_0^{\alpha_y} \int_0^{\alpha_x} J_{\text{pr}(n)}(x, y, k) dx dy.
\]

(A11)

Eq. (A11) with the aid of Eq. (A11) finally takes the form

\[
\langle \Psi_n(k) | C | \Psi_n(k) \rangle = \int_0^{\alpha_x} \int_0^{\alpha_y} r \times J_{\text{pr}(n)}(r, k) dx dy + \left( \frac{N_x - 1}{2} \alpha_x + \frac{N_y - 1}{2} \alpha_y \right) \times \int_0^{\alpha_x} \int_0^{\alpha_y} J_{\text{pr}(n)}(r, k) dx dy
\]

(A12)

where all space integrals are taken within one primitive cell adjacent to a system’s edge and located at the po-
of the state by a form of the state (assumed to take continuous values). This is accom-
derator Eq. (2) on a Bloch type state of the form that gives the action of the standard velocity op-

dynamic limit, have canceled each other.

±where the two terms of the right hand side of Eq. (A12.)

|⟨\Psi_n(t, k)\rangle| = 1 \sqrt{N} e^{iE_n(t)k^t e^{ikr}} |u_n(k)\rangle \text{ in a 2D system identical to the one of the previous subsection. Therefore, we have to calculate}

4. Explicit calculation of \langle C_{intr} \rangle_n

We calculate the electrons’ intrinsic circulation \langle C_{intr} \rangle given by Eq. (16) of the main text with respect to a Bloch eigenstate \langle \Psi_n(t, k) \rangle = H(r) |\Psi(t, k)\rangle = \text{expression of the right hand side of Eq. (A12).}

\langle n \Psi(k) | C_{intr} | n \Psi(k) \rangle = \frac{1}{N_x N_y} \int_0^{N_x a_x} \int_0^{N_y a_y} r \times \mathbf{J}_{pr(n)}(x, y, k) dx dy - \langle r \rangle_n \times \frac{1}{N_x N_y} \int_0^{N_x a_x} \int_0^{N_y a_y} \mathbf{J}_{pr(n)}(x, y, k) dx dy. \tag{A13}

The first term of the right hand side of Eq. (A13) is given by Eq. (A12). The electrons’ position expectation value \langle r \rangle_n is given by the 2D generalization of Eq. (A2), that is,

\langle r \rangle_n = \left( \frac{(N_x - 1)}{2} \alpha_x + \frac{(N_y - 1)}{2} \alpha_y \right) + \langle u_n(k) | r | u_n(k) \rangle_{cell} \tag{A14}

and the space integral of the local probability current density is easily truncated within one primitive cell adjacent to a system’s edge (located at the position origin) due to the cell periodicity of the probability current, thus giving

\frac{1}{N_x N_y} \int_0^{N_x a_x} \int_0^{N_y a_y} \mathbf{J}_{pr(n)}(x, y, k) dx dy = \int_0^{a_x} \int_0^{a_y} \mathbf{J}_{pr(n)}(x, y, k) dx dy \tag{A15}

Substituting Eq. (A12) and Eq. (A14) − (A15) into Eq. (A13) we finally obtain

\langle n \Psi(k) | C_{intr} | n \Psi(k) \rangle = \int_0^{a_x} \int_0^{a_y} (r - \langle u_n(k) | r | u_n(k) \rangle_{cell}) \times \mathbf{J}_{pr(n)}(x, y, k) dx dy \tag{A16}

where the two terms ± \left( \frac{(N_x - 1)}{2} \alpha_x + \frac{(N_y - 1)}{2} \alpha_y \right) \times \int_0^{a_x} \int_0^{a_y} \mathbf{J}_{pr(n)}(r, k) dx dy, each one undefined in the thermo-
dynamic limit, have canceled each other.

Appendix B: Action of the velocity operator \textbf{v} on a Block eigenstate \langle \Psi_n(t, k) \rangle and of the operator \textbf{r} − \langle \textbf{r} \rangle_n on a cell periodic state \langle u_n(k) \rangle

1. Action of \textbf{v} on a Block eigenstate \langle \Psi_n(t, k) \rangle

At first we derive a general k-derivative formula that gives the action of the standard velocity operator Eq. (2) on a Bloch type state of the form \langle \Psi(t, k) \rangle = e^{i\textbf{k} \cdot \textbf{r}} |\Phi(t, k)\rangle, where \textbf{k} is a static wave vector (assumed to take continuous values). This is accomplished by taking into account the specific Bloch type form of the state |\Psi(t, k)\rangle as well as the time evolution of the state by \textbf{i} \hbar \frac{d}{dt} |\Psi(t, k)\rangle = H(r) |\Psi(t, k)\rangle, that is governed by a static Hamiltonian H(r).

Under these conditions, the action of the position op-

operator on the state |\Psi(t, k)\rangle can be expressed as

\textbf{r} |\Psi(t, k)\rangle = -i \partial_k |\Psi(t, k)\rangle + ie^{i\textbf{k} \cdot \textbf{r}} \partial_k |\Phi(t, k)\rangle. \tag{B1}

Acting on both sides of Eq. (B1) with the Hamiltonian H(r) of the system, and taking into account that the Hamiltonian does not depend on the wavevector, that is \left[ H(r), \partial_k \right] = 0, we find

H(r) |\Psi(t, k)\rangle = -i \partial_k (H(r) |\Psi(t, k)\rangle) + ie^{i\textbf{k} \cdot \textbf{r}} H_k(r, k) |\partial_k \Phi(t, k)\rangle \tag{B2}

where the Hamiltonian H_k(r, k) is defined by \textbf{H}_k(r, k) = e^{-i\textbf{k} \cdot \textbf{r}} H(r) e^{i\textbf{k} \cdot \textbf{r}}. The term \partial_k (H(r) |\Psi(t, k)\rangle) of the right hand side of Eq. (B2) can be recast in the form

\partial_k (H(r) |\Psi(t, k)\rangle) = i r H(r) |\Psi(t, k)\rangle + e^{i\textbf{k} \cdot \textbf{r}} \left( \textbf{i} \hbar \frac{d}{dt} |\partial_k \Phi(t, k)\rangle \right) \tag{B3}
where we have used
\[ H(r) |\Psi(t, k)\rangle = i\hbar \frac{d}{dt} |\Psi(t, k)\rangle = e^{ik \cdot r} i\hbar \frac{d}{dt} |\Phi(t, k)\rangle, \]
as well as
\[ \partial_k \left( e^{ik \cdot r} i\hbar \frac{d}{dt} |\Phi(t, k)\rangle \right) = -\hbar e^{ik \cdot r} \frac{d}{dt} |\Phi(t, k)\rangle + e^{ik \cdot r} i\hbar \frac{d}{dt} [\partial_k |\Phi(t, k)\rangle] \]
and
\[ -i\hbar e^{ik \cdot r} \frac{d}{dt} |\Phi(t, k)\rangle = i \hbar \frac{d}{dt} \left( e^{ik \cdot r} |\Phi(t, k)\rangle \right) \]
= \[ i \hbar H(r) |\Psi(t, k)\rangle. \]

Substituting Eq. (B23) into Eq. (B22) we find that the action of commutator \[ [H(r), r] \] on the Bloch type state \[ |\Psi(t, k)\rangle \] is given by
\[ [H(r), r] |\Psi(t, k)\rangle = i e^{ik \cdot r} \left( H_k(r, k) - i\hbar \frac{d}{dt} \right) |\Phi(t, k)\rangle. \] (B4)

The action of the commutator on a stationary Bloch type state of the form \[ |\Psi_n(t, k)\rangle = e^{ik \cdot r} e^{i\Theta_n(t, k)} |u_n(k)\rangle \] where \( \Theta_n(t, k) \) is the dynamical phase with an additional \( k \)-dependent gauge phase, that is, \( \Theta_n(t, k) = -\frac{1}{\hbar}E_n(k)t + \Lambda(k) \) can be calculated by replacing \( |\Phi(t, k)\rangle = e^{i\Theta_n(t, k)} |u_n(k)\rangle \) within Eq. (B4). This gives
\[ [H(r), r] |\Psi_n(t, k)\rangle = i e^{ik \cdot r} e^{i\Theta_n(t, k)} \left( H_k(r, k) - i\hbar \frac{d}{dt} \right) |\Psi_n(t, k)\rangle \] (B5)
where we have used that \( \frac{d}{dt} |u_n(k)\rangle = 0 \), as well as \( \left( H_k(r, k) + \hbar \frac{d}{dt} \Theta_n(t, k) \right) |u_n(k)\rangle = 0 \). From Eq. (B5) we can deduce that the action of the standard velocity operator \( v \) on a stationary Bloch state is given from
\[ v |\Psi_n(t, k)\rangle = -\frac{1}{\hbar} e^{ik \cdot r} e^{i\Theta_n(t, k)} \left( H_k(r, k) - E_n(k) \right) |\partial_k u_n(k)\rangle + \frac{1}{\hbar} \partial_k E_n(k) |\Psi_n(t, k)\rangle. \] (B6)

2. Action of \( (r - \langle r \rangle) \) on a cell-periodic eigenstate \( |u_n(k)\rangle \)

We assume a Bloch type eigenstate in the form \[ |\Psi_n(t, k)\rangle = e^{ik \cdot r} e^{i\Theta_n(t, k)} |u_n(k)\rangle \] where \( \Theta_n(t, k) \) is the dynamical phase with an additional \( k \)-dependent gauge phase, that is, \( \Theta_n(t, k) = -\frac{1}{\hbar}E_n(k)t + \Lambda(k) \). The time-independent eigenstate \( |u_n(k)\rangle \) can be recast in the form
\[ |u_n(k)\rangle = e^{-ik \cdot r} e^{-i\Lambda(k)} |\Psi_n(k)\rangle \] (B7)
where the time-dependence has been eliminated as expected.

In the position representation and by using Eq. (B7), the action of the position operator on the eigenstate \( |u_n(k)\rangle \) can be transformed to a \( k \)-derivative identity given by
\[ r |u_n(k)\rangle = i [\partial_k u_n(k) - \partial_k \Lambda(k)] |u_n(k)\rangle - i e^{-ik \cdot r} e^{-i\Lambda(k)} |\partial_k \Psi_n(k)\rangle. \] (B8)

Accordingly, the expectation value of the position operator \( r \) with respect to the eigenstate \( |u_n(k)\rangle \) takes with the aid of Eq. (B8) the form
\[ \langle u_n(k) | r |u_n(k)\rangle = A_{nn}(k) - \partial_k \Lambda(k) - i \langle \Psi_n(k) | \partial_k \Psi_n(k) \rangle, \] (B9)
where \( A_{nn}(k) = i \langle u_n(k) | \partial_k u_n(k) \rangle \) is the Abelian Berry connection. By acting with Eq. (B8) on \( |u_n(k)\rangle \) and then subtracting the product from Eq. (B8) we find the identity
\[ (r - \langle r \rangle_n) |u_n(k)\rangle = (i \partial_k - A_{nn}(k)) |u_n(k)\rangle - i e^{-ik \cdot r} e^{-i\Lambda(k)} \left( [\partial_k |\Psi_n(k)\rangle - \langle \Psi_n(k) | \partial_k \Psi_n(k) \rangle |\Psi_n(k)\rangle \right). \] (B10)
By then using the one-band covariant derivative definition, namely, \( i \hat{\partial}_k |u_n(k)\rangle = (i \partial_k - A_{nn}(k)) |u_n(k)\rangle \), where \( \hat{\partial}_k \) is given by \( \hat{\partial}_k = \partial_k + i A_{nn}(k) \), Eq. (B10) takes the form
\[ (r - \langle r \rangle_n) |u_n(k)\rangle = i [\hat{\partial}_k u_n(k) - i e^{-ik \cdot r} e^{-i\Lambda(k)} \left( [\partial_k |\Psi_n(k)\rangle - \langle \Psi_n(k) | \partial_k \Psi_n(k) \rangle |\Psi_n(k)\rangle \right) + i \langle \Psi_n(k) | \partial_k \Psi_n(k) \rangle |u_n(k)\rangle. \] (B11)
We then expand the state $|\partial_k \Psi_n(k)\rangle$ on the complete basis of the Bloch eigenstates $|\psi_m(k')\rangle$ by using the closure relation $I = \sum_{m,k'} |\psi_m(k')\rangle \langle \psi_m(k')|$, that is, we substitute $|\partial_k \Psi_n(k)\rangle = \sum_{m,k'} \langle \psi_m(k')|\partial_k \psi_n(k)\rangle |\psi_m(k')\rangle$ which gives

$$ (r - \langle r \rangle_n) |u_n(k)\rangle = i |\tilde{\partial}_k u_n(k)\rangle - i \sum_{m,k'} \langle \psi_m(k')|\partial_k \psi_n(k)\rangle e^{i(\Lambda(k') - \Lambda(k))} e^{i(k' - k) \cdot r} |u_n(k')\rangle + i \langle \Psi_n(k)|\partial_k \Psi_n(k)\rangle |u_n(k)\rangle, $$

and then use the Hermitian conjugate of Eq. (B12) to evaluate the orbital magnetic moment of the electron, namely

$$ \mathbf{m}_n(k) = -\frac{e}{2c} \text{Im}[i \langle u_n(k)| (r - \langle r \rangle_n) \times (H_k(r,k) - E_n(k)) |\partial_k u_n(k)\rangle]. $$

This way, Eq. (B13) takes the form

$$ \mathbf{m}_n(k) = -\frac{e}{2c} \text{Im} \left[ \left( \partial_k u_n(k) \times (H_k(r,k) - E_n(k)) |\partial_k u_n(k)\rangle \right) \right] + \frac{e}{2c} \text{Im} \left[ \sum_{m,k'} \langle \psi_m(k')|\partial_k \Psi_n(k)\rangle^* \times e^{i(\Lambda(k') - \Lambda(k))} \left\langle u_m(k')| e^{i(k' - k) \cdot r} (H_k(r,k) - E_n(k)) |\partial_k u_n(k)\rangle \right\rangle_{cell} \right] - \frac{e}{2c} \text{Im} \left[ \langle \partial_k \Psi_n(k)|\Psi_n(k)\rangle \times \langle u_n(k)| H_k(r,k) - E_n(k) |\partial_k u_n(k)\rangle \right], $$

By then assuming that the states, $\partial_k u_n(r,k)$ and $u_m(r,k')$, as well as the Hamiltonian $H_k(r,k)$, are invariant with respect to real-space translations by $R$ (with $R$ being the real-space lattice vectors), the quantity $\langle u_m(k')| e^{i(k' - k) \cdot r} (H_k(r,k) - E_n(k)) |\partial_k u_n(k)\rangle$ truncates into a unit cell expression given from

$$ \langle u_m(k')| e^{i(k' - k) \cdot r} (H_k(r,k) - E_n(k)) |\partial_k u_n(k)\rangle = \sum_R e^{i(k' - k) \cdot R} \langle u_m(k')| e^{i(k' - k) \cdot r} (H_k(r,k) - E_n(k)) |\partial_k u_n(k)\rangle_{cell} = N \delta_{k',k} \left\langle u_m(k')| e^{i(k' - k) \cdot r} (H_k(r,k) - E_n(k)) |\partial_k u_n(k)\rangle_{cell} \right\rangle, $$

where $N$ is the total number of unit cells enclosed by the volume $V$ of the system, while $k'$ and $k$ are assumed to lie in the first Brillouin zone. By replacing Eq. (B15) into Eq. (B14) we find

$$ \mathbf{m}_n(k) = -\frac{e}{2c} \text{Im} \left[ \left( \partial_k u_n(k) \times (H_k(r,k) - E_n(k)) |\partial_k u_n(k)\rangle \right) \right] + \frac{e}{2c} \text{Im} \left[ \sum_{m,k'} \langle \partial_k \Psi_n(k)|\Psi_m(k')\rangle \times e^{i(\Lambda(k') - \Lambda(k))} N \delta_{k',k} \left\langle u_m(k')| e^{i(k' - k) \cdot r} (H_k(r,k) - E_n(k)) |\partial_k u_n(k)\rangle_{cell} \right\rangle \right] - \frac{e}{2c} \text{Im} \left[ \langle \partial_k \Psi_n(k)|\Psi_n(k)\rangle \times \langle u_n(k)| H_k(r,k) - E_n(k) |\partial_k u_n(k)\rangle \right], $$

which finally gives

$$ \mathbf{m}_n(k) = -\frac{e}{2c} \text{Im} \left[ \left( \partial_k u_n(k) \times (H_k(r,k) - E_n(k)) |\partial_k u_n(k)\rangle \right) \right] - \frac{e}{2c} \text{Im} \left[ \sum_{m \neq n} \langle \psi_n(k)|\partial_k \psi_m(k)\rangle \times \langle u_m(k)| (H_k(r,k) - E_n(k)) |\partial_k u_n(k)\rangle \right], $$

where we have used $\langle \partial_k \Psi_n(k)|\Psi_m(k')\rangle = -\langle \Psi_n(k)|\partial_k \Psi_m(k')\rangle$ that is valid due to $m \neq n$, as well as, $N \langle u_m(k)| (H_k(r,k) - E_n(k)) |\partial_k u_n(k)\rangle_{cell} = \langle u_m(k)| (H_k(r,k) - E_n(k)) |\partial_k u_n(k)\rangle$. Eq. (B17) is Eq. (87) of the main text. As a final step, we find an expression for $\langle \psi_n(k)|\partial_k \psi_m(k)\rangle$, provided that $n \neq m$, and then replace it in the
sum of Eq. (B17). This is accomplished by the off-diagonal Hellmann-Feynman theorem that we derive in Appendix C.

Appendix C: Derivation of the off-diagonal Hellmann-Feynman theorem and the matrix elements $\langle \psi_n(k)|\partial_k \psi_m(k) \rangle$

We develop an off-diagonal Hellmann-Feynman theorem by starting from the eigenvalue equation

$$ (H(r) - E_m(k)) |\psi_m(k)\rangle = 0. \quad (C1) $$

where $H(r)$ is the initial system’s Hamiltonian. Specifically, for the purpose of calculations of this work, we use the initial Hamiltonian of the system which does not depend on the wavevector $k$, that is, $\partial_k H(r) = 0$. The result that we derive, is easily extended to include a Hamiltonian that has explicit parameter dependence by simply adding to it the term that has the derivative of the Hamiltonian with respect to the parameter.

By assuming that the crystal momentum takes continuous values, we act with the momentum gradient operator $\partial_k$ on Eq. (C1) obtaining

$$ -\partial_k E_m(k) |\psi_m(k)\rangle + (H(r) - E_m(k)) |\partial_k \psi_m(k)\rangle = 0. \quad (C2) $$

and then take the inner product of Eq. (C2) with $\langle \psi_n(k)|$ which gives

$$ -\partial_k E_m(k) \delta_{nm} + \langle \psi_n(k)| (H(r) - E_m(k)) |\partial_k \psi_m(k)\rangle = 0. \quad (C3) $$

We now take into account a possible anomaly of the momentum gradient operator due to the non-Hermitian effect, that emerges whenever the gradient operator $\partial_k$ breaks the domain of definition $D_H$ of the Hamiltonian $H(r)$. In this framework, the wavefunctions $\psi_m(r, k)$ and $\partial_k \psi_m(r, k)$ fulfill different boundary conditions over the edges of the system, and as a result they don’t belong within the same domain of definition, that is, $\psi_m(r, k) \in D_H$ while $\partial_k \psi_m(r, k) \notin D_H$. Therefore, whenever the non-Hermitian effect emerges, the term $\langle \psi_n(k)| (H(r) - E_m(k)) |\partial_k \psi_m(k)\rangle$ entering Eq. (C3) is not zero as a result of the following non-trivial inequality

$$ \langle H_k(r, k) \psi_n(k) |\partial_k \psi_m(k)\rangle = \langle \psi_n(k)|H_k(r, k)\rangle^\dagger \partial_k \psi_m(k) \rangle \neq \langle \psi_n(k)|H_k(r, k)\partial_k \psi_m(k)\rangle. $$

We treat this non-Hermitian effect by expressing the term $\langle \psi_n(k)|H(r) |\partial_k \psi_m(k)\rangle$ as

$$ \langle \psi_n(k)|H(r) |\partial_k \psi_m(k)\rangle = \langle H(r) \psi_n(k) |\partial_k \psi_m(k)\rangle - S_{nm}(k) \quad (C4) $$

where the $S_{nm}(k)$ term represents the non-Hermitian effect and is a boundary quantity. Its explicit boundary integral form is given below. In this respect, by taking into account Eq. (C4), Eq. (C3) takes the form

$$ \partial_k E_m(k) \delta_{nm} = (E_n(k) - E_m(k)) \langle \psi_n(k)|\partial_k \psi_m(k)\rangle - S_{nm}(k), \quad (C5) $$

which for $n \neq m$ gives $\langle \psi_n(k)|\partial_k \psi_m(k)\rangle$ as a function of $S_{nm}(k)$, given by

$$ \langle \psi_n(k)|\partial_k \psi_m(k)\rangle = \frac{S_{nm}(k)}{(E_n(k) - E_m(k))}. \quad (C6) $$

We now give the explicit integral form of $S_{nm}(k)$. Specifically, (i) by using Eq. (C4) as the definition of the $S_{nm}(k)$, (ii) by working in the position representation, and (iii) after an integration by parts (assuming a 3D system), the matrix elements of the non-Hermitian term $S_{nm}(k)$ are always transformed, due to symmetry of the integrands, into a boundary quantity that is given by

$$ S_{nm}(k) = \langle \Psi_n(k)| (H(r)^+ - H(r) ) |\partial_k \Psi_m(k)\rangle. \quad (C8) $$

It is now intuitively useful to give the extension of Eq. (C5) to the one that includes the explicit dependence of the Hamiltonian on a static parameter, in order to show the necessity of a non-Hermitian boundary term that solves a “paradox” concerning the band theory. First we present the “paradox” and then we show how this is resolved by taking into account the non-Hermitian term $S_{nm}(k)$. When one uses the cell periodic eigenstates and applies the Hellmann-Feynman theorem into the equation $\langle u_n(k)|H_k(r, k)|u_m(k)\rangle = E_n(k)$, one finds the standard velocity expectation value with respect to the dispersion relation derivative, that is $\langle u_n(k)|\partial_k H_k(r, k)|u_m(k)\rangle = \partial_k E_n(k) \neq 0$. On the other hand, if one uses the Bloch eigenstates, that is applies the Hellmann-Feynman theorem into the equation $\langle \psi_n(k)|H(r)\psi_n(k)\rangle = E_n(k)$, one deduces that $\partial_k E_n(k) = 0$. These sorts of subtleties are attributed to non-Hermitian boundary terms that are not properly taken into account. Specifically, by assuming a Hamiltonian $H(r, R)$, where $R$ is a general parameter, then Eq. (C5) takes the form

$$ \partial_R E_m(R) \delta_{nm} = (E_n(R) - E_m(R)) \langle \psi_n(R)|\partial_R \psi_m(R)\rangle + \langle \psi_n(R)|\partial_R H(r, R) |\psi_m(R)\rangle - S_{nm}(R) \quad (C9) $$

where $|\psi_n(R)\rangle$ are the eigenstates of the Hamiltonian. By way of an example, using the diagonal form of Eq. (C5) and assuming $R \equiv k$ as well as an initial Hamiltonian $H(r)$ we find $\partial_k E_n(k) = -S_{nn}(k)$. In
this manner, one will deduce that the bands are always flat (or equivalently that the group velocity is always zero) if the non-Hermitian boundary contribution is not taken into account, which will lead to an apparent “paradox”. Using now the Bloch form eigenstate

\[ |\Psi_n(k)\rangle = e^{i\mathbf{k} \cdot \mathbf{r}} e^{i\Lambda(k)} |u_n(k)\rangle \]

into the boundary term

\[ S_{n}(k) = \langle H(\mathbf{r}) \psi_n(k) | \partial_k \psi_n(k) \rangle - \langle \psi_n(k) | H(\mathbf{r}) | \partial_k \psi_n(k) \rangle, \]

as well as by taking into account Eq. (30) and the explicit form of the boundary velocity definition Eq. (4) of the main text, the relation between the boundary velocity and the standard (group) velocity for stationary states \( \langle v_0 \rangle_n = - \langle v \rangle_n \) is restored and the “paradox” is resolved.

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1. K. -T. Chen and P. A. Lee, Phys. Rev. B 86, 195111 (2012).
2. A. Marrazzo and R. Resta, Phys. Rev. Lett. 116, 137201 (2016).
3. R. Bianco and R. Resta, Phys. Rev. B 93, 174417 (2016).
4. S. R. Park, J. Han, C. Kim, Y. Y. Koh, C. Kim, H. Lee, H. J. Choi, J. H. Han, K. D. Lee, N. J. Hur, M. Arita, K. Shimada, H. Namatame, and M. Taniguchi, Phys. Rev. Lett. 108, 046805 (2012).
5. B. Kim, C. H. Kim, P. Kim, W. Jung, Y. Kim, Y. Koh, M. Arita, K. Shimada, H. Namatame, M. Taniguchi, J. Yu, and C. Kim, Phys. Rev. B 85, 195402 (2012).
6. J. -H. Park, C. H. Kim, J. -W. Rhim, and J. H. Han, Phys. Rev. B 85, 195401 (2012).
7. D. Go, J. -P. Hanke, P. M. Buhl, F. Freimuth, G. Bihlmayer, H. -W. Lee, Y. Morkousov, and S. Bigel, Sci. Rep. 7, 4674 (2017).
8. R. F. W. Bader, Atoms in MoleculesA Quantum Theory (Oxford University Press, Oxford, 1990).
9. R. F. W. Bader and P. L. A. Popelier, Int. J. Quantum Chem. 45, 189-207 (1993).
10. R. F. W. Bader and T. A. Keith, Int. J. Quantum Chem. 60, 373-379, (1996).
11. R. F. W. Bader and C. F. Matta, Int. J. Quantum Chem. 85, 592-607 (2001).
12. R. F. W. Bader and T. A. Keith, J. Chem. Phys. 99, 3683 (1993).
13. J. G. Esteve, Phys. Rev. D 34, 674 (1986).
14. J. G. Esteve, Phys. Rev. D 66, 125013 (2002).
15. R. N. Hill, Am. J. Phys. 41, 736 (1973).
16. J. G. Esteve, F. Falceto, C. G. Canal, Phys. Lett. A 374, 819 (2010).
17. R. Resta, Phys. Rev. Lett. 80, 1800 (1998).
18. J. W. Taylor, J. A. Duffy, A. M. Bebb, M. R. Lees, L. Bouchenoire, S. D. Brown, and M. J. Cooper, Phys. Rev. B 66, 161319(R) (2002).
19. H. J. Gotsis and I. I. Mazin, Phys. Rev. B 68, 224427 (2003).
20. S. Qiao, A. Kimura, H. Adachi, K. Iori, K. Miyamoto, T. Xie, H. Namatame, M. Taniguchi, A. Tanaka, T. Muro, S. Imada, and S. Suga, Phys. Rev. B 70, 134418 (2004).
21. T. Thonhauser, Int. J. Mod. Phys. B 25, 1429 (2011).
22. T. Thonhauser, D. Ceresoli, D. Vanderbilt, and R. Resta, Phys. Rev. Lett. 95, 137205 (2005).
23. D. Ceresoli, T. Thonhauser, D. Vanderbilt, and R. Resta, Phys. Rev. B 74, 024408 (2006).
24. D. Xiao, J. Shi, and Q. Niu, Phys. Rev. Lett. 95, 137204 (2005).
25. D. Xiao, M. -C. Chang and Q. Niu, Rev. Mod. Phys. 82, 1959 (2010).
26. M. -C. Chang and Q. Niu, Phys. Rev. B 53, 7010 (1996).
27. J. Shi, G. Vignale, D. Xiao, and Q. Niu, Phys. Rev. Lett. 99, 197202 (2007).
28. K. -T. Chen and P. A. Lee, Phys. Rev. B 84, 205137 (2011).
29. R. Resta, J. Phys.: Condens. Matt. 22, 123201 (2010).
30. R. Bianco and R. Resta, Phys. Rev. Lett. 110, 087202 (2013).
31. A. Malashevich, S. Coh, I. Souza, and D. Vanderbilt, New J. Phys. 12, 053032 (2010).
32. S. M. Lloyd, M. Babiker, G. Thirunavukarsu and J. Yuan, Rev. Mod. Phys. 89, 035004 (2017).
33. K. Y. Bliokh, I. P. Ivanov, G. Guzzinzi, L. Clark, R. Van Boxem, A. Beche, R. Juchtmans, M.A. Alonso, P. Schattschneider, F. Nori and J. Verbeeck, Phys. Rep. 690, 1-70 (2017).
34. The one-band covariant derivative \( \tilde{\partial}_k \) can alternatively be defined as \( \tilde{\partial}_k = (1 - |u_n(k)|)^2 |u_n(k)| \partial_k \) without changing any of the final results.
35. R. Resta, D. Ceresoli, T. Thonhauser, and D. Vanderbilt, Chem. Phys. Chem. 6, 1815 (2005).
36. A. Malashevich, D. Vanderbilt and I. Souza, Phys. Rev. B 83, 092407 (2011).