Nonlinear Hall Effect with Time-Reversal Symmetry: Theory and Material Realizations

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The appearance of a Hall conductance necessarily requires breaking of time-reversal symmetry, either by an external magnetic field or by the internal magnetization of a material. As a second response, however, Hall dissipationless transverse currents can appear even in time-reversal symmetric conditions provided the material is non-centrosymmetric. This non-linear Hall effect has a quantum origin: it is related to the geometric properties of the electronic wavefunctions and encoded in the dipole moment of the Berry curvature. Here, the general theory underpinning this effect is reviewed and various material platforms where non-linear Hall transverse responses have been found are discussed. On the theoretical front, the link between the non-linear Hall effect and the Berry curvature dipole is discussed using Boltzmann transport theory. On the material front, different platforms, including topological crystalline insulators, transition metal dichalcogenides, graphene, and Weyl semimetals are reviewed.

1. Introduction

The electric Hall effect—the phenomenon originally observed by Edwin H. Hall in 1879—is the production of a transverse voltage in current carrying conductors subject to an external out-of-plane magnetic field. Studies of the Hall effect have led to important discoveries in condensed matter physics. These include the quantization of the Hall conductance[1] and its interpretation in terms of the topological properties of the Landau levels,[2] which have inaugurated the search for topological phases of matter.[3,4] There is an intimate relation between topology and the Hall effect. The quantum wavefunctions of the electrons in a solid can be in fact endowed with a non-trivial geometric structure. The geometric properties of the wavefunctions, encoded in a quantity called Berry curvature, yield a bending of the electron trajectories in ferromagnetic conductors. This bending, which represents a quantum analogue of the classical Lorentz force, is the origin of the anomalous Hall effect (AHE). Although the AHE has been originally observed by Hall himself and the first underpinning microscopic theories developed in the 1950s by Karplus and Luttinger,[5,6] the fundamental understanding of its intrinsic part in terms of concepts based on geometry and topology has been achieved only recently.[7,8] Since then, an important area of research has concerned the identification of magnetic quantum materials displaying a sizeable AHE both in its unquantized[9] and quantized version.[10,11]

Hall effects cannot instead probe the non-trivial geometric properties of the Bloch states in time-reversal invariant materials with broken inversion symmetry. This is because the Berry curvature of a system with time-reversal symmetry is an odd function of the crystal momentum \(k\). Its integral weighed by the equilibrium Fermi distribution function is then forced to vanish: Kramers’ theorem ensures that states at \(k\) and \(-k\) are either both populated or not populated. It has been recently established,[12–14] however, that this assertion holds true only as long as the linear response regime is considered, that is, for Hall voltages that are linearly proportional to the external electric field. Non-linear Hall currents that are quadratic in the external electric field can appear even in time-reversal symmetric conditions. This non-linear effect has an intrinsic contribution directly related to a quantity that can be seen as the dipole moment of the Berry curvature.[14] The non-linear Hall effect (NLHE) due to the Berry curvature dipole (BCD) has a quantum origin precisely as the intrinsic AHE, but cannot be quantized since it always requires a finite Fermi surface. It is also related to photogalvanic effects—where the geometric properties of the wavefunctions also come into play—involving interband transitions at optical frequencies,[15–27] but with the important difference that the NLHE is governed by intraband processes involving electrons near the Fermi surface.

This characteristic makes the NLHE due to BCD not only a unique toolbox to probe the geometric properties of electronic wavefunctions in time-reversal invariant materials. The NLHE can be used for instance to detect the ferroelectric distortion of the so-called ferroelectric metals, LiOsO\(_3\) being an important material example, which cannot be studied by means of traditional...
ferroelectric techniques due to the presence of free carriers.\[^{18}\] Furthermore, new quantum technologies could directly make use of this effect. The quadratic transverse current-voltage characteristic could be in fact used to rectify\[^{19}\] and detect terahertz radiation\[^{20}\] directly. In addition, such Hall rectifiers would have a number of advantages including the simplicity of the device architecture that would facilitate integration on-chip and mass production.

The aim of this work is to review the fundamental theory and the material realizations of this recently discovered quantum effect. We have structured this review as follows. In Section 2 we discuss the theory underpinning the NLHE with time-reversal symmetric conditions using Boltzmann transport theory. In Section 3 we discuss the appearance of this effect in 2D quantum materials characterized by a strong spin–orbit coupling. In Section 4 we review the mechanism responsible for the NLHE in spin–orbit free 2D graphene. In Section 5 we consider the realization of this effect in bulk non-centrosymmetric 3D crystals. Finally, in Section 6 we draw our conclusions.

## 2. Theory of the Non-Linear Hall Effect in Time-Reversal Symmetric Conditions

### 2.1. Symmetry Constraints on the Non-Linear Hall Effect

In this section we follow ref.\[^{21}\], and present an analysis of the constraints imposed by crystalline symmetries for the occurrence of the NLHE with time-reversal symmetry. As a warmup, let us first consider the crystalline symmetry constraints on the conventional Hall effect found in the linear response regime. Generally speaking, the electric current response to an external electric field is captured by the linear conductivity tensor defined by

\[
\mathbf{J}_L = \sigma_{\alpha\beta} \mathbf{E}_{\beta} \quad (1)
\]

The off-diagonal tensor components regulating transverse currents can be separated into symmetric parts, which appear in systems with sufficiently low symmetry (typically when \(\alpha, \beta\) do not correspond to principal crystallographic directions\[^{22}\]), and a Hall antisymmetric part that, as a consequence of Onsager reciprocity relations\[^{23}\] requires the presence of a time-reversal symmetry breaking field. In 2D systems, the single antisymmetric conductivity tensor component defines the Hall conductivity

\[
\sigma_{n} = \frac{\epsilon_{\alpha\beta} \sigma_{\alpha\beta}}{2} \quad (2)
\]

with \(\epsilon_{\alpha\beta}\) the 2D Levi-Civita symbol. To identify the crystalline symmetry constraints on \(\sigma_{n}\) we first recall that a generic point group symmetry can be represented by an orthogonal matrix \(\mathcal{O}\). Since the current and the electric fields transform as vectors under a generic coordinate change, the conductivity tensor must transform according to \(\mathcal{O}^T \sigma \mathcal{O}\). This transformation rule implies that the antisymmetric Hall conductivity transforms as a pseudodscalar

\[
\sigma_{n} = \text{det}(\mathcal{O}) \sigma_{n} \quad (3)
\]

An immediate consequence of the equation above is that the presence of a point-group symmetry with \(\text{det}(\mathcal{O}) = -1\), for example a mirror line, forces the Hall conductance to vanish.\[^{24}\]

Let us now consider the current response at second-order in electric fields. This defines a non-linear conductivity tensor

\[
\mathbf{j}_n = \chi_{\alpha\beta\gamma} \mathbf{E}_\beta \mathbf{E}_\gamma \quad (4)
\]

In strict analogy with the linear conductivity we can separate the non-linear tensor \(\chi_{\alpha\beta\gamma}\) into components that contribute to the electrical power dissipation \(j_n \mathbf{E}_n\), and dissipationless Hall components. Contrary to \(\sigma_{n}\), these non-linear Hall components are not forced to vanish by time-reversal invariance. They can be identified by antisymmetrizing the first index with either the second or the third—both choices are equivalent because the tensor is by construction symmetric in the last two indices. In the particular case of 2D systems, there are thus two independent components of the non-linear dissipationless Hall conductance reading

\[
\chi_{L\beta} = \frac{\epsilon_{\alpha\beta\gamma} \chi_{\alpha\beta\gamma}}{2} \quad (5)
\]

which transform as a pseudovector under a point group symmetry, that is

\[
\chi_{L\beta} = \text{det}(\mathcal{O}) \mathcal{O}_{\alpha\beta} \chi_{L\alpha} \quad (6)
\]

In this case the presence of a mirror line only forces the non-linear Hall pseudovector to be orthogonal to the mirror line itself. Therefore, \(\chi_{L\beta}\) can be non-vanishing. On the contrary, the presence of two or more mirror lines requires \(\chi_{L\beta}\) to correspond to the null vector. Similarly, if the crystal is centrosymmetric the non-linear Hall response is forced to be zero. Note also that the different transformation properties of the linear (Equation (2)) and non-linear (Equation (5)) conductivity tensors imply that in certain crystalline structures the dissipationless Hall currents are exclusively non-linear, even if time-reversal is explicitly broken. As an example, in crystals with \(C_1\) point group symmetry the linear Hall conductance \(\sigma_{L}\) vanishes independent of the presence of time-reversal symmetry. On the contrary \(\chi_{L\beta}\) will be only orthogonal to the unique mirror line of the crystal.

Following similar arguments, it is possible to derive the symmetry constraints on the (non)linear conductivity tensor in a 3D material. The three independent components of the linear Hall conductance given by \(\sigma_{L\beta} = \epsilon_{\alpha\beta\gamma} \sigma_{\alpha\beta\gamma}/2\) transform as a pseudovector. Therefore, precisely as the non-linear Hall conductance of 2D systems, the Hall vector of a 3D material must be normal to any mirror plane. The presence of two independent mirror planes forces all components of \(\sigma_{L\beta}\) to vanish. The 3D non-linear Hall conductivity has instead nine independent components that transform as a rank-two pseudotensor. This tensor can be decomposed into a symmetric and an antisymmetric part.\[^{14}\] The antisymmetric part transforms as a vector, and is generally non-vanishing in the ten polar point groups \(C_n\) and \(C_{nv}\) where \(n = 1, 2, 3, 4, 6\). For these groups, the polar axis determines the direction of the non-linear Hall vector. The existence of a non-vanishing symmetric part of the 3D non-linear Hall conductance strongly depends on the presence of mirror symmetries. All non-centrosymmetric crystal point groups without left-handed symmetries can have a non-vanishing symmetric part of the non-linear Hall conductance. The only crystal point groups with mirror symmetries that allow for a non-linear Hall tensor are instead \(C_{1h}\), \(C_{2h}\), and \(S_d\). As we will see in the next section,
the non-linear Hall conductance can be directly linked to the BCD using the Boltzmann equation approach in the constant relaxation time approximation.

2.2. Non-Linear Hall Effect Due to Berry Curvature Dipole

We now employ the semiclassical Boltzmann transport framework for a simple single band model to relate the non-linear Hall conductance to the BCD. We recall that in the absence of externally applied magnetic fields, the semiclassical equations of motion accounting for the anomalous velocity term\(^{19,25,26}\) can be written as

\[
\mathbf{f} = \frac{e}{\hbar} \mathbf{v}_k \epsilon(k) + \frac{e}{\hbar} \mathbf{E} \times \Omega_k
\]

(7)

where \(\epsilon\) is the energy dispersion of the metal in question, \(\mathbf{E}\) is the driving electric field, and \(\Omega_k\) is the Berry curvature defined as \(\Omega_{k} = \epsilon_{abc} \partial_a \mathbf{A}_b \). Here \(\mathbf{A}_k\) is the Berry connection associated to the Bloch waves \(|u_k\rangle\) with crystalline momentum \(k\). To proceed further, we use that the electronic distribution function \(f_{\mathbf{k},\tau}\), satisfies the semiclassical Boltzmann equation

\[
\partial_t f_{\mathbf{k},\tau} + \mathbf{v}_k f_{\mathbf{k},\tau} + \mathbf{E} \cdot \nabla \epsilon f_{\mathbf{k},\tau} = I_{\text{coll}}(\epsilon)
\]

(8)

where the collision integral in the relaxation time approximation reads

\[
I_{\text{coll}}(\epsilon) = -\frac{(f_{\mathbf{k},\tau} - f^0_{\mathbf{k}})}{\tau}
\]

(9)

In the equation above \(\tau\) indicates an intraband scattering time and \(f^0_{\mathbf{k}}\) the equilibrium distribution function. We are interested in a stationary and homogeneous solution to the Boltzmann equation. Using Equations (7) and (8) we have

\[
\mathbf{E} \cdot \nabla \epsilon f_{\mathbf{k},\tau} = -\frac{(f_{\mathbf{k},\tau} - f^0_{\mathbf{k}})}{\tau}
\]

(10)

Next, we expand the distribution function in a series as \(f_{\mathbf{k},\tau} = f^0_{\mathbf{k}} + f^1_{\mathbf{k}} + f^2_{\mathbf{k}} + \cdots\) where the term \(f^n_{\mathbf{k}}\) is understood to vanish to the \(\mathbf{E}^n\) order. One then finds the following structure for the linear and non-linear terms in the distribution function

\[
f^1_{\mathbf{k}} = -\frac{e}{\hbar} \mathbf{E} \partial_\epsilon f^0_{\mathbf{k}}
\]

(11)

\[
f^2_{\mathbf{k}} = \frac{e^2}{\hbar^2} \mathbf{E}^2 \epsilon f^0_{\mathbf{k}} \partial_\epsilon \partial_{\mathbf{k}} f^0_{\mathbf{k}}
\]

We now can compute the current using the relation \(j = \epsilon \int d^2k/(2\pi)^2 t_{\mathbf{k}}\). At linear order in the electric field we have

\[
j_\alpha = \frac{e^2}{\hbar^2} \int \frac{d^2k}{(2\pi)^2} \epsilon_{\beta\gamma\delta} \partial_\delta f^0_{\mathbf{k}} \epsilon_{\gamma\delta}(\mathbf{k}) \langle E_\beta \rangle
\]

(12)

In the equation above, the first term in the right hand side is the usual semiclassical contribution to the conductance, which can be expressed in terms of the electronic group velocities. This term can provide a finite contribution to the transverse resistance in low-symmetric crystals. However, such contribution is clearly symmetric in the \(\alpha \leftrightarrow \beta\) exchange and therefore does not enter in the Hall conductance. The second term on the right hand side corresponds instead to the well-known intrinsic contribution to the anomalous Hall conductance. It is controlled by the Berry phases accumulated by the particle motion on the Fermi surface.\(^{19}\) In the presence of time-reversal symmetry, the Berry curvature \(\Omega_k\) is an odd function of the momentum. Consequently, the Hall conductance vanishes in perfect agreement with Onsager relations.\(^{22}\) We next consider the non-linear response of the current \(\alpha E^2\). It is simple to show that it takes the following form

\[
j_\alpha = \frac{e^3}{\hbar^4} \int \frac{d^2k}{(2\pi)^2} \epsilon_{\beta\gamma\delta} \partial_{\delta} f^0_{\mathbf{k}} \epsilon_{\gamma\delta}(k) \partial_\epsilon f^0_{\mathbf{k}} \langle E_\beta E_\gamma \rangle
\]

(13)

The first term, which is of entirely semiclassical origin, vanishes in time-reversal symmetric condition since it involves the three index tensor \(\epsilon_{\beta\gamma\delta}(\mathbf{k}) \partial_\delta f^0_{\mathbf{k}} \partial_{\mathbf{k}} f^0_{\mathbf{k}}\) that is odd under time-reversal. After integration by parts, the non-vanishing non-linear conductivity can be therefore written as

\[
\chi_{\alpha\beta\gamma} = \frac{e^3}{\hbar^4} \int \frac{d^2k}{(2\pi)^2} \epsilon_{\beta\gamma\delta} \partial_{\delta} f^0_{\mathbf{k}} \langle E_\beta \rangle\langle E_\gamma \rangle
\]

(14)

We therefore have that in time-reversal symmetric conditions the dissipationless Hall non-linear current is regulated by the first moment of the Berry curvature, the BCD,\(^{15}\) over the occupied states

\[
D_{\beta\gamma} = \int \frac{d^2k}{(2\pi)^2} \langle \partial_\delta f^0_{\mathbf{k}} \Omega_{\mathbf{k} \beta} \rangle f^0_{\mathbf{k}}
\]

(15)

The BCD is subject to the symmetry constraints introduced in the preceding section for the non-linear Hall conductance. In 2D systems, for instance, the Berry curvature is a pseudoscalar and therefore the BCD behaves as a pseudovector precisely as \(\chi_{\alpha\beta\gamma}\) does.

In our foregoing discussion, we have considered the dc limit. When accounting for an ac driving electric field, non-linear Hall currents yield a current response at twice the driving frequency with the addition of a rectified current. Specifically for a driving electric field \(\mathbf{E}(t) = \text{Re}[\mathbf{E} e^{i\omega t}]\), with \(\mathbf{E} \in \mathbb{C}\), the resulting current at twice the frequency \(f_{2\omega} = \omega E_{\mathbf{k}}\mathbf{E}^\dagger\mathbf{E}\) while the rectified current \(j^0 = \chi_{\alpha\beta\gamma} E^\dagger\mathbf{E}\). The ac non-linear response function takes the following form

\[
\chi_{\alpha\beta\gamma} = \frac{e^3}{2\hbar^2(1 + i\omega\tau)} \int \frac{d^2k}{(2\pi)^2} \epsilon_{\beta\gamma\delta} \langle \partial_\delta f^0_{\mathbf{k}} \Omega_{\mathbf{k} \beta} \rangle f^0_{\mathbf{k}}
\]

(16)

It is interesting to note that at frequencies above the width of the Drude peak \(\omega \tau \gg 1\) but below the interband transition threshold, the non-linear response function becomes independent of...
the scattering time and therefore provides a direct measure of the geometric properties of the electronic wavefunctions.

2.3. Disorder-Induced Contributions to the Non-Linear Hall Effect

The BCD does not completely determine the NLHE of a non-centrosymmetric quantum material. Using either a quantum Boltzmann transport approach or a semiclassical Boltzmann theory beyond the constant relaxation time approximation, it can be shown that other disorder-mediated contributions to the non-linear Hall conductance exist. These “extrinsic” contributions are the non-linear counterparts of the side-jump and skew-scattering contributions appearing in the linear AHE. In this section we review the Boltzmann semiclassical transport framework following ref. [29], to which we refer the readers interested in further details.

Let us start out by rewriting the collision integral appearing in the kinetic equation (Equation (8)) as

\[ I_{\text{coll}}(j_l) = - \sum_p \left( \alpha_p j_l - \alpha_p f_p \right) \]

where the label \( l \) is a composition a band and momenta indices \((n, k)\) whereas \( \sum_p = \sum_n \int d^3k/(2\pi)^3 \). In addition, \( \alpha_p \) is the disorder averaged scattering rate between the Bloch waves with quantum numbers \( l \) and \( l' \). The scattering rate \( \alpha_{p\gamma} \) can be related to the T-matrix element via

\[ \alpha_{p\gamma} = \frac{2\pi}{\hbar} |T_{p\gamma}|^2 \delta(e_i - e_f) \]

The scattering T matrix is defined as \( T_{p\gamma} = \langle l' | \hat{V}_{\text{imp}} | \gamma \rangle \) with \( \hat{V}_{\text{imp}} \) indicating the impurity potential operator whereas \( |\gamma\rangle \) represents the eigenstate of the full Hamiltonian \( \hat{H} = \hat{H}_0 + \hat{V}_{\text{imp}} \) satisfying the Lippman-Schwinger equation

\[ |\psi_l\rangle = |l\rangle + \sum_{\gamma} \frac{\hat{V}_{\text{imp}}}{e_i - e_{\gamma} + i\epsilon} |\gamma\rangle \]

For weak disorder one can approximate the scattering state \( |\psi_l\rangle \) by a truncated series in powers of \( V_{\text{imp}} = \langle l' | \hat{V}_{\text{imp}} | l' \rangle \) as

\[ |\psi_l\rangle = |l\rangle + \sum_{\gamma} \frac{V_{\text{imp}}}{e_i - e_{\gamma} + i\epsilon} |\gamma\rangle + \cdots \]

Inserting this relation in the expression for the T-matrix element, we can expand the scattering rate in powers of the disorder strength as

\[ \alpha_{p\gamma} = \alpha_{p\gamma}^{(2)} + \alpha_{p\gamma}^{(3)} + \alpha_{p\gamma}^{(4)} + \cdots \]

The scattering rate \( \alpha_{p\gamma}^{(2)} = 2\pi(|V_{\text{imp}}|^2) \delta(e_i - e_f)/\hbar \) is symmetric under the \( l \leftrightarrow l' \) exchange. The higher-order corrections instead contain both a symmetric and an antisymmetric term. The symmetric components of \( \alpha_{p\gamma}^{(1,4)} \) can be neglected since they only renormalize the second-order scattering rate \( \alpha_{p\gamma}^{(2)} \). On the contrary, the antisymmetric contributions to \( \alpha_{p\gamma}^{(3,4)} \) yield the non-linear skew-scattering contribution to the NLHE with time-reversal symmetry. To show this, we first go back to the Boltzmann equation and rewrite explicitly the collision integral using the symmetric and antisymmetric contributions as follows:

\[ \frac{\epsilon}{\hbar} \mathbf{E} \cdot \nabla f_l = - \sum_p \alpha_p^{(2)} (f_l - f_p) - \sum_p \alpha_p^{(4)} (f_l + f_p) \]

where now \( \alpha_p^{(4)} \) contains the antisymmetric contributions of both \( \alpha_p^{(3)} \) and \( \alpha_p^{(4)} \). The equation above, however, does not account for the microscopic displacement \( \delta r_p \) experienced by a wavepacket when scattering from a generic state \( l \) to \( l' \). Assuming smooth impurity potentials the gauge-invariant expression for this coordinate shift, usually referred to as side-jump, reads as

\[ \delta r_p = \langle u_l | i \hat{\mathbf{a}}_k u_r \rangle - \langle u_l | i \hat{\mathbf{a}}_k u_r \rangle - \hat{D}_{k,k} \text{arg}[\langle u_l | u_r \rangle] \]

where \( \text{arg} \) is the phase of the complex number and we introduced the operator \( \hat{D}_{k,k} = \delta_k + \delta_{-k} \). In the presence of the external driving electric field the microscopic displacement \( \delta r_p \) yields an energy shift \( \Delta U_p = -e \mathbf{E} \cdot \delta r_p \) that should be taken into account in the scattering rate. Specifically, the symmetric second-order scattering rate has to be modified as

\[ \alpha_p^{(2)} \rightarrow \alpha_p^{(2)} = \frac{2\pi}{\hbar} \langle |V_{\text{imp}}|^2 \rangle \delta(e_i - e_f - e \mathbf{E} \cdot \delta r_p) \]

\[ = \frac{2\pi}{\hbar} \langle |V_{\text{imp}}|^2 \rangle \delta(e_i - e_f) + e \mathbf{E} \cdot \delta r_p \frac{\partial}{\partial e_i} \delta(e_i - e_f) \]

where we have used the antisymmetric property (cf. Equation (23)) of the side-jump \( \delta r_p \). The Boltzmann equation (Equation (22)) is then modified as

\[ \frac{\epsilon}{\hbar} \mathbf{E} \cdot \nabla f_l = - \sum_p \left[ \alpha_p^{(2)} + e \mathbf{E} \cdot \delta r_p \frac{\partial}{\partial e_i} \delta(e_i - e_f) \right] \]

where we introduced the quantity

\[ \delta r_p = \langle u_l | i \hat{\mathbf{a}}_k u_r \rangle - \langle u_l | i \hat{\mathbf{a}}_k u_r \rangle - \hat{D}_{k,k} \text{arg}[\langle u_l | u_r \rangle] \]

To proceed further, we decompose the distribution function into three different terms, that is, \( f_l = f_l^{\text{int}} + g_l^{\text{skew}} + g_l^{\text{dis}} \), where the intrinsic distribution function \( f_l^{\text{int}} = f_l^{\text{int}} + g_l^{\text{skew}} + f_l^{\text{dis}} \) indicates the equilibrium distribution function. We next seek an approximate solution to the Boltzmann equation (Equation (26)) by decomposing it into three (time-independent) equations reading

\[ \frac{\epsilon}{\hbar} \mathbf{E} \cdot \nabla f_l^{\text{int}} = - \sum_p \alpha_p^{(2)} (g_l^{\text{dis}} - g_i^{\text{dis}}) \]

\[ \frac{\epsilon}{\hbar} \mathbf{E} \cdot \nabla g_l^{\text{skew}} = - \sum_p \alpha_p^{(2)} (g_l^{\text{skew}} - g_i^{\text{skew}}) - e \mathbf{E} \cdot \sum_p \delta r_p (f_l^{\text{int}} - f_p) \]

\[ \frac{\epsilon}{\hbar} \mathbf{E} \cdot \nabla g_l^{\text{dis}} = - \sum_p \alpha_p^{(2)} (g_l^{\text{dis}} - g_i^{\text{dis}}) - \sum_p \alpha_p^{(4)} (g_i + g_l^{\text{dis}}) \]

As before, we expand the three terms \( g_l^{\text{dis}}, g_l^{\text{skew}}, \) and \( g_l^{\text{dis}} \) in a series where each term \( g_l^{\text{dis}} \) vanishes as \( F^* \). In addition, the term in the
collision integral containing the symmetric scattering \( a_r^{(i)} \) will be solved in the relaxation time approximation. Assuming the latter to be constant for simplicity, we find that the linear and quadratic terms \( \delta g \) correspond to Equation (11) as expected. Next, we determine the anomalous \( g_{\text{dis}}^{\text{adia}} \) distribution due to the coordinate shift \( \delta r_i \). At linear order we have

\[
0 = -\frac{g_{\text{dis}, 1}^{\text{adia}}}{\tau} - eE \cdot \sum f^{(i)}_0 = f^{(i)}_0 \right) \tag{29}
\]

Introducing the velocity contribution due to the accumulation of coordinate shifts after many scattering events\([32,33]\) \( \psi^i_l = \sum a_l^{(i)} \delta r_i \), and after straightforward manipulations, the linear anomalous distribution term can be recast as

\[
g_{\text{dis}, 1}^{\text{adia}} = e\tau E \cdot \psi^i_l \mathbf{v}_l \frac{\partial f^{(i)}_0}{\partial \epsilon_l} \tag{30}
\]

The quadratic contribution to the anomalous distribution function is instead determined by the equation

\[
\frac{\tau}{\hbar} E \cdot \nabla_k g_{\text{dis}, 1}^{\text{adia}} = -eE \cdot \sum f^{(i)}_0 (g^i_l - g^i_l) \tag{31}
\]

Using Equation (30) and the expression for the linear intrinsic distribution function Equation (11), we find

\[
g_{\text{dis}, 1}^{\text{adia}} = -\frac{e^2 \tau}{\hbar} E \cdot \nabla_k \left( E \cdot \psi^i_l \mathbf{v}_l \frac{\partial f^{(i)}_0}{\partial \epsilon_l} \right) + \frac{e^2 \tau}{\hbar} E \cdot \sum f^{(i)}_0 \left( [E \cdot \nabla_k f^{(i)}_0 - E \cdot \nabla_k f^{(i)}_0] \right) \tag{32}
\]

Next, we turn to the skew-scattering term \( g_{sk} \). From the third equation in Equation (28), we find the linear order contribution

\[
g_{sk}^{(1)} = \frac{e^2 \tau}{\hbar} \sum f^{(i)}_0 \left( [E \cdot \nabla_k f^{(i)}_0 + E \cdot \nabla_k f^{(i)}_0] \right) \tag{33}
\]

Using the equation above, we can also determine the first non-linear contribution to the skew-scattering distribution. It reads:

\[
g_{sk}^{(1)} = \frac{e^2 \tau}{\hbar} \left\{ E \cdot \nabla_k \sum f^{(i)}_0 \left( [E \cdot \nabla_k f^{(i)}_0 + E \cdot \nabla_k f^{(i)}_0] \right) \right\} + \sum f^{(i)}_0 \left( [E \cdot \nabla_k (E \cdot \nabla_k f^{(i)}_0) + E \cdot \nabla_k (E \cdot \nabla_k f^{(i)}_0)] \right) \tag{34}
\]

Having in our hands both the linear and quadratic contributions to the anomalous and skew-scattering distribution functions, we next evaluate the response current to a driving electric field \( j = e \sum \mathbf{i} f_l \). In doing so, we note that the side-jump velocity explicitly enters into the semiclassical equation of motion\([9,26,29-33]\)

\[
j_l = \frac{1}{\hbar} \nabla_k \epsilon_l + \frac{e}{\hbar} E \times \Omega_i + \psi^i_l \tag{35}
\]

This implies that in the linear response regime there are three disorder-mediated contributions beyond the semiclassical and anomalous Hall conductance of Equation (12). There is a first contribution due to the anomalous side-jump distribution that yields a conductivity

\[
\alpha_{\text{si}}^{(1)} = \frac{e^2 \tau}{\hbar} \sum f^{(i)}_0 \frac{\partial f^{(i)}_0}{\partial \epsilon_l} \tag{36}
\]

In addition, the side-jump velocity appearing in the equation of motion contributes with an additional conductivity

\[
\alpha_{\text{si}}^{(2)} = -\frac{e^2 \tau}{\hbar} \sum f^{(i)}_0 \frac{\partial f^{(i)}_0}{\partial \epsilon_l} \tag{37}
\]

We point out that we have neglected terms \( \propto \psi^i_l g_{\text{dis}, 1}^{\text{adia}, 1} \), since they are of higher-order in the scattering rate \( \omega \). Finally, the skew-scattering contribution to the distribution function leads to the conductivity

\[
\alpha_{sk}^{\text{adia}} = -\frac{e^2 \tau}{\hbar} \sum f^{(i)}_0 \frac{\partial f^{(i)}_0}{\partial \epsilon_l} \tag{38}
\]

In systems with broken time-reversal symmetry, Equations (36)–(38) provide the side-jump and skew-scattering contributions to the anomalous Hall conductance. Note that Equation (38) can be split into two different contributions corresponding to the antisymmetric scattering rates \( a_l^{(i)} \) and \( a_l^{(i)} \). In time-reversal symmetric conditions these extrinsic contributions to the Hall conductance are forced to vanish, precisely as the anomalous Hall conductance due to the Berry curvature does. This is because the coordinate shift \( \delta r_i \), and consequently the side-jump velocity \( \psi^i_l \), are even under time-reversal. Since the conventional group velocity \( \alpha \nabla_k \) is odd under time-reversal, one finds that the side-jump conductivities \( \alpha^{(1,2)}_{sk} \) are identically zero. The same holds true for the skew-scattering contribution since the antisymmetric scattering rate is odd under time-reversal.

We now evaluate the non-linear disorder-induced conductivity. Using the aforementioned symmetry constraints, it is easy to show that the terms quadratic in the driving electric field where the anomalous velocity is coupled to the distribution functions \( g_{\text{dis}, 1}^{\text{adia}} \) and \( g_{\text{dis}, 1}^{\text{adia}} \) are forced to vanish by time-reversal. As a result, we have that the only Berry curvature mediated term corresponds to the dipole of Equation (14). In perfect analogy with the linear conductivity, there are three disorder-induced non-linear conductivities. The first contribution comes from the second-order anomalous distribution function \( g_{\text{dis}, 2}^{\text{adia}} \). From Equation (32) and after simple manipulations it can be recast as

\[
\lambda^{(2)}_{sk} = \frac{e^2 \tau}{\hbar} \sum f^{(i)}_0 \left( \nabla_k \mathbf{v}^i_l + \mathbf{M}^i_l \right) \nabla_k \epsilon_l + \left( \nabla_k \nabla_k \epsilon_l \right) \frac{\partial f^{(i)}_0}{\partial \epsilon_l} \tag{39}
\]

where we introduced the tensor

\[
\mathbf{M}^i_l = \frac{2\pi}{\hbar} \sum \left( \nabla_k \left( [|\mathbf{v}^i_l|^2]_{\text{dis}} \delta r_i \right) \right) \nabla_k \left( [|\mathbf{v}^i_l|^2]_{\text{dis}} \delta r_i \right) \tag{40}
\]
The contribution due to the side-jump velocity can be instead put as
\[
\chi^{\alpha\beta}_{\alpha\beta} = \frac{e^2}{\hbar} \sum_j \sum_i V_{ji}^0 \nabla_{\alpha} V_{ji}^0 f_i^0.
\]
(41)

Finally, the non-linear skew scattering distribution function yields the additional conductivity
\[
\chi^{\alpha\beta}_{\alpha\beta} = \frac{e^2}{\hbar} \sum_{\beta} \sum_{\alpha} \int \left( \nabla_{\alpha} V_{\beta}^0 - \nabla_{\alpha} V_{\beta}^0 \right) \nabla_{\beta} V_{\alpha}^0 f_i^0
- \left( \nabla_{\beta} V_{\alpha}^0 - \nabla_{\beta} V_{\alpha}^0 \right) \nabla_{\beta} V_{\alpha}^0 f_i^0.
\]
(42)

Equations (39)–(42) represent the disorder-induced terms in the non-linear Hall conductivity in the dc limit assuming a constant relaxation time. As mentioned above, these results can be easily generalized to a driving a.c. electric field and a general relaxation time (see ref. [29] for further details). In closing this section, we point out that the disorder-induced contributions to the non-linear Hall conductance have a dependence in the impurity concentration \( n_i \) given by \( y^\nu (n, V_i^0) \), with \( V_i^0 = (V_i^0)_{\text{dBZ}} \) and \( V_i \) the random disorder strength. This also implies that precisely as the BCD contribution Equation (14), the disorder-mediated corrections to the non-linear Hall conductance grow linearly with the relaxation time. Nevertheless, the different contributions to the non-linear Hall conductance can be experimentally separated using the scaling between the non-linear Hall signal and the conventional longitudinal (linear) resistivity, in analogy with the scaling used in the AHE.[14,35]

3. Strongly Spin–Orbit Coupled 2D Materials

3.1. Tilted Massive Dirac Cones

Beside the general symmetry constraints discussed in Section 2.1, the intrinsic Berry curvature-mediated contribution to the non-linear Hall conductance is subject to other point-group symmetry restrictions. These are of primary importance in identifying materials that possess substantial BCD. Let us first consider the specific role played by rotational symmetries. As long as time-reversal symmetry is preserved, all systems with an evenfold rotation symmetry \( C_n \) (with \( n = 2, 4, 6 \)) cannot have a finite BCD. This is because the composed symmetry \( C_n \Theta \) with \( \Theta \) the time-reversal operator, is an antiunitary symmetry that squares to one. Moreover this symmetry acts locally in momentum space since it brings the 2D momentum \( k \) back to itself. These two properties imply that the Berry curvature is forced to vanish for all momenta in the 2D Brillouin zone (BZ).[36] Consequently, a non-vanishing Berry curvature can only appear in 2D crystals where there is either a threefold rotation symmetry or all rotation symmetries are broken. For the latter, and as discussed in Section 2.1, the presence of a mirror line still allows for a non-vanishing BCD that is forced to be orthogonal to the mirror line. In the absence of mirror symmetries instead, the BCD will not be pinned to any specific direction. In the remainder we will discuss systems with a single mirror line symmetry, that is, with point group symmetry \( C_\nu \). In order to have a sizable Berry curvature, the low-energy electronic properties of such systems must be described by massive Dirac cones. Furthermore, the absence of rotational symmetries implies that there is no fermion multiplication theorem,[37] and the minimum number of massive Dirac cones allowed by symmetry is two.[38] To preserve the mirror symmetry these two massive Dirac cones will be located specularly with respect to the mirror-symmetric line of the 2D BZ. To make things concrete, consider for instance the reflection symmetry to map a point with coordinates \((x, y)\) to \((x, -y)\). The massive Dirac cones will then be centered around two valleys \( \Lambda_{1,2} = \{k_x, \pm k_y\} \). The effective Hamiltonian close to these valleys can be derived by accounting for all symmetry-allowed terms in a \( k \cdot p \) expansion. Time-reversal symmetry gives the constraint on the effective Hamiltonian \( \Theta^{-1} \mathcal{H}_{\text{eff}} (k_x, k_y) \Theta = \mathcal{H}_{\text{eff}} (-k_x, -k_y) \). The time-reversal operator can be represented as \( \Theta = i \sigma_z \tau_x \) where the Pauli matrix vectors \( \sigma \) and \( \tau \) act in spin and valley space respectively, whereas \( K \) is the complex conjugation. Similarly, the mirror symmetry gives the constraint \( \mathcal{M}^{-1} \mathcal{H}_{\text{eff}} (k_x, k_y) \mathcal{M} = \mathcal{H}_{\text{eff}} (k_x, -k_y) \). The mirror symmetry operator takes the form \( \mathcal{M} = -i \sigma_z \tau_x \) since it exchanges the valleys, as time-reversal does, and acts in spin space as exp \( -i \sigma_x \tau_x / 2 \). Retaining terms up to linear order in momentum \( k \) and neglecting intervalley mixing terms—this condition amounts to keep only symmetry allowed terms \( \sigma \tau \tau \)—the low-energy continuum Hamiltonian gets the following form:

\[
\mathcal{H}_{\text{eff}} = \alpha \tau_x \sigma_z k_y + (\nu \cdot k_x \sigma_y - \nu \cdot k_y \sigma_x) \otimes \tau_x + m \sigma_z
\]
(43)

In the equation above we have neglected a term of the form \( \alpha \tau_x \sigma_z \) since this term shifts in a time-reversal symmetric manner the two valleys \( \Lambda_{1,2} \), and can be thus reabsorbed in the effective Hamiltonian by a proper redefinition of the momentum \( k_x \).

Equation (43) corresponds to the low-energy theory of a massive Dirac cone except for the term proportional to \( \alpha \), which produces a tilt as shown in Figure 1a.

The presence of this tilt term is key for the occurrence of a finite BCD,[14,12,20] as we now discuss. It is straightforward to show that the Berry curvature is independent of the tilt strength and can be written as

\[
\Omega_{k_x} = \pm \frac{\tau \nu \nu \cdot m}{2 (m^2 + \nu^2 k_x^2 + \nu^2 k_y^2)^{3/2}}
\]
(44)

where the \( \pm \) sign refers to the conduction and valence bands respectively, and \( \tau = \pm 1 \) for the two valleys \( \Lambda_{1,2} \). In each valley the Berry curvature is an even function of the momentum \( k \) measured relatively to the Dirac points. Therefore, the BCD density \( \partial_{\nu} \Omega_{k_x} \) is an odd function of the momentum. The contribution to the BCD coming from each valley is identically zero in the absence of a tilt term. The situation is different for \( a \neq 0 \). In this case the Fermi lines become elliptical, and the contribution to the BCD in each valley is different from zero (cf. Figure 1b–e). In addition, the contribution from the two different valleys is same since the elliptical distortion of the Fermi lines is opposite in the two valleys. As a final result, we have that the BCD density is directly proportional to the tilt parameter \( a \). Another way to understand that the finite value BCD is entirely due to the tilt term is to
transform $D_y$ as a line integral over the Fermi line of the system as

$$D_y = \sum_k \int \frac{d^3k}{(2\pi)^2} \Omega_{k_y} v_k^y \times \delta(e - e_F)$$

(45)

In the absence of a tilt term, this integral vanishes in each valley since the Berry curvature is constant on the Fermi lines whereas the group velocity in the $\hat{y}$ direction is equal but opposite on the opposite sides of the Fermi surface. Tilting the Dirac cones allows for a mismatch between left and right movers in each valley (see Figure 2a,b) leading to a finite contribution to the BCD. Furthermore, the contribution to the dipole coming from the two valleys is equal since the opposite mismatch between left and right movers is compensated by the opposite values of the Berry curvature. Using Equation (45) it is possible to provide an analytical expression for the BCD in systems with tilted massive Dirac cones. Consider for simplicity the case in which $v_x = v_y = v$, and assume the tilt parameter $a$ to be small as compared to the Fermi velocity $v$. Expanding the Dirac delta as

$$\delta(e - e_F) = \delta(e^0 - e_F) + a v k_y \partial_{k_y} \delta(e^0 - e_F),$$

with $e^0$ indicating the energy of the untitled massive Dirac cone, the BCD can be found to be

$$D_y = \frac{3a}{4\pi} \frac{m}{v_F^2} \left[ e_F^2 - m^2 \right]$$

(46)

where we considered the Fermi energy to be in the conduction band. It is important to note that as a function of the chemical potential, the BCD displays a characteristic non-monotonous behavior[14] (see Figure 2c). A similar feature is also found when explicitly computing the disordered-averaged contributions to the NLHE discussed in the previous section.[21,29] The overall contribution, however, does not cancel out and is still finite.

3.2. Surface States of Topological Crystalline Insulators

The surface states of the topological crystalline insulator SnTe[39-41] represent a paradigmatic example of tilted massive Dirac cones. This makes SnTe a prime material platform for the realization of the quantum NLHE in time-reversal symmetric conditions. Generally speaking, the group-IV tellurides have a high-temperature rocksalt crystal structure with a face-centered cubic BZ (cf. Figure 3). The BZ is bounded by six square faces and eight hexagonal faces.[39] The centers of the latter, commonly denoted by $L$, represent the equivalent high-symmetry points of the BZ where the fundamental gap of the SnTe or PbTe is located. The band structure in the immediate vicinity of the four equivalent $L$ points can be captured using a four-band $k \cdot p$ model[42] that spans spin space and the $p$-orbital space of the anion (Te) and cation (Pb,Sn). In PbTe, the valence band is derived from the $p$-orbital of the anion while the conduction band from the cation Pb. On the contrary, SnTe has an inverted band ordering with the valence band derived from the cation Sn and the conduction band from Te. The inverted ordering of the bands of SnTe as compared to PbTe establishes the former as a
Figure 2. a,b) Contour plot of the group velocity $v_g$ in a pair of tilted massive Dirac cones. The parameter set is same as in Figure 1. c) Behavior of the Berry curvature dipole in a system with a pair of tilted massive Dirac cones as regulated by Equation (46).

Figure 3. Left panel: High-temperature rocksalt crystal structure of SnTe. Right panel: Corresponding Brillouin zone with the high-symmetry points $L$, the Brillouin zone center $\Gamma$ and the mirror symmetric plane. We also show the (001) surface BZ projection with highlighted high-symmetry lines.

topological crystalline insulator. The bulk crystalline topology of the material comes about the non-trivial mirror Chern number associated to the $\Gamma L_1 L_2$ plane of the BZ (see Figure 3), which is left invariant by the (110) mirror symmetry of the rocksalt crystal structure. The non-trivial value of the mirror Chern number implies the presence of counterpropagating midgap modes on the surface projections of the mirror invariant plane.$^{[39,43]}$ This, for instance, applies to the $\Gamma - \bar{X}_1$ line of the (001) surface BZ. Since the mirror Chern number associated to the $\Gamma L_1 L_2$ plane $n_{s,1} = 2$, there will be two pairs of counterpropagating edge modes along the $\Gamma - \bar{X}_1$ line. In addition, since the left and right edge modes belong to the different $\pm i$ mirror sectors, their crossings cannot be gapped. On the contrary, away from the $\Gamma - \bar{X}_1$ the absence of mirror symmetry allows for the gapping of the edge modes. The crossings on the $\Gamma - \bar{X}_1$ line of the (001) surface BZ are the Dirac points of two topologically protected surface Dirac cones. By rotational symmetry, such surface Dirac cones also appear along the $\Gamma - \bar{X}_2$ line. One can derive the electronic characteristics of these four surface Dirac cones by using a 2D $\mathbf{k} \cdot \mathbf{p}$ theory close to the $\bar{X}_{1,2}$ points of the surface BZ.$^{[44]}$ This can be found by simply noticing that the $\bar{X}_{1,2}$ points of the surface BZ are invariant under a twofold rotation symmetry $C_2$, and the two mirror line symmetries $M_{x,y}$—from here onwards we denote with $\hat{x}$ the (110) direction perpendicular to the mirror plane. As in our former analysis, these symmetry operations, together with time-reversal symmetry, constrain the terms allowed in the $\mathbf{k} \cdot \mathbf{p}$ expansion for the surface Dirac cones. Furthermore, the...
representation of the four symmetries can be derived by noticing that the \( \bar{X}_1 \) points of the (001) surface BZ correspond to the surface projections of two of the four equivalent \( L \) points of the BZ (see Figure 3). Imagine now that instead of considering an atomically sharp interface between the vacuum and the material bulk, one would consider a smooth interface separating SnTe from PbTe. Then, one would expect Dirac-like domain wall states, each of which comes from the change in the mass gap in one specific \( L \) point of the BZ. At \( \bar{X}_1 \) one would then expect two different flavors of Dirac-like states. Consequently, the minimal surface \( \mathbf{k} \cdot \mathbf{p} \) theory should account for such a flavor degree of freedom together with the spin degree of freedom. This clearly holds true even when the smooth interface is substituted by an atomically sharp interface. With this in mind, we can proceed to find the representations of the symmetry operations that constraint the surface low-energy theory. Let us explicitly consider the low-energy theory for the surface states projected onto the \( \bar{X}_1 \) point of the surface BZ. The theory close to the \( \bar{X}_1 \) point can be obtained following the same strategy.

The internal time-reversal symmetry does not act on the flavor degree of freedom. Therefore it can be represented, as usual, by \( \Theta = i \sigma_y \mathcal{K} \) where \( \mathcal{K} \) is the complex conjugation and the Pauli vector \( \sigma \) acts in spin space. The twofold rotation operator \( C_{\bar{x}} \) interchanges the \( L_{\bar{1},2} \) valleys while it can be represented in spin space by \( -i \sigma_x / \sqrt{2} \). As a result, the twofold rotation operator is represented by \( C_{\bar{x}} = -i \tau_x \sigma_z \). Similarly to the twofold rotation operation \( C_{\bar{x}} \), also the mirror symmetry \( M_{\bar{x}} \) interchanges the \( L_1 \) point with \( L_2 \). Hence, this mirror symmetry can be represented as \( M_{\bar{x}} = -i \sigma_y \tau_x \). On the contrary, the mirror symmetry \( M_{\bar{x}} = -i \sigma_x \tau_y \) since it does not interchange the two projected \( L \) points. With this, we can write the surface \( \mathbf{k} \cdot \mathbf{p} \) theory away from the \( \bar{X}_1 \) point of the surface BZ. Specifically, by retaining flavor mixing terms up to zeroth order in momentum the low-energy theory can be found to be

\[
H_{k_p} = m \tau_x \sigma_0 + \delta \tau_y \sigma_0 + (v_x k_x \sigma_y - v_y k_y \sigma_z) \otimes \tau_0
\]  

(47)

As expected, the surface states are gapped specifically on the \( k_z = 0 \) line, that is, along the \( \bar{X}_1 - \bar{M} \) direction of the surface BZ. On the contrary the \( M_{\bar{x}} \) symmetry guarantees the presence of two zero-energy Dirac points for \( k_y = \pm v / \sqrt{m^2 + \delta^2} \) on the \( k_z = 0 \) line. In perfect accord with the foregoing general symmetry analysis, the in-gap surface states realize two Dirac cones located at \( \Lambda_{1,2} \) with an effective Hamiltonian

\[
H_{\text{Dirac}} = \bar{v}_s \delta k_x \sigma_y - v_y \delta k_y \sigma_z
\]  

(48)

where we introduced the momentum \( \delta k = \mathbf{k} - \Lambda_{1,2} \) and the renormalized velocity \( \bar{v}_s = v_s \delta / \sqrt{m^2 + \delta^2} \). As mentioned above, this form of the surface states for SnTe has been found by neglecting flavor mixing term \( \tau_y k_{x,y,z} \) linear in momentum. If the latter were to be considered, the following perturbation should be added to the original surface \( \mathbf{k} \cdot \mathbf{p} \) Hamiltonian:

\[
\Delta H_{k_p} = (\alpha_x k_x \sigma_y - \alpha_y k_y \sigma_z) \otimes \tau_0 + \beta \tau_0 \sigma_0 \tau_0 + \gamma k_x \sigma_z \tau_z
\]  

(49)

Projecting this term in the low-energy Hamiltonian of Equation (48) is modified in two different ways. First, it leads to an additional renormalization of the Fermi velocity \( \bar{v}_s \). Second, it yields a tilt of the surface Dirac cones. The corresponding low-energy theory reads

\[
H_{\text{Dirac}} = a \bar{v}_s \delta k_x \sigma_y + \bar{v}_s \delta k_y \sigma_z - v_y \delta k_y \sigma_z
\]  

(50)

where the tilt parameter \( a \) is directly proportional to the \( \mathbf{k} \cdot \mathbf{p} \) parameters \( \alpha, \beta \) whereas \( \chi = \pm 1 \) distinguishes the \( \Lambda_{1,2} \) valleys.

The absence of a surface energy gap does not allow for a finite Berry curvature. The latter, however, naturally arises\(^{[46,47]}\) when considering a ferroelectric distortion whereby the Sn and Te atoms are displaced along different directions. SnTe is known to undergo a structural transition at low temperatures\(^{[48–50]}\) that involves precisely such a ferroelectric distortion. Besides yielding a finite ferroelectric polarization, this structural distortion breaks completely the rotational symmetry\(^{[51]}\) Moreover if the displacement vector is along the \( \bar{x} \) direction, the structural distortion breaks the \( \mathbf{M}_x \) mirror symmetry, whereas a displacement in the orthogonal direction leads to a loss of the \( \mathbf{M}_y \) reflection symmetry. Using the preceding symmetry analysis, it can be shown that breaking the \( \mathbf{M}_x \) symmetry changes the crossings of the states along the \( \Gamma - \bar{X}_1 \) line into avoided level crossings, and ultimately the Dirac cones centered at \( \Lambda_{1,2} \) acquire a mass gap. Breaking instead the \( \mathbf{M}_y \) symmetry preserves massless Dirac fermions close to the \( \bar{X}_1 \) point of the surface BZ.\(^{[45]}\) The situation is of course reversed when considering the surface states located close to the \( \bar{X}_1 \) point of the surface BZ. All in all, we therefore have that a ferroelectric distortion with the displacement vector oriented along a principal crystallographic direction of the surface BZ will result in the gapping of two out of the four (001) surface Dirac cones of SnTe.

To concretely show how a mass gap for the surface Dirac cones at \( \Lambda_{1,2} \) appears when the \( \mathbf{M}_y \) reflection symmetry is broken, it is sufficient to notice that in this situation an additional symmetry-allowed term has to be included in the \( \mathbf{k} \cdot \mathbf{p} \) Hamiltonian of Equation (47). It reads

\[
H_{k_p}^{M_y} = w_{x,y} \tau_0 \tau_z
\]  

(51)

Projecting this term onto the low-energy surface state Hamiltonian, we find that the ferroelectric distortion yields two opposite masses for the two surface Dirac fermions centered at \( \Lambda_{1,2} \). Therefore, the full Hamiltonian can be recast as

\[
H_{\text{Dirac}} = a \bar{v}_s \delta k_x \sigma_y + \bar{v}_s \delta k_y \sigma_z - v_y \delta k_y \sigma_z + \beta \chi \tau_z
\]  

(52)

where \( \chi = \pm 1 \) distinguishes the \( \Lambda_{1,2} \) valleys. We have therefore reached the massive tilted Dirac fermion model introduced in the preceding section and characterized by a non vanishing BCD.

### 3.3. Transition Metal Dichalcogenide Monolayers

Having established the occurrence of a finite BCD at the topological surface states of SnTe, we next show its appearance in 2D crystals characterized by a strong spin–orbit coupling. Due to the presence of massive Dirac cones, transition metal dichalcogenides (TMDs) in their so-called 1H form (see Figure 4a) have been proposed as candidate materials carrying a sizable BCD.\(^{[52]}\) Because of the concomitant presence of a threefold rotation symmetry and a vertical mirror symmetry, 1H-TMDs do not satisfy
the symmetry constraints discussed in Section 2.1. Consequently an external perturbation lowering the symmetry, namely uniaxial strain, needs to be applied.

Generally speaking, 1H monolayers of group-VI dichalcogenides MX₂ (with M=Mo,W and X=S, Se, Te) have a direct band-gap in the visible frequency range\(^{[53,54]}\) with conduction and valence bands edges that are located at the corners of the 2D hexagonal BZ. As a result, the low-energy properties of these systems are very similar to graphene but with two important differences. First, inversion symmetry is explicitly broken thus implying a non-vanishing Berry curvature.\(^{[55,56]}\) Second, TMDs have a strong spin–orbit coupling resulting from the \(d\)-band of the heavy metal atom. The appearance of massive Dirac cones can be immediately understood by first neglecting spin–orbit coupling all together. Density functional theory calculations\(^{[57-60]}\) show that the electronic band structure consists of partially filled \(d\)-bands of the heavy metal ion lying between M-X \(s\) – \(p\) bonding and antibonding bands. The trigonal prismatic coordination of the transition metal ions (see Figure 4a) splits its \(d\)-bands into a single 1D representation—the \(d_{z^2}\) orbital—and two different 2D representations that differ from each other in the ±1 eigenvalue of the reflection symmetry with respect to the (horizontal) mirror plane. Specifically, the \(d_{x^2−y^2}\) and \(d_{xy}\) orbitals form the so-called irreducible \(E\) representation, whereas the \(d_{xz}\) and \(d_{yz}\) orbitals give rise to the so-called \(E'\) 2D irreducible representation.\(^{[61]}\) At the \(\Gamma\) point of the BZ the valence and conduction states close to the Fermi level are given by the single \(d_{z^2}\) orbital and the twofold degenerate states composed of the \(d_{x^2}\) and \(d_{y^2−z^2}\) orbitals. These two degenerate states split along the \(\Gamma−K\) line thus allowing to describe the low-energy properties in terms of an effective two-band model. Since the little group at the \(K\) point is \(C_{6v}\), the states forming the effective low-energy doublet at the \(K\) point are given by the combined orbitals \(d_{z^2}\) and \(d_{xy} ± id_{x^2−y^2}\). Note that the absence of a vertical mirror symmetry \(\sigma_v\) in the little group guarantees the splitting of the \(E\) doublet at the \(K\) point. In addition, time-reversal symmetry guarantees that the states at the \(K\) and \(K'\) points, which are related to each other by time-reversal symmetry, are given by \(d_{xy} ± i d_{x^2−y^2}\) with \(\tau\) the valley index. The effective Hamiltonian away from the \(K, K'\) of the BZ can now be derived using 2D \(\mathbf{k} \cdot \mathbf{p}\) theory. To do so, we notice that the threefold rotation symmetry operator can be represented as \(C_3 = \exp(−i\pi \sigma_z/3)\) whereas the time-reversal operator \(\Theta = \tau_y \mathbf{K}\). Finally, the mirror symmetry interchanging the valleys can be simply represented as \(M = \tau_x\). The presence of these symmetries allows for a Dirac mass \(\Delta /2\) where \(\Delta\) corresponds to the TMD direct gap, while the triad of Pauli matrices \(\sigma_{x,y,z}\) now acts in the orbital space. Using the transformation of momenta under the threefold rotation symmetry one finds to linear order in momentum a isotropic Dirac theory of the form

\[
H^{0\text{\text{-}TMD}} = v_F (\tau k_x \sigma_z + k_y \sigma_y) + \frac{\Delta}{2} \sigma_z \tag{53}
\]

Next, we can explicitly include the atomic \(\mathbf{L} \cdot \mathbf{S}\) spin–orbit coupling of the metal \(d\) orbitals. The ensuing effective Hamiltonian\(^{[55]}\) can then be recast in the form

\[
H^{\text{TMD}} = H^{0\text{-TMD}} - \lambda \tau \frac{s_z - 1}{2} s_z \tag{54}
\]

with \(s_z\) indicating the spin degrees of freedom, and \(\lambda\) the halved splitting of the valence band edge caused by spin–orbit coupling. Note that the eigenstates of the effective \(\mathbf{k} \cdot \mathbf{p}\) Hamiltonian are common eigenstates of the spin in the direction perpendicular to the 2D TMD sheet due to the presence of the horizontal mirror symmetry \(M\). The low-energy Hamiltonian in Equation (54) corresponds to two copies (but with different gaps) of the effective Hamiltonian for the surface states of topological crystalline insulators without the tilt term. The absence of the latter is due to the threefold rotation symmetry, which, in turn, implies the existence of three vertical mirror symmetries, and forces the BCD to vanish. However, the application of uniaxial strain can lower the point group symmetry making the tilt term symmetry allowed and the BCD finite. The presence of a strain-induced tilt term cannot be captured in an effective \(\mathbf{k} \cdot \mathbf{p}\) theory considering strain terms at lowest order. However, a microscopic model based on \textit{ab initio} derived Wannier functions with strain effects incorporated by varying the interatomic bond length\(^{[62]}\) shows the appearance of a finite BCD in complete agreement with the symmetry analysis. The size of the BCD is, however, much smaller than the one theoretically predicted to occur on the surface states of SnTe. The latter has been estimated to be in the nm range,\(^{[14]}\) whereas BCDs of the order of \(10^{-2}\) Å are expected in the 1H structure of both WSe₂\(^{[52]}\) (see Figure 4b) and MoSe₂.\(^{[63]}\)

Although the hexagonal structure is the most energetically favorable one, TMD monolayers are present also in a different structural form: the so-called 1T\(_h\) phase. It corresponds to the bulk T\(_h\) phase in which WTe₂ and MoTe₂ realize Weyl semimetals.\(^{[64-67]}\) The monolayer 1T\(_h\) phase intrinsically
symmetry of these two symmetries implies the presence of the inversion fractional translation \( t \) mirror symmetry. A twofold rotation \( \theta = \mathbf{K} \).

At the other high-symmetry momenta, that is, \( \Gamma = \{0,0\} \) and \( Y = \{0,\pi\} \) the screw rotation eigenvalues are instead real \( \pm 1 \). As a result, time-reversal symmetry does not imply any additional degeneracy. For even fillings, these symmetry properties can lead to a symmetry-enforced “topological” semimetal along the \( \Gamma - X \) (or \( Y - M \)) screw line (see the sketch in Figure 5b). Close to the Dirac point on the screw line the linear dispersion is completely anisotropic. In addition, a tilt term \( k_x \sigma_y \) is symmetry allowed. Density functional theory band structures in the absence of spin–orbit coupling (see Figure 5c,d) confirmed the presence of tilted massless Dirac cones both in MoTe\(_2\) and WTe\(_2\). This topological semimetal protected by screw rotation becomes a quantum spin-Hall insulating state when the intrinsic spin–orbit coupling is turned on.\( ^{[68]} \) In this case, the Berry curvature is identically zero due to the concomitant presence of inversion and time-reversal symmetry. However, breaking inversion symmetry via either an externally applied electric field or considering a structural distortion to the non-centrosymmetric 1T phase, all the conditions for the appearance of a BCD are met. Both these situations have been theoretically studied using density functional theory calculations.\(^ {[32,74]} \) In particular, it has been shown that WTe\(_2\) in the 1T phase possess BCDs of the order of \( 10^{-1} \) Å. Larger values have been instead found using the tunability provided by the external electric field in the 1T phase both in WTe\(_2\) and MoTe\(_2\) monolayers. Even more importantly, a BCD of the order of \( 10^{3} \) Å has been measured in WTe\(_2\).\(^ {[75]} \) Similarly to the density functional theory calculation studies, these experiments have highlighted a large tunability of the BCD.

3.4. Bilayer Transition Metal Dichalcogenides

Sizable BCDs have been theoretically predicted\(^ {[76]} \) and experimentally verified in bilayer\(^ {[77]} \) and few-layer\(^ {[78]} \) WTe\(_2\). TMD bilayers, in particular, display dipoles of the order of a few nanometers, one order of magnitude larger than the values predicted and experimentally observed in the electrically activated 1T phase of TMD monolayers, and four order magnitudes larger than the one predicted in 1H monolayers. Moreover the size of the dipole can be additionally tuned with the application of an out-of-plane electric field. The origin of such a large BCD in TMD bilayers can be understood by considering a simple mechanics of hybridization between Dirac fermions appearing in two isolated monolayers.\(^ {[68]} \) Assume for simplicity that on the screw lines of the TMD monolayers the Dirac cones have a vanishingly small tilt term. In the unrealistic case in which the two layers are completely decoupled the bilayer will then feature two massless Dirac cones one on top of each other (see Figure 6a). Consequently, the electronic band structure of the bilayer system will be twofold degenerate at all wavevectors. Next, we can assume that the two layers are coupled but stacked without any relative displacement in the \( x - y \) plane. The interlayer coupling will energetically split the Dirac cones, and thus remove the twofold degeneracy of the bands. However, the Dirac
points on the screw lines will still be present (see Figure 6b) since the screw rotation symmetry remains unbroken. Finally, one can consider the stacking experimentally realized in, for example, WTe$_2$. The relative displacement between the two layers breaks the screw rotation symmetry. Therefore, the Dirac cones acquire a mass and Berry curvature (see Figure 6c). Moreover, since the original Dirac cones have opposite chirality the Berry curvature of the resulting massive Dirac cones are opposite. After they become gapped, these untitled Dirac cones yield a strong BCD since the right moving states and the left moving states are characterized by an opposite Berry curvature. Adding now the effect of the spin–orbit coupling and the original tilt of the Dirac cones does not change qualitatively any of the conclusion.

4. Berry Curvature Dipole in the Absence of Spin–Orbit Coupling

The mechanism at work in bilayer TMDs does not strictly require the presence of titled massive Dirac cones, neither of a sizable spin–orbit coupling. This feature highlights the possibility to observe the non-linear Hall effect even in 2D materials made of light elements. Graphene has been put forward as a paradigmatic example of a spin–orbit-free material with a non-vanishing BCD.[79] Importantly, experimental signatures of a non-linear Hall effect with time-reversal symmetry have been recently found in corrugated bilayer graphene.[80] As we will discuss below, the origin of the non-linear Hall effect in graphene does not stem from the Dirac cone shifting mechanism of bilayer WTe$_2$. It is instead the warping of the Fermi surface the physical characteristic responsible for the non-zero value of the BCD.

4.1. Uniaxially Strained Monolayer Graphene

The wallpaper group of monolayer graphene is $p6mm$. It is generated by the point group $C_{6v}$ and in-plane translations. The point group is generated by a threefold rotation symmetry, a mirror symmetry and a twofold rotation. Since spin–orbit coupling can be neglected all together in graphene, the twofold rotation coincides with inversion symmetry. As a result, the Berry curvature identically vanishes. A possible way to open up a gap and break inversion symmetry is to induce a sublattice imbalance,[81] that is, a charge density wave instability. This can be achieved for instance by placing graphene on a lattice-matched substrate. Density functional theory calculations[82] first identified hexagonal boron nitride as a substrate yielding a band gap of the order of 25 meV. The small nominal lattice mismatch between graphene and hexagonal boron nitride can also lead to a large moiré superlattice characterized by the generation of mini Dirac cones at the expense of a full band gap opening.[83–86] Signatures of a commensurate-incommensurate transition for graphene on top of hexagonal boron nitride[87] have revealed that both these situations can occur in practice: moiré gapless regions are separated by the gapped commensurate ones of interest for our discussion below. As for the case of TMD monolayers in the 1H phase, the point group $C_{6v}$ of gapped graphene does not allow for a non-vanishing BCD. However, the application of uniaxial strain lowers the symmetry of the system to $C_3$ and in principle allows for the onset of a non-linear Hall effect. Let us now examine the electronic characteristic of a graphene layer in the presence of uniaxial strain. To do so, we start out from the graphene tight-binding Hamiltonian[88] in its simplest form, that is, considering

![Figure 6. Sketch (top panels) and density functional theory band structures (bottom panels) of WTe$_2$ assuming a vanishing interlayer coupling (a), an hypothetical bilayer structure preserving the screw rotation symmetry (b) and the actual stacking that breaks the screw rotation symmetry and yields massive Dirac cones (c). The density functional theory band structures are reproduced with permission.[81] Copyright 2016, American Physical Society.](https://www.advquantumtech.com)
only hopping processes between nearest neighbor atomic sites. It reads:

\[ H_{MLG} = -\sum_{ij} t_{ij} a_i^\dagger b_j + \text{c.c.} - \frac{\Delta}{2} \sum_i a_i^\dagger a_i + \frac{\Delta}{2} \sum_i b_i^\dagger b_i \]  

(55)

where \( a_i^\dagger \) and \( b_i^\dagger \) are creation (annihilation) operators on the A and B sublattices respectively. In the equation above, \( \Delta \) indicates the substrate-induced band gap, the subscript \( i \) runs over all unit cell positions, and we introduced the three nearest neighbor vectors

\[ \delta_1 = \frac{a}{\sqrt{3}} \left\{ \sqrt{3}, \frac{1}{2} \right\}, \quad \delta_2 = \frac{a}{\sqrt{3}} \left\{ \frac{-\sqrt{3}}{2}, \frac{1}{2} \right\}, \quad \delta_3 = \frac{a}{\sqrt{3}} \{0, -1\} \]  

(56)

Furthermore, the presence of strain implies that the hopping amplitudes \( t_{ij} \) explicitly depend on the nearest neighbor vectors. Specifically, \( t_{ij} = t_0 (1 - \beta \delta_{ij}) \) where \( t_0 \) is the hopping amplitude for the pristine threefold rotation symmetric honeycomb lattice, the lattice parameter \( \beta \) can be determined by Raman spectroscopy whereas the relative distance changes \( \delta_{ij} \) can be expressed in terms of the strain tensor components \( e_{ij} \) as

\[ \delta_{ij} = \frac{\delta_i \delta_j}{a^2 e_{ij}} \]  

(57)

To proceed further, we go to momentum space and write the Bloch Hamiltonian as

\[ H_{MLG} = -\sum_{\mathbf{q}} t_{\mathbf{q}} \left( \delta_{\mathbf{q}0} \delta_{\mathbf{q}} e^{-i(\mathbf{K}^0, \mathbf{q})} \frac{\Delta}{2} \right) \]  

(58)

where we have rewritten the momenta as \( \mathbf{k} = \mathbf{K}^0 + \mathbf{q} \) since we are interested in the electronic properties close to the \( \mathbf{K} \) or \( \mathbf{K}' \) valleys of the BZ given by \( \mathbf{K} = \{4\pi/3a, 0\} \) and \( \mathbf{K}' = \{-4\pi/3a, 0\} \).

The Bloch Hamiltonian can be then expanded to linear order in the small momenta \( \mathbf{q} \). Using simple vector identities and assuming an anisotropic biaxial strain with \( e_{xx} \neq e_{yy} \neq 0 \) and \( e_{xy} \equiv 0 \) the continuum low-energy Hamiltonian near the two valleys of the BZ can be recast as

\[ H_{\mathbf{q}} = \xi v_{\mathbf{q}} \sigma_x + v_{\mathbf{q}} A_{\mathbf{q}} \sigma_z + v_{\mathbf{q}} \sigma_x \frac{\Delta}{2} \sigma_z \]  

(59)

where \( \xi \approx \pm 1 \) is the valley index. In the equation above, \( A_{\mathbf{q}} = \sqrt{3} \beta (e_{xx} - e_{yy})/2a \) is the well-known strain-induced “pseudo”-gauge field\(^{89-91} \) whereas \( v_{\mathbf{q}} = \sqrt{3} t_0 a/2 \) is the Fermi velocity of the Dirac carriers in unstrained samples. In addition, \( v_{\mathbf{q}} = v_\xi [1 - \beta (e_{xx} + e_{yy})]/4 \) and \( v_{\mathbf{q}} = v_\xi [1 - \beta (e_{xx} + 3e_{yy})]/4 \) are renormalized Fermi velocities that become anisotropic when explicitly considering the linear coupling between momentum and strain.\(^{92} \) The Dirac cones explicitly acquire an anisotropic character, consistent with the reduction of the point group symmetry. The warping of the Fermi surface can be instead captured by keeping terms up to quadratic order in the momentum \( \mathbf{q}^2 \). They read

\[ \Delta H_{\mathbf{q}} (\mathbf{q}) = (\xi \gamma_2^2 - \lambda_1 \gamma_3^2) \sigma_y + 2 e_{\mathbf{q}} q_x \gamma_3 \sigma_x + 2 e_{\mathbf{q}} q_y \gamma_1 \sigma_y + 2 e_{\mathbf{q}} q_z \gamma_2 \sigma_z \]  

(60)

where \( \gamma_1 = \pm \frac{\Delta}{2} \) and \( v_0 = \frac{\Delta}{2} \) are two strain independent parameters with the dimension of a velocity. Specifically, \( v_0 \) is the Fermi velocity of the Dirac electrons in each monolayer and is thus related to the intralayer hopping amplitude \( \gamma_1 \). By contrast, the velocity \( v_\xi \) is related to the so-called “skew” interlayer hopping amplitude \( \gamma_2 \), connecting the \( A_1 \) and \( B_1 \) sites. The \( A_1 \) and \( B_1 \) lie on top of each other and are coupled by the interlayer coupling \( \gamma_1 \). Strain effects enter via two pseudo-gauge fields \( A_{\mathbf{q}} \).\(^{96} \) Assuming mechanical stresses applied along the principal crystallographic directions, the pseudogauge fields \( A_{\mathbf{q}} \) are related to the elastic properties of the material. Finally, the different on-site potentials in the two layers \( \pm \Delta/2 \) are due to an externally applied electric field.\(^{97} \) For energies near the Fermi level, the states coupled by \( \gamma_1 \) can be eliminated through a Schrieffer-Wolff transformation.\(^{98} \)
Figure 7. Berry curvature and dipole density for unstrained (left panels) and strained (right panels) monolayer graphene. When strain is present the deformation of the Fermi surface leads to a finite value of the dipole. Note that we have considered for simplicity the trigonal warping term that respects the threefold rotation symmetry, that is, $\lambda_1 = \lambda_2 = \lambda_3$. The distortion of the Fermi surface is therefore entirely due to the anisotropic Fermi velocity.

After a gauge transformation $k_x \rightarrow k_x - A_0$, one obtains the effective $2 \times 2$ Hamiltonian

$$H_6 = \left[ -\frac{1}{2m} (k_x^2 - k_y^2) + \xi v_3 k_x + w \right] \sigma_x$$

$$- \left( \frac{1}{m} k_x k_y + \xi v_3 \right) \sigma_y + \frac{\Delta}{2} \sigma_z$$

where we introduced the effective mass $m = \gamma_1/2v_0^2$ and the strain coupling $w = 1/2 \gamma_1 (\epsilon_{xx} - \epsilon_{yy})(\beta_3 - \beta_0)$. The inclusion of the skew interlayer hopping has a twofold effect. First, it gives an explicit trigonal warping to the Fermi surface. Second, and most important, it changes the topology of the Fermi surface at low energies. In the absence of strain for instance, the low-energy quadratic band crossing point occurring for $v_3 = 0$ is changed in favour of the appearance of four Dirac cones, one of which is located at the K and K’ points of the BZ. The remaining three “leg” Dirac cones, with a Berry phase opposite to the central cone one, are arranged in a three-fold rotation symmetric fashion (see Figure 8a) and have a distance in momentum given by $k_{L} = m v_3$. The Lifshitz transition where the Fermi surface changes topology\cite{95} occurs at $\epsilon_L = m v_3^2/2$ in the $\Delta = 0$ inversion-symmetric case. The appearance of a non-vanishing BCD in the system can be understood considering the Berry curvature properties in this strain-free ($w = 0$) case.\cite{99} As shown in Figure 8a the central Dirac cone has a $C_3$ symmetric Berry curvature and thus it gives a vanishing contribution to the BCD. When taken by themselves, the leg Dirac cones instead have only a mirror symmetric Berry curvature profile and therefore their contribution to the BCD is non-zero. Each gapped leg Dirac cone is described by the low-energy Hamiltonian introduced for monolayer graphene with a warping term such that $\lambda_1 = \lambda_2 = \lambda_3$. However, the contributions of the leg Dirac cones cancel each other due to the global threefold rotation symmetry. Once strain is introduced, the perfect cancellation of the leg Dirac cone contributions is lost and a finite overall BCD appears. In addition, the central massive Dirac cone also yields a non-zero contribution to the BCD for $w \neq 0$. As explicitly shown in Figure 8b strain promotes additional changes in the topology of the Fermi surface marked by Lifshitz transition. Moreover, it can also lead to Dirac cone annihilation processes as shown for the inversion symmetric case in ref.\cite{96}. Independent of the specific fermiology, the system always develops a sizable total BCD. The existence of various Lifshitz transition is imprinted instead in the presence of cusp and inflection points in the behavior of...
Figure 8. a) Berry curvature and Berry curvature dipole density in gated bilayer graphene in the absence of strain below the Lifshitz transition. b) Same with homogeneous uniaxial strain. Beside yielding a non-vanishing Berry curvature dipole, the uniaxial strain also promotes a Lifshitz transition. c) Berry curvature dipole in bilayer graphene assuming a gate-induced gap $\Delta = 10 \text{ meV}$ and various strains as a function of the carrier density measured in units of $\kappa_L^2$ with $\kappa_L = 0.035 \text{nm}^{-1}$. Panel (c) is reproduced with permission. [79] Copyright 2019, American Physical Society.
the BCD as a function of the carrier density (see Figure 8c). Importantly for a strain term \( w = -5e_1 \), which corresponds roughly to a 1% strain, and a for gate-induced gap \( \Delta = 10 \text{ meV} \) the BCD \( D_\delta \approx 1 \text{ nm} \) assuming a carrier density \( n \approx 10^{11} \text{ cm}^{-2} \). As mentioned above, this value is comparable to the one experimentally found in bilayer WTe\(_2\) and can be boosted by an order of magnitude for smaller values of the gate-induced gap. Remarkably, dipoles in the tens of nanometer scale have been recently found in the corrugated bilayer graphene nanoarchitectures of ref. [80]. We also note that the conspiracy of strain and warping of the Fermi surface has been shown to yield various features\(^{[99]}\) appearing when built-in electric fields are present.

5. 3D Materials

Although the NLHE with time-reversal symmetry finds a natural realization in 2D crystals, it can also arise in 3D bulk crystals. TaTe\(_2\), a type-II Weyl semimetal ternary compound,\(^{[101-103]}\) has been recently shown to possess a NLHE surviving even at room temperature.\(^{[104]}\) Generally speaking, a finite BCD appears in 3D Weyl semimetals with tilted cones,\(^{[105-107]}\) be them either of type-I or of strongly overtitled type-II. This can be understood again considering \( \mathbf{k} \cdot \mathbf{p} \) theory. Let us analyze, for simplicity, a Weyl semimetal with an isotropic Fermi velocity. Its effective low-energy Hamiltonian reads

\[
\mathcal{H}_\text{Weyl} = \chi v_0 \sum_{i=x,y,z} k_i \sigma_i + u_i k_i I
\]

where \( \chi = \pm 1 \) is the chirality (the topological charge) of the Weyl cone,\(^{[108]}\) and the tilt direction has been chosen to be the \( \hat{a} \) direction. This continuum theory describes a type-II Weyl semimetal for \( |u_x/v_0| > 1 \), whereas for \( |u_x/v_0| < 1 \) the cone is of the type-I form. Since the total topological charge in the full BZ of a system to have identical vanishing, each Weyl cone has to come with a partner of opposite chirality. In addition, time-reversal symmetry implies that each Weyl cone has a time-reversed partner of the same chirality. The total number of Weyl cones in a time-reversal symmetric topological semimetal is therefore \( 4n \), with \( n \) integer. It is possible to show that each Weyl cone yields a finite BCD. This can be seen already in the untitled \( u_x \equiv 0 \) limit. Using that the Berry curvature of a single Weyl cone is \( \mathbf{\Omega} = \chi \mathbf{k}/(2|\mathbf{k}|^2) \) and that the carrier velocity is \( \mathbf{v} = v_0 \hat{\mathbf{k}} \), the components of the BCD pseudotensor read as

\[
D_{xx} = D_{yy} = D_{zz} = \frac{\chi}{3} \frac{1}{4\pi^2}
\]

whereas the off-diagonal components identically vanish. We emphasize that there are inconsistencies in the literature as it concerns the BCD of a single Weyl cone.\(^{[109]}\) We refer the reader to ref. [105] for a discussion on this point. Since the BCD depends exclusively on the topological charge of the Weyl nodes, each of the symmetric components \( D_{ij} \) averages to zero when summed over all nodes of a Weyl semimetal. This holds as long as the tilt of the Weyl cones is neglected. Assuming instead a sizable tilt term, the situation changes qualitatively. The diagonal nonvanishing components of the BCD indeed acquire a specific dependence on the dimensionless parameter \( \delta = u_x/v_0 \). These have been evaluated in ref. [105] and read

\[
D_{yx} = D_{yx} = \frac{1}{8\pi^2} \frac{1}{\delta^3} \left( \frac{\delta + \frac{\delta^2 - 1}{2} \log \frac{1 + \delta}{1 - \delta}}{1 - \delta} \right)
\]

\[
D_{xx} = \frac{1}{4\pi^2} \frac{\delta^2 - 1}{\delta^4} \left( \frac{\delta - \frac{1}{2} \log \frac{1 + \delta}{1 - \delta}}{1 - \delta} \right)
\]

The equations above reduce to Equation (63) in the \( \delta \rightarrow 0 \) limit. In addition, it is interesting to note that, independent of the tilt term, the trace of the BCD pseudotensor is the universal quantity \( \text{Tr}D = \chi/(4\pi^2) \). Finally, as explicitly shown in Figure 9a, the off-diagonal components of the pseudotensor vanish. The explicit \( \delta \)-dependence of the dipole components \( D_{ij} \) can make the total BCD finite in a generic Weyl semimetal. This is because the dipole tensors of the Weyl nodes related by time-reversal symmetry are same and are not entirely cancelled by the tensors corresponding to the Weyl nodes with opposite topological charge. Specifically, this occurs in materials, such as SrSi\(_2\),\(^{[110]}\) where Weyl nodes of opposite topological charge are not related to each other by any point group symmetries. Materials with additional mirror symmetries, TaAs being a paradigmatic example,\(^{[111-114]}\) are forced to have a vanishing total BCD for the simple reason that Weyl nodes of opposite charge are mapped by the mirror symmetry, and therefore constrained to have opposite Berry curvatures.

Although this feature is in agreement with the fact that a 3D material with mirror symmetries cannot have a symmetric BCD pseudotensor, it does not justify why the antisymmetric part of the BCD should be identically zero. Density functional theory calculations have shown that TaAs has a large dipole\(^{[116]}\) with \( D_{xy} = -D_{yx} \neq 0 \) that is symmetry-allowed. The resolution of this paradox comes from the fact that higher-order terms in momentum \( \mathbf{k} \) can change the properties of the Berry curvature. This can be demonstrated considering a \( \mathbf{k} \cdot \mathbf{p} \) model for a pair of Weyl nodes in the presence of a mirror symmetry.\(^{[115]}\) It reads

\[
\mathcal{H} = v_x k_x \sigma_x + v_y k_y \sigma_y + \frac{k_z^2 - \lambda}{2m} \sigma_z + u_x k_x I
\]

This model predicts the presence of two Weyl nodes at \( k_z = \pm \sqrt{\lambda} \) with a corresponding Fermi velocity \( v_x = \sqrt{\lambda/m} \). Figure 9b shows the corresponding \( D_{xy} \) dipole surface density assuming a perfectly isotropic Fermi velocity for the two Weyl cones. As compared to the result obtained using the linear Weyl effective Hamiltonian (cf. Figure 9a), it is clear that the model Equation (65) yields a finite antisymmetric BCD (cf. Figure 9) in agreement with the density functional theory calculations results for the type-I TaAs and the type-II MoTe\(_2\) Weyl semimetals.

It is interesting to note that in the \( \lambda < 0 \) parameter range the model in Equation (65) predicts an insulating state with a gap \( \Delta = (|\lambda|/m) \). Even in this regime, there is a finite dipole (surface) density antisymmetric component (see Figure 9c), provided the system can be doped with charge carriers and thus possesses a finite Fermi surface. Remarkably the Rashba semiconductor BiTeI can realize both the \( \lambda > 0 \) and the \( \lambda < 0 \) regimes of this model. BiTeI\(^{[117]}\) has been predicted to become a strong 3D topological
Figure 9. a) Berry curvature dipole line density $\Omega_{kxvy}$ evaluated on the $k_z = 0$ plane for a pair of Weyl nodes using the effective $k \cdot p$ Hamiltonian for isolated cones. The dipole $D_{xy}$ clearly vanishes by symmetry. b) Same using the model Equation (65) for the creation of a pair of Weyl nodes. In this case there isn't any symmetry forcing the dipole to be zero. c) Berry curvature dipole line density on the $k_z = 0$ plane for the model Equation (65) in the insulating regime. Provided there is a finite Fermi surface, the Berry curvature dipole is non-vanishing. d) Berry curvature dipole as a function of pressure in BiTeI as obtained using density functional theory calculations. The inset shows the behavior in the topological insulating region while approaching the topological phase transition to a Weyl semimetal. Panel (d) is reproduced with permission.[115] Copyright 2018, American Physical Society.

6. Conclusions

In this concluding section, we summarize what has been achieved with the recent studies on the NLHE in time-reversal symmetric conditions, and also point out possible directions for future research on this recently discovered phenomenon. Being regulated by the Berry curvature dipole, the time-reversal symmetric NLHE can be used as a direct probe of the geometry of the Bloch states in non-magnetic systems. This intrinsic quantum property can be only unveiled in crystals with unusually low crystalline symmetry. Bilayer WTe$_2$ is a paradigmatic example of a material fulfilling such symmetry requirements. And indeed its non-vanishing BCD has been directly observed.[77] The crystalline symmetry requirements for a non-vanishing BCD can be however also achieved using the capability of externally applied fields to lower the point group symmetry of a crystal. Externally applied electric fields, for instance, break inversion symmetry and therefore allow for a time-reversal symmetric NLHE even in materials, which, in their pristine form have a vanishing Berry curvature. This scheme has been successfully applied in the quantum spin Hall 1T$'$ phase of transition metal insulator[118] at moderate pressures $> 3$ GPa. The topological and semiconducting phases are separated by an intermediate Weyl semimetal phase.[119] Both “topological” phase transition can be therefore captured by the model in Equation (65) assuming that changing the pressure the parameter $\lambda$, or equivalently the bulk gap $\Delta$, is varied. Figure 9d shows the behavior of the antisymmetric BCD $d_z = (D_{xy} - D_{yx})/2$ computed in a recent density functional theory calculation study[115] for various carrier density. It highlights how the BCD gets strongly enhanced while approaching the Weyl semimetal phase. This is in agreement with the fact that the model of Equation (65) predicts a divergent antisymmetric BCD in the insulating regime when the $\Delta \to 0$ limit is taken (cf. the inset in Figure 9d). As a result, non-linear Hall measurements can provide a unique signature of the pressure-induced topological phase transition[120] in BiTeI, even if local order parameters are absent. It has been recently proposed that 3D Weyl semimetals can host a gigantic non-linear Hall effect that derives entirely from a surface BCD. This effect is caused by a divergence of the Berry curvature occurring over an entire “hot-line” of the surface Brillouin zone, and generally accompanies the Fermi arcs of Weyl semimetals.[121]
dichalcogenides.[32] Mechanical deformations are yet another knob that can be used to decrease the crystalline symmetry of materials and eventually allow for a NLHE. Contrary to external electric fields, strain does not break the centrosymmetry of a crystal. However, it can reduce the rotational symmetry to make this effect visible. The ability of strain to induce finite BCDs can be also employed to design novel strain tensors based on metals.[122] In principle, also externally applied magnetic field could be used to lower the point-group symmetry and meet the NLHE requirements. A planar magnetic field, in particular, breaks the time-reversal invariance. However, the absence of Lorentz force combined with the presence of a residual mirror symmetry can guarantee the complete absence of a linear dissipationless Hall conductance thus making the non-linear Hall effect the only visible effect. This phenomenon has been dubbed anomalous non-linear planar Hall effect.[36]

Independent of the presence and nature of the external perturbation, the appearance of the time-reversal symmetric NLHE was originally believed to necessitate a substantial spin–orbit coupling. However, the experimental demonstration of non-linear transverse currents in strained (bilayer) graphene[60] has shown that this effect could be also pursued in systems made of light elements, where the presence of spin–orbit coupling could be neglected all together. This has opened new material avenues for studies of the NLHE with time-reversal symmetry. Twisted bilayer graphene—a material structure where correlated insulating behavior[123] and superconductivity[124] have been shown to arise—has been recently suggested to host a substantial BCD[125,126] on the order of tens of nanometers. In twisted bilayer graphene strain with an opposite sign in the two graphene layers has been imaged in STM experiments.[127] Moreover, when encapsulated with hexagonal boron nitride the inversion symmetry of twisted bilayer graphene is broken. As a result, all symmetry requirements for a finite BCD are fulfilled. We note that finite BCDs might even occur in short-range superlattices as the ones with tripled unit cells realized by depositing graphene on hexagonal III-VI semiconductors.[128] In these heterostructures, the graphene Dirac cones are folded at the center of the Brillouin zone. The system might then realize a Dirac semimetal phase similar in nature to the one considered in ref. [129], and for which sizable BCDs have been predicted.

We conclude by mentioning that non-linear transverse currents in the presence of time-reversal symmetry have been suggested to occur also in the strong 3D topological insulators of the $\text{Bi}_2\text{Te}_3$ material class.[130] The anomalous single surface Dirac cones in these materials are characterized by an intrinsic chirality that enables a novel skew scattering[131] similar to the one predicted in unstrained bilayer graphene.[19] However, it is important to note that the non-linear response found in these materials does not represent a dissipationless non-linear Hall conductance, and is therefore compatible with the trigonal symmetry of the $\text{Bi}_2\text{Te}_3$ surface states.[132] Finally, non-linear responses using the topological surface states of $\text{Bi}_2\text{Te}_3$ have been demonstrated to occur also in the presence of external planar magnetic fields.[133]

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Conflict of Interest

The author declares no conflict of interest.

Keywords

Berry curvature dipole, graphene, topological crystalline insulators, transition metal dichalcogenides, Weyl semimetals

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[1] K. v. Klitzing, G. Dorda, M. Pepper, Phys. Rev. Lett. 1980, 45, 494.
[2] D. J. Thouless, M. Kohmoto, M. P. Nightingale, M. den Nijs, Phys. Rev. Lett. 1982, 49, 405.
[3] M. Z. Hasan, C. L. Kane, Rev. Mod. Phys. 2010, 82, 3045.
[4] X.-L. Qi, S.-C. Zhang, Rev. Mod. Phys. 2011, 83, 1057.
[5] R. Karpplus, J. M. Luttinger, Phys. Rev. 1954, 95, 1154.
[6] J. M. Luttinger, Phys. Rev. 1958, 112, 739.
[7] T. Jungwirth, Q. Niu, A. H. MacDonald, Phys. Rev. Lett. 2002, 88, 207208.
[8] F. D. M. Haldane, Phys. Rev. Lett. 2004, 93, 206602.
[9] N. Nagaosa, J. Sinova, S. Onoda, A. H. MacDonald, N. P. Ong, Rev. Mod. Phys. 2010, 82, 1539.
[10] F. D. M. Haldane, Phys. Rev. Lett. 1988, 61, 51.
[11] C.-Z. Chang, J. Zhang, X. Feng, J. Shen, Z. Zhang, M. Guo, K. Li, Y. Ou, P. Wei, L.-L. Wang, Z.-Q. Ji, Y. Feng, S. Ji, X. Chen, J. Jia, X. Dai, Z. Fang, S.-C. Zhang, K. He, Y. Wang, L. Lu, X.-C. Ma, Q.-K. Xue, Science 2013, 340, 167.
[12] E. Deyo, L. E. Golub, E. L. Ivchenko, B. Spivak, arXiv:0904.1917, 2009.
[13] J. E. Moore, J. Orenstein, Phys. Rev. Lett. 2010, 105, 026805.
[14] I. Sodemann, L. Fu, Phys. Rev. Lett. 2015, 115, 216806.
[15] F. de Juan, A. G. Grushin, T. Morimoto, J. E. Moore, Nat. Commun. 2017, 8, 15995.
[16] T. Morimoto, N. Nagaosa, Sci. Adv. 2016, 2, 5.
[17] B. Sadhukhan, T. Nag, Phys. Rev. B 2021, 103, 14.
[18] R.-C. Xiao, D.-F. Shao, W. Huang, H. Jiang, Phys. Rev. B 2020, 102, 024109.
[19] H. Isobe, S.-Y. Xu, L. Fu, Sci. Adv. 2020, 6, 13.
[20] Y. Zhang, L. Fu, arXiv:2101.05842, 2021.
[21] S. Nandy, I. Sodemann, Phys. Rev. B 2019, 100, 195117.
[22] J. Wu, A. T. Bollinger, X. He, I. Božović, Nature 2017, 547, 432.
[23] L. Onsager, Phys. Rev. 1931, 37, 405.
[24] C. Fang, M. J. Gilbert, B. A. Bernevig, Phys. Rev. B 2012, 86, 115112.
[25] G. Sundaram, Q. Niu, Phys. Rev. B 1999, 59, 14915.
[26] D. Xiao, M.-C. Chang, Q. Niu, Rev. Mod. Phys. 2010, 82, 1959.
[27] C. Xiao, Z. Z. Du, Q. Niu, Phys. Rev. B 2019, 100, 165422.
[28] E. J. König, M. Dzero, A. Levchenko, D. A. Pesin, Phys. Rev. B 2019, 99, 155404.
[29] Z. Z. Du, C. M. Wang, S. Li, H.-Z. Lu, X. C. Xie, Nat. Commun. 2019, 10, 3047.
[30] N. A. Sinitsyn, Q. Niu, A. H. MacDonald, Phys. Rev. B 2006, 73, 075318.
[31] N. A. Sinitsyn, A. H. MacDonald, T. Jungwirth, V. K. Dugaev, J. Sinova, Phys. Rev. B 2007, 75, 045315.
[32] N. A. Sinitsyn, J. Phys.: Condens. Matter 2007, 20, 023201.
[33] N. A. Sinitsyn, Q. Niu, J. Sinova, K. Nomura, Phys. Rev. B 2005, 72, 045346.
[34] Y. Tian, L. Ye, X. Jin, Phys. Rev. Lett. 2009, 103, 087206.
