

First-principles investigations on the Berry phase effect in spin–orbit coupling materials



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ABSTRACT

In recent years, the Berry phase as a fascinating concept has made a great success for interpreting many physical phenomena. In this paper, we review our past works on the Berry phase effect in solid materials with spin–orbit coupling. Firstly, we developed an exact method for directly evaluating the Berry curvature and anomalous Hall conductivity, then the intrinsic mechanism of anomalous Hall effect was quantitatively confirmed in bcc Fe and $\text{CuCr}_2\text{Se}_{4-x}\text{Br}_x$. An effective method was proposed to decompose the anomalous Hall effect into the intrinsic and extrinsic contributions. We also developed computational methods for the spin Hall conductivity and anomalous Nernst conductivity. Secondly, we developed a powerful method for computing the Z_2 topological invariant without consideration of special symmetry. We predicted many topological insulators in three-dimensions, including half-Heusler, chalcopyrite, strained InSb, core-holed Ge and InSb, $\text{Bi}_2\text{Te}_3/\text{BiTeI}$ heterostructure, and in two-dimensions, including silicene, germanene, stanene, X-hydride/halide ($X = \text{N–Bi}$) monolayers and Bi_4Br_4 . We also predicted the quantum anomalous Hall effect in magnetic atoms adsorbed graphene and half-passivated BiH, the quantum valley Hall effect and topological superconducting in silicene and n -doped BiH. Finally, the summary of our past works and the further outlooks are discussed.

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1. Introduction

The Berry phase effect [1], which is defined as that the nondegenerate eigenstate definitely comes back to itself but with an extra phase difference when the system is adiabatically evolved along a closed path in the parameter space, has recently caused a great deal of interest in a variety of fields in physics. The Berry phase has proved its importance due to three key physical properties [2,3]. First, the Berry phase is gauge invariant in the sense that multiplying the eigenstate by an overall phase factor does not change the Berry phase within multiples of 2π . This property makes the Berry curvature physically observable. Second, the Berry phase is geometrical because it can be expressed in terms of local geometrical quantities along a loop in the parameter space. This property makes the Berry phase computable in practice. Finally, the Berry phase is analogous to gauge field theory and differential geometry. This makes the Berry phase a beautiful and intuitive concept.

In crystalline solid, the band structure within the independent electron approximation provides a natural starting point to study

the Berry phase effect. The band structure for a given system is determined by the following Hamiltonian:

$$H = \frac{\hat{p}^2}{2m} + V(\mathbf{r}), \quad (1)$$

where $V(\mathbf{r} + \mathbf{a}) = V(\mathbf{r})$ is the periodic potential with $\mathbf{a}$ the Bravais lattice vector. The $\mathbf{k}$ -dependent Hamiltonian reads as $e^{-i\mathbf{k}\cdot\mathbf{r}}He^{i\mathbf{k}\cdot\mathbf{r}}$ and its eigenstate can be written as $u_{n\mathbf{k}}(\mathbf{r}) = e^{-i\mathbf{k}\cdot\mathbf{r}}\psi_{n\mathbf{k}}(\mathbf{r})$, which is in fact the periodic part of the Bloch function $\psi_{n\mathbf{k}}(\mathbf{r})$. Since the Brillouin zone (BZ) can be regarded as the parameter space and $\mathbf{k}$ varies in the momentum space, the Berry phase for Bloch state can be expressed as,

$$\gamma_n = \oint_C d\mathbf{k} \cdot \mathcal{A}_n(\mathbf{k}), \quad (2)$$

where the integrand is usually known as the Berry connection, defined as

$$\mathcal{A}_n = i\langle u_n(\mathbf{k}) | \nabla_{\mathbf{k}} | u_n(\mathbf{k}) \rangle. \quad (3)$$

It should be emphasized that the path C must be a closed path in the BZ such that γ_n is a gauge-invariant quantity. In analogy to electrodynamics, it is useful to introduce the Berry curvature from the Berry connection,

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$$\Omega_n(\mathbf{k}) = \nabla_{\mathbf{k}} \times \mathcal{A}_n. \quad (4)$$

Then according to Stokes's theorem, the Berry phase can also be written as a surface integral

$$\gamma_n = \int_{\mathcal{S}} d\mathcal{S} \cdot \Omega_n(\mathbf{k}), \quad (5)$$

where $\mathcal{S}$ is an arbitrary surface enclosed by the path $\mathcal{C}$. The Berry curvature is an intrinsic quantity, which provides a local description of the geometric properties in the parameter space. Now, we have recognized that the Berry curvature plays an essential role in the description of the dynamics of the Bloch electrons. Thus, the Berry curvature is a more fundamental quantity in a large class of applications of the Berry phase.

In solid materials, especially for those with large spin-orbit coupling (SOC), the Berry phase has manifested itself having deep relations with various emergent quantum phenomena [3], including anomalous Hall effect, spin Hall effect, valley Hall effect, anomalous thermoelectric effect, electronic polarization, orbital magnetization, magnetoresistance, magneto-optic effect, and three/two-dimensional (3D/2D) topological insulator. The first-principles calculation within the density functional theory played an important role to understand the Berry phase in vast situations because the quantitative comparison with experimental results becomes possible. In the past decade, our research group has paid much attention to these kinds of studies and produced very fruitful works.

In this paper, we review our first-principles investigations on the Berry phase effect in real materials with SOC. The rest of this paper is organized as follows. In Section 2, we review the first-principles calculations of the anomalous Hall conductivity, spin Hall conductivity, anomalous Nernst conductivity, Chern number, and Z_2 topological invariants, which all have been implemented in our homemade package based on the full-potential linearized augmented plane-wave (FP-LAPW) formalism. In Section 3, we focus on the anomalous Hall effect, spin Hall effect, and anomalous Nernst effect, and show that the intrinsic mechanism dominates at certain cases. Then, 3D and 2D topological materials as very hot topics in recent years are discussed in Sections 4 and 5, respectively. In Section 6, we also introduce briefly our studies on group-VI dichalcogenide monolayers. Finally, in Section 7, we give a brief summary of our works on the Berry phase effect in solid materials with prominent spin-orbit coupling and presents some outlooks in further studies.

2. Computational methods and formulas

In this section, we review the computational methods of anomalous Hall conductivity, spin Hall conductivity, anomalous Nernst conductivity, Chern number, and Z_2 topological invariants, following a brief introduction of the FP-LAPW formalism. The central job is to calculate various physical quantities, such as the velocity, parity, and time-reversal operators. The physical pictures for these fascinating quantum phenomena are schematically shown in Fig. 1.

2.1. FP-LAPW formalism

In relativistic SOC calculations, the Bloch wavefunctions (BFs) of electrons have the two-component form,

$$\Psi_{nk}(\mathbf{r}) = \begin{bmatrix} \psi_{nk}^{\uparrow}(\mathbf{r}) \\ \psi_{nk}^{\downarrow}(\mathbf{r}) \end{bmatrix}, \quad (6)$$

where the arrows refer to the up and down spin components. The periodic part of the BFs is $u_{nk}(\mathbf{r}) = e^{-i\mathbf{k}\cdot\mathbf{r}} [\psi_{nk}^{\uparrow}(\mathbf{r}) \quad \psi_{nk}^{\downarrow}(\mathbf{r})]^T$, where T

is the transpose operator. Within the FP-LAPW framework, the unit cell is often divided into the muffin-tin and interstitial regions [4–6]. Correspondingly, the BFs of electrons are also divided into two parts. In the muffin-tin region, the BFs are written as

$$\psi_{nk}^{\sigma,\alpha}(\mathbf{r}) = \sum_{lm} \left[A_{lm}^{\sigma,\alpha}(n, \mathbf{k}) u_{l,1}^{\sigma,\alpha} + B_{lm}^{\sigma,\alpha}(n, \mathbf{k}) \dot{u}_{l,1}^{\sigma,\alpha} + C_{lm}^{\sigma,\alpha}(n, \mathbf{k}) u_{l,2}^{\sigma,\alpha} + D_{lm}^{\sigma,\alpha}(n, \mathbf{k}) u_{l,1/2}^{\sigma,\alpha} \right] Y_{lm}(\hat{\mathbf{r}}^{\alpha}), |\mathbf{r} - \mathbf{r}^{\alpha}| \in R_{\alpha}, \quad (7)$$

where the α -th atom sphere has the radius of R_{α} and the position of $\mathbf{r}^{\alpha}$ and σ stands for the spin index. $u_{l,1}^{\sigma,\alpha}$ is the radial solutions of scalar-relativistic Schrödinger equation at linear energy $E_{l,1}^{\alpha}$ of $l = s, p$, or d orbitals; $\dot{u}_{l,1}^{\sigma,\alpha}$ is the energy derivatives of $u_{l,1}^{\sigma,\alpha}$; $u_{l,2}^{\sigma,\alpha}$ and $u_{l,1/2}^{\sigma,\alpha}$ are the radial functions of the local orbitals adding to the $u_{l,1}^{\sigma,\alpha}$ and $\dot{u}_{l,1}^{\sigma,\alpha}$ for semi-core states, which can improve the variational freedom of standard basis functions; $Y_{lm}(\hat{\mathbf{r}}^{\alpha})$ is spherical harmonics with the angular momentum index lm . The expansion coefficients in Eq. (7) are

$$\begin{aligned} A_{lm}^{\sigma,\alpha}(n, \mathbf{k}) &= \sum_j z_{nkj}^{\sigma} \tilde{A}_{lm}^{\sigma,\alpha}(\mathbf{k} + \mathbf{K}_j) + \sum_{j_0} z_{nkj_0}^{\sigma} \tilde{A}_{l_0m_0}^{\sigma,\alpha}(\mathbf{k} + \mathbf{K}_{j_0}) \delta_{l,l_0} \delta_{m,m_0}, \\ B_{lm}^{\sigma,\alpha}(n, \mathbf{k}) &= \sum_j z_{nkj}^{\sigma} \tilde{B}_{lm}^{\sigma,\alpha}(\mathbf{k} + \mathbf{K}_j) + \sum_{j_0} z_{nkj_0}^{\sigma} \tilde{B}_{l_0m_0}^{\sigma,\alpha}(\mathbf{k} + \mathbf{K}_{j_0}) \delta_{l,l_0} \delta_{m,m_0}, \\ C_{lm}^{\sigma,\alpha}(n, \mathbf{k}) &= \sum_{j_0} z_{nkj_0}^{\sigma} \tilde{C}_{l_0m_0}^{\sigma,\alpha}(\mathbf{k} + \mathbf{K}_{j_0}) \delta_{l,l_0} \delta_{m,m_0}, \\ D_{lm}^{\sigma,\alpha}(n, \mathbf{k}) &= \sum_{j_0} z_{nkj_0}^{\sigma} \tilde{D}_{l_0m_0}^{\sigma,\alpha}(\mathbf{k} + \mathbf{K}_{j_0}) \delta_{l,l_0} \delta_{m,m_0}, \end{aligned} \quad (8)$$

in which the $\tilde{A}_{lm}^{\sigma,\alpha}$ and $\tilde{B}_{lm}^{\sigma,\alpha}$ are the coefficients of LAPW basis, while only $\tilde{A}_{lm}^{\sigma,\alpha}$ is used in APW basis; $\tilde{A}_{l_0m_0}^{\sigma,\alpha}$, $\tilde{B}_{l_0m_0}^{\sigma,\alpha}$, $\tilde{C}_{l_0m_0}^{\sigma,\alpha}$ and $\tilde{D}_{l_0m_0}^{\sigma,\alpha}$ are the coefficients of local orbital basis. These coefficients can be determined by continuous differentiable conditions at the boundaries of muffin-tin sphere [7].

On the other hand, in the interstitial region, the plane waves are simply used to construct the BFs,

$$\psi_{nk}^{\sigma}(\mathbf{r}) = \frac{1}{\sqrt{\Omega}} \sum_j z_{nkj}^{\sigma} e^{i(\mathbf{k} + \mathbf{K}_j) \cdot \mathbf{r}}, \quad \mathbf{r} \in I, \quad (9)$$

where z_{nkj}^{σ} is the expansion coefficient with spin index σ , band index n , wave vector $\mathbf{k}$, and reciprocal-lattice vector $\mathbf{K}_j$ up to a largest cutoff value $|\mathbf{k} + \mathbf{K}_j| \leq \mathbf{K}_{max}$; Ω is volume of unit cell.

Once the ground states are obtained via the self-consistent field solution, the BFs can be used to further compute many physical properties as will be introduced following.

2.2. Anomalous Hall conductivity

Within the semiclassical transport theory, the equations of motion are modified by including the Berry phase correction to the group velocity [8,9],

$$\dot{\mathbf{x}} = \frac{1}{\hbar} \frac{\partial \varepsilon_n(\mathbf{k})}{\partial \mathbf{k}} - \dot{\mathbf{k}} \times \Omega_n(\mathbf{k}) \quad (10)$$

$$\hbar \dot{\mathbf{k}} = -e\mathbf{E} - e\dot{\mathbf{x}} \times \mathbf{B} \quad (11)$$

where ε_n is the eigenvalue of Bloch electrons and $\Omega_n(\mathbf{k})$ is the Berry curvature of Bloch electrons, defined as

$$\Omega_n(\mathbf{k}) = -\text{Im}(\nabla_{\mathbf{k}} u_{nk} | \times | \nabla_{\mathbf{k}} u_{nk} \rangle) \quad (12)$$

with the periodic part of eigenstate u_{nk} . The Berry curvature drives an anomalous transverse velocity in the presence of an electric field

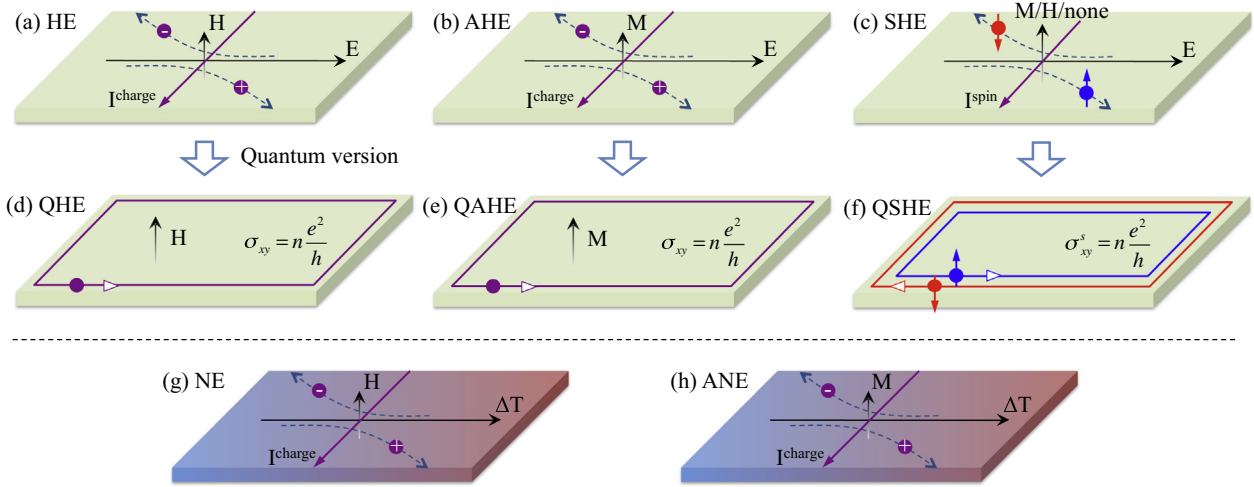


Fig. 1. Schematic plots of Hall family effects turned up in this work: (a) Hall effect, (b) anomalous Hall effect, (c) spin Hall effect; the quantum versions of (a–c), (e) quantum Hall effect, (e) quantum anomalous Hall effect, (f) quantum spin Hall effect; (g) Nernst effect, (h) anomalous Nernst effect. H, M, E, and ΔT are the magnetic field, magnetization, electric field, and temperature gradient, respectively. $I^{\text{charge}}/I^{\text{spin}}$ are the transverse charge/spin Hall currents; $\sigma_{xy}/\sigma_{xy}^s$ are the transverse charge/spin Hall conductivities with quantized values (n is an integer).

[3], which is responsible for the intrinsic contribution to the anomalous Hall effect [10].

According to the Kubo-formula [10,11], the Berry curvature can be recast to

$$\Omega_{n,z}(\mathbf{k}) = -\sum_{n' \neq n} \frac{2\text{Im}\langle \psi_{n\mathbf{k}} | \mathbf{v}_x | \psi_{n'\mathbf{k}} \rangle \langle \psi_{n'\mathbf{k}} | \mathbf{v}_y | \psi_{n\mathbf{k}} \rangle}{(\omega_{n'} - \omega_n)^2}, \quad (13)$$

where $\mathbf{v}_{x,y}$ are the velocity operators and eigenvalue $\varepsilon_n = \hbar\omega_n$. One can naturally evaluate the total Berry curvature for all occupied bands at individual $\mathbf{k}$ point,

$$\Omega_z(\mathbf{k}) = \sum_n f_n \Omega_{n,z}(\mathbf{k}), \quad (14)$$

where f_n is the Fermi–Dirac distribution function. Then, the intrinsic anomalous Hall conductivity (IAHC) can be calculated by the integration of total Berry curvature over the Brillouin zone (BZ):

$$\sigma_{xy} = -\frac{e^2}{h} \int_{\text{BZ}} \frac{d^3k}{(2\pi)^3} \Omega_z(\mathbf{k}). \quad (15)$$

2.3. Spin Hall conductivity

Similar to the IAHC, the intrinsic spin Hall conductivity (ISHC) is written as the integration of spin Berry curvature in the BZ,

$$\sigma_{xy}^s = \frac{e}{h^2} \int_{\text{BZ}} \frac{d^3k}{(2\pi)^3} \Omega_z^s(\mathbf{k}), \quad (16)$$

with

$$\Omega_z^s(\mathbf{k}) = \sum_n f_n \Omega_{n,z}^s(\mathbf{k}). \quad (17)$$

Again using the Kubo-formulas [12,13], the spin Berry curvature is expressed as,

$$\Omega_{n,z}^s(\mathbf{k}) = -\sum_{n' \neq n} \frac{2\text{Im}\langle \psi_{n\mathbf{k}} | \mathbf{j}_x | \psi_{n'\mathbf{k}} \rangle \langle \psi_{n'\mathbf{k}} | \mathbf{v}_y | \psi_{n\mathbf{k}} \rangle}{(\omega_{n'} - \omega_n)^2}, \quad (18)$$

where $\mathbf{j}_x$ is defined as the spin current operator $\frac{1}{2}(\hat{s}_z v_x + v_x \hat{s}_z)$ and $\hat{s}$ stands for the Pauling matrix. Using Eqs. (17) and (18), we can easily calculate the SHC.

2.4. Anomalous Nernst conductivity

In a ferromagnet, the Hall voltage could also arise when a thermal gradient instead of an electric field is applied. This phenomenon, due to the relativistic SOC, is referred to as the anomalous Nernst effect (ANE). Within this Berry-phase formalism, the intrinsic anomalous Nernst conductivity (IANC) can be written as [14]

$$\alpha_{xy} = \frac{1}{T} \frac{e}{h} \sum_n \int_{\text{BZ}} \frac{d\mathbf{k}}{(2\pi)^3} f_{n\mathbf{k}} \Omega_{n,z}(\mathbf{k}) \times [(\varepsilon_{n\mathbf{k}} - \mu) f_{n\mathbf{k}} + k_B T \ln(1 + e^{-\beta(\varepsilon_{n\mathbf{k}} - \mu)})], \quad (19)$$

where μ is the chemical potential, k_B is the Boltzmann constant. The BZ integration of the Berry curvature for all the occupied bands is very similar to the calculations of IAHC and ISHC. Further, the IANC has a direct relation to the IAHC, given by

$$\alpha_{xy} = -\frac{1}{e} \int d\epsilon \frac{\partial f}{\partial \mu} \sigma_{xy}(\epsilon) \frac{\epsilon - \mu}{T}. \quad (20)$$

2.5. Chern number

In 2D systems, with either external magnetic field or internal magnetic exchange field, there may appear chiral edge states on the boundary, which are intimately related to the topological property of the bulk Bloch states. These topological phenomena are so-called quantum Hall effect (QHE) or quantum anomalous Hall effect (QAHE), which can be characterized by the quantized charge Hall conductance,

$$\sigma_{xy} = C \frac{e^2}{h} \quad (21)$$

where C is an integer known as the Chern number [11,15] being deeply related to the Berry phase of Bloch electrons. The Chern number can be calculated from the integration of Berry curvature in 2D BZ,

$$C = \frac{1}{2\pi} \sum_n \int_{\text{BZ}} d^2k \Omega_n \quad (22)$$

The Chern number, as a topological invariant, can be used to distinguish the topological insulator and ordinary insulator in 2D magnetic systems with broken time-reversal symmetry [16].

2.6. Z_2 topological invariants

In the non-magnetic system, i.e., with time-reversal symmetry, the topological materials can be characterized by the Z_2 topological invariants [17,18]. Further considering the spatial inversion symmetry, there are two kinds of methods to calculate Z_2 topological invariants.

For the materials with spatial inversion symmetry, Z_2 topological invariants can be simply evaluated by the parity method [19]. In 3D systems, there are four independent invariants $v_0; (v_1 v_2 v_3)$:

$$(-1)^{v_0} = \prod_i \delta_i, \quad (23)$$

$$(-1)^{v_k} = \prod_{n_k=1, n_{j \neq k}=0,1} \delta_{i=(n_1 n_2 n_3)}. \quad (24)$$

where δ_i is the product of parity eigenvalues for occupied bands at time-reversal invariant momenta, $\Gamma_{i=(n_1 n_2 n_3)} = \frac{1}{2}(n_1 \mathbf{G}_1 + n_2 \mathbf{G}_2 + n_3 \mathbf{G}_3)$; $\mathbf{G}_{1,2,3}$ are primitive reciprocal-lattice vectors and $n_{1,2,3}$ is equal to 1 or 0. $v_0 \neq 0$ indicates a strong topological insulator (STI); if $v_0 = 0$, but not all of v_1, v_2 , and v_3 are equal to zero, the system is called weak topological insulator (WTI); $v_0 = v_1 = v_2 = v_3 = 0$ indicates an ordinary insulator. In 2D systems, there is only one independent invariant, that is, $v_0 = 1$ means a topological insulator, while $v_0 = 0$ means an ordinary insulator.

To obtain the Z_2 topological invariants in the spatial inversion symmetric systems, the key job is to calculate the eigenvalues of parity operator at each time-reversal invariant momenta, i.e., $\langle \Psi_{n\Gamma}(\mathbf{r}) | P | \Psi_{n\Gamma}(\mathbf{r}) \rangle$. The parity operator P is defined as $\{I; \mathbf{t}\}$, where I is an inverse operation making $\mathbf{r} \rightarrow -\mathbf{r}$ and $\mathbf{t}$ is a translational operation. The derivation of parity eigenvalue within the FP-LAPW formalism have been discussed in detail in our previous work [7].

On the other hand, for the materials without spatial inversion symmetry, the parity criterion cannot be applied. However, one can still calculate the Z_2 topological invariants by using a more complex method with lattice division in the BZ [20], which is deeply related to the Berry phase of bulk valence electrons. Fu and Kane first demonstrated [21] that under the time-reversal constraints, the Z_2 topological invariants can be expressed as

$$Z_2 = \frac{1}{2\pi} \left[\oint_{\partial B^+} d\mathbf{k} \cdot \mathcal{A}(\mathbf{k}) - \int_{B^+} d^2 k \mathcal{F}(\mathbf{k}) \right] \bmod 2, \quad (25)$$

where B^+ and ∂B^+ represent half of BZ and its boundary respectively, which is schematically plotted in Fig. 2. The integrands in Eq. (25) are the Berry connection

$$\mathcal{A} = i \sum_n \langle u_n(\mathbf{k}) | \nabla_{\mathbf{k}} u_n(\mathbf{k}) \rangle \quad (26)$$

and the Berry curvature

$$\mathcal{F}(\mathbf{k}) = \nabla_{\mathbf{k}} \times \mathcal{A}(\mathbf{k})|_{\mathbf{z}}, \quad (27)$$

where $|u_n(\mathbf{k})\rangle$ is the periodic part of BFs. From the aspect of numerical calculation, the finite element expressions of the Berry connection and Berry curvature are needed, given by,

$$\mathcal{A}_{\mu}(\mathbf{k}_j) = \text{Im} \log U_{\mu}(\mathbf{k}_j), \quad (28)$$

and

$$\mathcal{F}(\mathbf{k}_j) = \text{Im} \log U_{\mu}(\mathbf{k}_j) U_{\nu}(\mathbf{k}_j + \boldsymbol{\mu}) U_{\mu}^{-1}(\mathbf{k}_j + \boldsymbol{\nu}) U_{\nu}^{-1}(\mathbf{k}_j), \quad (29)$$

respectively. Here, the central quantity is the so-called link variable,

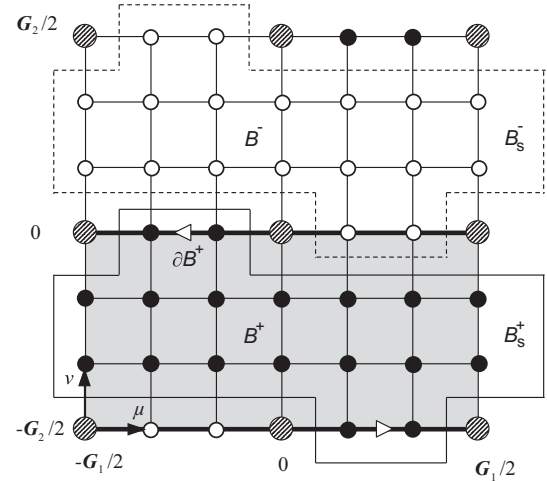


Fig. 2. A schematic presentation of lattice division of 2D BZ. Only shaded region B^+ is needed due to the time-reversal symmetry. The thick lines indicate the boundary ∂B^+ and the open arrows denote their directions. All k points are classed into: B_s^+ , B_s^- , and B_s^0 , labeled by small solid, small open and large shaded circles, respectively. Adapted from Ref. [7].

$$U_{\mu}(\mathbf{k}_j) = \frac{\det \langle \tilde{u}_m(\mathbf{k}_j) | \tilde{u}_n(\mathbf{k}_j + \boldsymbol{\mu}) \rangle}{|\det \langle \tilde{u}_m(\mathbf{k}_j) | \tilde{u}_n(\mathbf{k}_j + \boldsymbol{\mu}) \rangle|}, \quad (30)$$

in which $\boldsymbol{\mu}$ is the unit vector on the uniformed $\mathbf{k}$ -mesh of BZ and $|\tilde{u}_m(\mathbf{k}_j)\rangle$ is the periodic part of BFs applied by the time-reversal constraints

$$|u_n(-\mathbf{k})\rangle = \Theta |u_n(\mathbf{k})\rangle, \quad \mathbf{k} \in B_s^+, \quad (31)$$

$$|u_{2n}(-\mathbf{k})\rangle = \Theta |u_{2n-1}(\mathbf{k})\rangle, \quad -\mathbf{k} \text{ and } \mathbf{k} \in B_s^0, \quad (32)$$

and also the periodic gauge

$$|u_n(\mathbf{k} + \mathbf{G}_j)\rangle = e^{-i\mathbf{G}_j \cdot \mathbf{r}} |u_n(\mathbf{k})\rangle. \quad (33)$$

The calculations of overlap matrices related to time-reversal symmetry and periodic gauge have been discussed in detail in our previous work [7].

In 3D systems, there are four independent planes, $T(Z_0)$, $T(Z_1)$, $T(X_0)$ and $T(Y_0)$, which are plotted in Fig. 3. On each plane, one can correspondingly calculate the Z_2 topological invariants, z_0 , z_1 , x_0 , and y_0 , respectively. Following Refs. [22–24], we further denote four independent Z_2 invariants by $v_0; (v_1 v_2 v_3)$, with the relation of $v_0 = (z_0 + z_1) \bmod 2$, $v_1 = x_0$, $v_2 = y_0$ and $v_3 = z_1$. Using these four invariants, topological insulators can be further

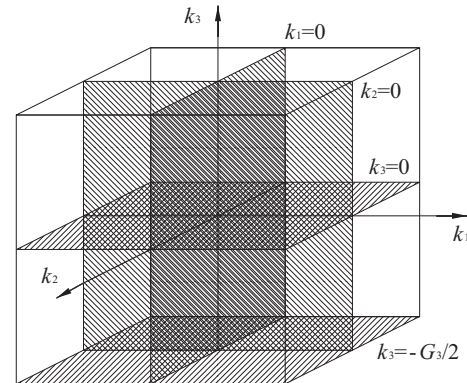


Fig. 3. A schematic presentation of four independent planes in 3D BZ, $T(Z_0)$, $T(Z_1)$, $T(X_0)$ and $T(Y_0)$, which locate at $k_3 = 0$, $k_3 = -G_3/2$, $k_1 = 0$, and $k_2 = 0$, respectively. Adapted from Ref. [7].

classified into STI and WTI, as above mentioned. In 2D systems, there is only one planes $T(Z_0)$, therefore, only one topological invariants ν_0 exists and thus there is not the well definition of WTI.

In addition to our method, there appeared other approaches to compute the Z_2 topological invariants, which are based on the evolution of the Wannier charge centers [25,26].

3. Anomalous Hall, spin Hall, and anomalous Nernst effects

In solid materials, the spin–orbit coupling is responsible for various phenomena of transverse transports, e.g., the anomalous Hall effect (AHE) [27,28], spin Hall effect (SHE) [29], and anomalous Nernst effect (ANE) [30], which have long been concerned in the fundamentally physical interest and practical applications.

3.1. First-principles study on the intrinsic AHE

AHE was discovered more than a century ago but its microscopic origin has not been very clear until recently. Within the semiclassical theory, there are three contributions to the AHE [31]: the intrinsic contribution [32], which comes solely from the electronic structure of pristine crystal and relates deeply to the Berry phase of Bloch electrons; the extrinsic skew-scattering contribution [33,34], which arises from an asymmetric scattering of electrons and is proportional to the impurity concentration; the extrinsic side-jump contribution [35,36], which is also essentially driven by the scattering of electrons off impurities but does not depend on the concentration of impurities.

The dominated microscopic mechanisms existing in various types of ferromagnets has for over several decades been discussed. On the experimental part, an empirical relation between the magnetization and the Hall resistivity was proposed: $\rho_H = R_0 H + R_1 M(T, H)$, which can be roughly used to judge the intrinsic and extrinsic contributions depending on the behavior of anomalous Hall coefficient R_1 as a function of the longitudinal resistivity ρ_0 . On the theoretical part, most of calculations comparing the intrinsic and extrinsic contributions of the AHE from a microscopic point of view have been performed for very simple models not immediately linked to real materials, such that a crucial corollary was still not obtained in any system. This continuous debating and confusing were on-going until to the breakthrough in the year of 2004. At that time, Yao et al. [10] first pointed out that the Berry phase related intrinsic contribution is prominently dominated in ferromagnetic metal Fe by using accurate first-principles FP-LAPW calculations. At the same time, Fang et al. [37] studied the AHE in ferromagnetic SrRuO_3 and also demonstrated the importance of intrinsic mechanism via the picture of magnetic monopoles in momentum space.

Using Eq. (15), the calculated IAHC of Fe is $751 (\Omega\text{cm})^{-1}$, in reasonable agreement with experimental value of $1032 (\Omega\text{cm})^{-1}$. This calculation uncovered the vital role of intrinsic mechanism, which originates from the Berry phase of Bloch electrons. The Berry curvature $\Omega_{n,z}$ usually has large peaks around the nearly degenerated bands, e.g., near the point H in Fig. 4. The σ_{xy} is always strongly enhanced when the Fermi level across the SOC induced small band gap because the Berry curvature has opposite signs for the upper and lower bands and only lower band is occupied. Fig. 5 shows the map distribution of Berry curvature $\Omega_{n,z}$ and the relevant Fermi surface. The $\mathbf{k}$ points with largest $\Omega_{n,z}$ act essentially as a magnetic monopole in momentum space, which drives an anomalous velocity and is responsible for the emergence of AHE. Physically, the AHE can be viewed as the charily of magnetic monopole in momentum space, represented by the extreme Berry curvature.

This conclusion in 3d transition metals has been further confirmed by other theoretical calculations, such as Fe [38–40], Co

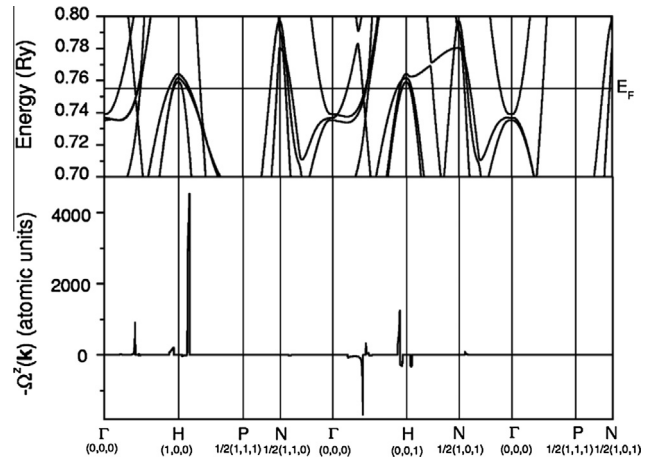


Fig. 4. First-principles calculation of the band structure (top panel) and Berry curvature (bottom panel) of Fe. Adapted from Ref. [10].

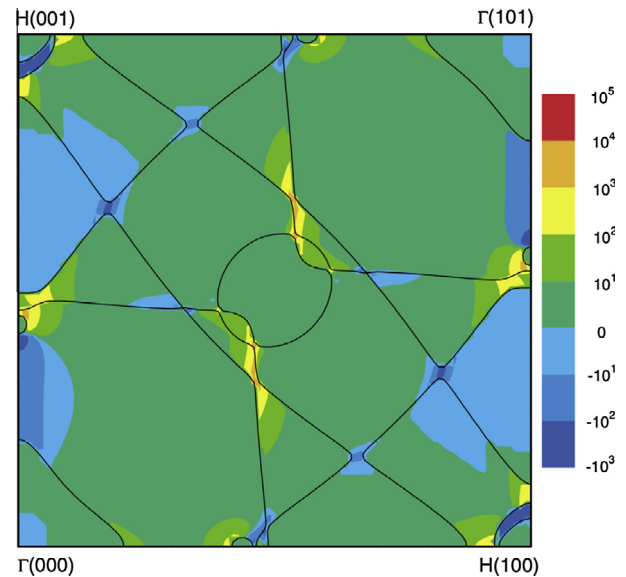


Fig. 5. First-principles calculation of the Fermi surface (solid lines) and Berry curvature (color map) of Fe in the (010) plane. Adapted from Ref. [10]. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

[39,40], Ni [39,40]. Besides the pure transition metals, we have also extended the study of intrinsic AHE to magnetic spinel $\text{CuCr}_2\text{Se}_{4-x}\text{Br}_x$ [41], magnetic thinfilm Mn_5Ge_3 [42]. In $\text{CuCr}_2\text{Se}_{4-x}\text{Br}_x$, the calculated IAHC as a function of electron-doping can reasonably capture the feature of sign changes comparing with experimental observations, as present in Fig. 6, which again exemplifies the underlying mechanism of Berry phase. In Mn_5Ge_3 , the calculated IAHC is $964 (\Omega\text{cm})^{-1}$, in excellent agreement with the experimental measurement of $860 (\Omega\text{cm})^{-1}$. Furthermore, a realistic method for separating the intrinsic and extrinsic contributions to the AHE has been successfully developed [42].

3.2. First-principles study on the intrinsic SHE

The spin current in the SHE can be regarded as two anomalous Hall currents, which propagate in opposite directions and separately carry spin-up and spin-down electrons. In principle, the microscopic mechanisms of the AHE are equivalent to those

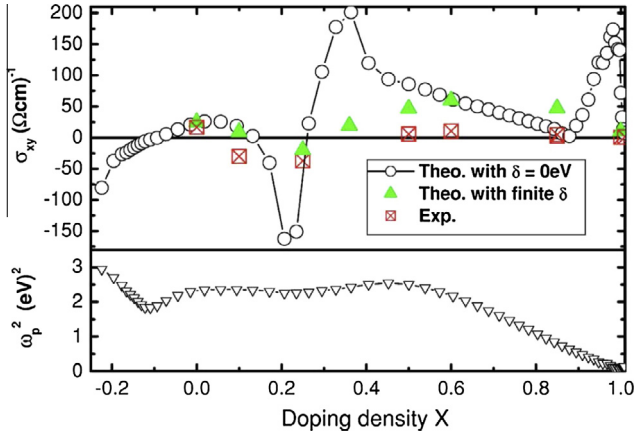


Fig. 6. The calculated IAHC (open circles and solid triangles) and experimental results (square crosses) as a function of doping x in $\text{CuCr}_2\text{Se}_{4-x}\text{Br}_x$ (upper panel). δ is a small parameter representing the finite lifetime broadening of the eigenstates, which can be determined from the plasma frequency (lower panel). Adapted from Ref. [41].

responsible for the SHE. Similar to the AHE, the SHE also has intrinsic (impurity independent) and extrinsic (impurity driven) parts from the experimental observations. The only difference between the AHE and SHE is that the ferromagnetic order is needed for the former one, while the latter one exists also in nonmagnetic materials.

The existence of SHE has been experimentally confirmed in 2D hole gas [43] and 3D electron film [44]. Although many theoretical studies based on certain model Hamiltonians have attempted to provide physical pictures for the understanding of microscopic mechanism, the intrinsic or the extrinsic origin of the SHE is still not clear. Taking advantage of parameter-free first-principles calculation, we studied the intrinsic SHE in various systems, including semiconductors (Si and GaAs) [12,13], simple metals (W and Au) [12], and group-VI dichalcogenides MX_2 ($M = \text{Mo}, \text{W}$; $X = \text{S}, \text{Se}$) [45].

Fig. 7 shows the calculated band structure and ISHC σ_{xy}^s as functions of the Fermi level for bulk Si. At zero temperature and clean limit, the maximum of σ_{xy}^s is $50 (\Omega\text{cm})^{-1}$ for hole-doped Si, which mainly comes from the contributions of heavy hole bands at Γ point; on the other hand for electron-doped Si, the σ_{xy}^s is negative and reach its maximum of $-50 (\Omega\text{cm})^{-1}$, which comes from the contribution of s orbitals at X point. The sign of σ_{xy}^s is the same

as that of ordinary Hall effect, i.e., positive for hole doping and negative for electron doping. The effects of temperature and disorder can be taken into account by modifying the Fermi distribution f_{nk} by adding a parameter of finite lifetime broadening δ in the Berry curvature. The results show that temperature and disorder change the ISHC very much in the electron-doped case, while not so dramatic for the hole-doped one. There are similar results for another semiconductor GaAs, e.g., Fig. 1 in Ref. [12].

Fig. 8 shows the calculated band structure and ISHC σ_{xy}^s as functions of the Fermi level for bulk Au. At zero temperature and clean limit, the σ_{xy}^s has a large value of $731 (\Omega\text{cm})^{-1}$, which is very expectable due to the strong SOC in Au. These results are similar to another simple metal W but with opposite sign of σ_{xy}^s , e.g., Fig. 3 in Ref. [12]. W has negative σ_{xy}^s with hole-type conductivity, while Au has positive σ_{xy}^s with electron-type conductivity. For W and Au, the signs of σ_{xy}^s are opposite with their carrier type, thus this is different from the situation of GaAs and Si.

Group-VI dichalcogenides MX_2 ($M = \text{Mo}, \text{W}$; $X = \text{S}, \text{Se}$) have van der Waals layered structures and each monolayer is consisted of one M and two X atoms with strongly covalent bondings. Due to the presence of inversion symmetry breaking in monolayer MX_2 , the charge carriers acquire an opposite Berry curvature at K and K' points, as seen in Fig. 9(a) and (b), such that the net IAHC is zero by the integration of Berry curvature in the whole BZ. However, spin Berry curvature has the same sign at K and K' points, as seen in Fig. 9(c) and (d), which results in a finite ISHC. At hole-doping concentration $n_h = 1.0 \times 10^{-13} \text{ cm}^{-2}$, the calculated σ_{xy}^s is up to $1.3 \times 10^{-2} e^2/h$, which is comparable to that in $p(n)$ -doped semiconductors GaAs, Si, Ge, and AlAs [12,13]. We also calculated the σ_{xy}^s in inversion-symmetric bulk MX_2 and found that it is about one order of magnitude smaller than that of monolayer.

3.3. First-principles study on the intrinsic ANE

The IANC α_{xy} depends only on the band structure and Berry curvature, so it can be evaluated for crystals based on first-principles methods. We previously studied the intrinsic ANE as a function of doping concentration x in the magnetic spinel $\text{CuCr}_2\text{Se}_{4-x}\text{Br}_x$ [14], as shown in Fig. 10. One can see that the calculated α_{xy} is quantitatively in agreement with the experimental data except for the data point at $x = 0.25$, where is a rather special point because it was experimentally reported [46] that for some unknown reasons, α_{xy} is not really proportional to temperature.

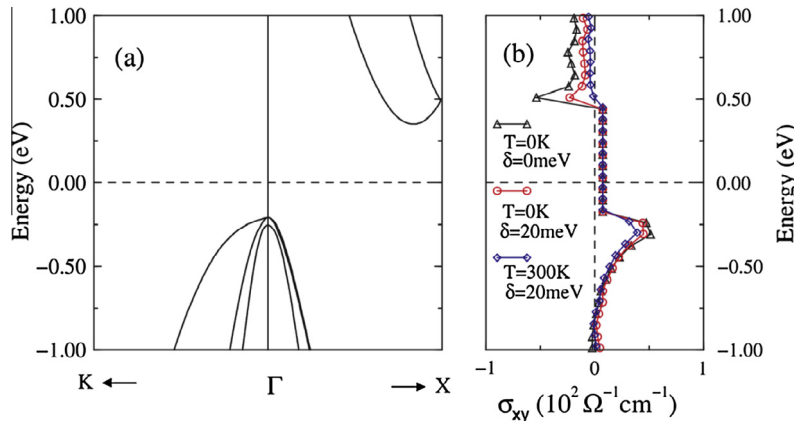


Fig. 7. The calculated band structure (a) and ISHC σ_{xy}^s (b) as function of the Fermi level for bulk Si. Note: the unit of ISHC has been multiplying a factor of $2e/h$ to be consistent with that of IAHC. Adapted from Ref. [12].

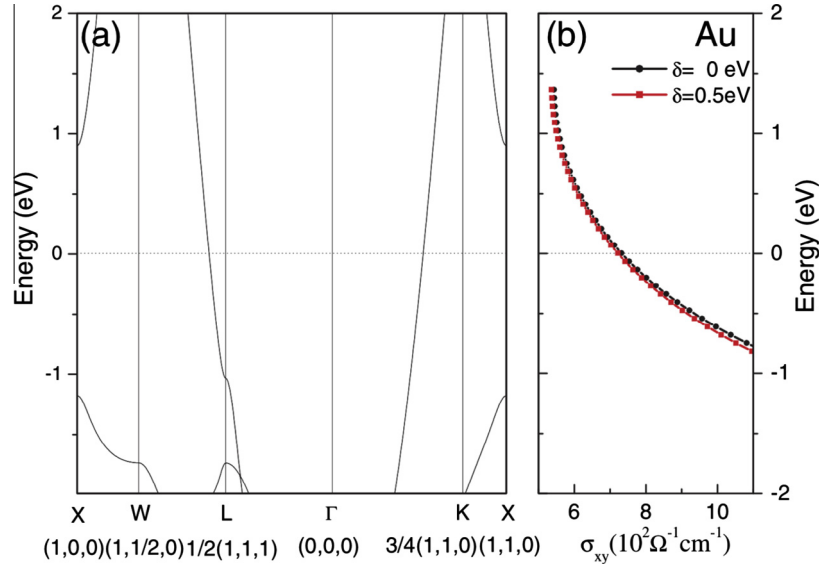


Fig. 8. The calculated band structure (a) and ISHC σ_{xy}^s (b) as function of the Fermi level for bulk Au. Note: the unit of ISHC has been multiplying a factor of $2e/h$ to be consistent with that of IAHC. Adapted from Ref. [12].

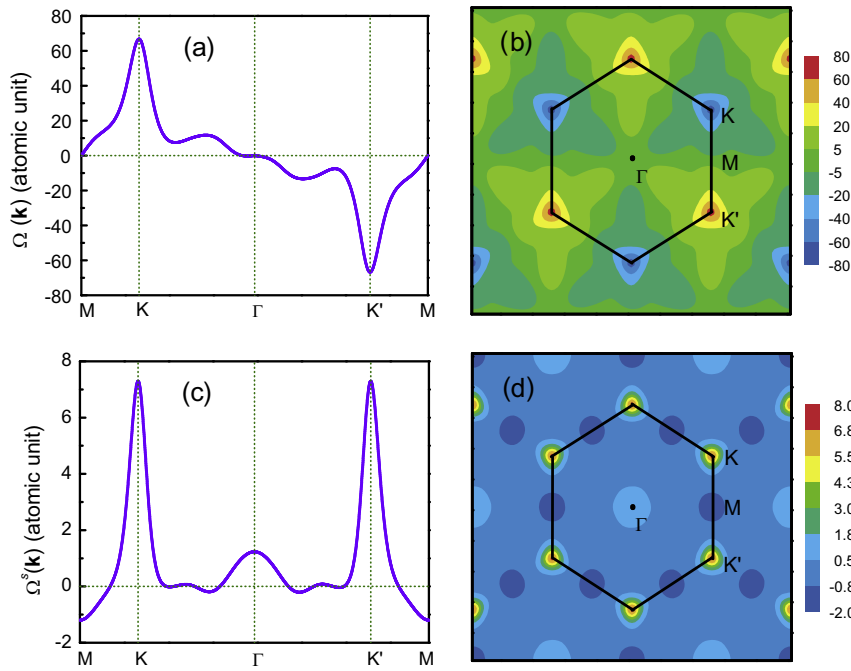


Fig. 9. The ordinary and spin Berry curvatures of monolayer MoS₂ along the high-symmetry lines (a and c), and in the 2D k -plane (b and d), respectively. Adapted from Ref. [45].

At low temperatures, the Mott relation between the electrical and thermoelectric conductivities can be established,

$$\alpha_{xy} = \frac{\pi^2}{3} \frac{k_B^2 T}{e} \sigma'_{xy}(\epsilon_F),$$

where ϵ_F indicates the Fermi energy. A proportional relation between α_{xy} and temperature is expected from above Mott relation. In fact, this is followed strictly by all the data points at other doping densities, but not at $x = 0.25$. More detailed experimental results are clearly needed for a careful comparison with our calculations.

The oscillatory behavior of α_{xy} results from the complicated band structure and occurs when the Fermi energy goes through a region of SOC induced band gap [41]. We predicted a pronounced peak-valley structure around $x = 0.3$, while the available

experimental data is too sparse to capture it. Nevertheless, there is an indirect experimental evidence [47] for this peak because it occurs at a place where the AHC has a sudden change of sign and magnitude around the doping concentration $x = 0.3$. Such a correlation is just expected from above Mott relation. Furthermore, the Mott relation has also been used to study the ANE and the AHE in proximity-induced ferromagnetic Pt and Pd, and their potential relations to the SHE from other theoretical work [48].

4. Two-dimensional topological materials

Two-dimensional (2D) layered materials, such as successfully fabricated graphene [49–51], silicene [52–54], germanene, stanene, X-hydride/halide ($X = N-Bi$) monolayers, Bi₄Br₄, and graphite

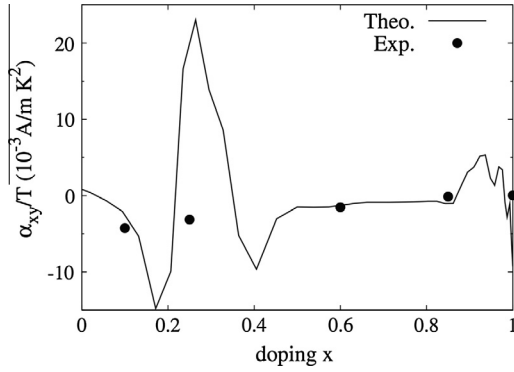


Fig. 10. The intrinsic anomalous Nernst conductivity α_{xy} of $\text{CuCr}_2\text{Se}_{4-x}\text{Br}_x$ as a function of the Br content x . Solid circles are experimental values. Adapted from Ref. [14].

like metal–organic framework [55], are a hotspot in the fields of condensed matter physics and material science due to their novel low-energy Dirac electronic behaviors and promising applications in electronics. In this section, we will review our group's works on novel quantum states of matter with nontrivial topological properties, such as 2D Z_2 topological insulator states, 2D Chern topological insulator states, and topological superconductivity in these 2D layered materials.

4.1. 2D Z_2 TIs

4.1.1. Graphene

The quantum spin Hall effect (QSHE), a new quantum state of matter with nontrivial topological properties, has garnered great interest in the fields of condensed matter physics and materials science due to its scientific importance as a novel quantum state and its technological applications in spintronics. QSH phase with time-reversal invariance, which is characterized by Z_2 topological invariant [18,56], is gapped in the bulk and conduct charge and spin in gapless edge states without dissipation at the sample boundaries.

Although the concept of QSHE, also known as 2D Z_2 TIs, was first proposed in graphene, our subsequent works showed that the band gap opened by SOC is extremely small ($\sim 10^{-6}$ eV), which is in fact a second order process for graphene, such that the QSH effect can occur only at an unrealistically low temperature [57]. Currently, the major challenge is to find suitable materials with larger SOC gap for QSHE. In the following, we will introduce several kinds of QSH insulators with a large SOC gap, which we proposed in the last few years.

4.1.2. Silicene, germanene, and stanene

Using first-principles methods, we have recently demonstrated, by exploiting adiabatic continuity and the direct calculation of the Z_2 topological invariant, that 2D low-buckled honeycomb silicene, germanene and stanene can realize the QSHE, with a sizable gap opened at the Dirac points due to their larger SOC and low-buckled structures [58,59]. The geometric structure of freestanding silicene, germanene and stanene is low-buckled as plotted in Fig. 11(a) and (b). Fig. 11(c)–(e) shows that for native silicene, germanene and stanene, the size of the QSHE gap are respectively 1.55 (18 K), 23.9 (277 K) and 73.5 (854 K) meV, higher than the liquid helium, the liquid nitrogen, and room temperature, respectively.

Starting from symmetry considerations and the tight-binding method in combination with first-principles calculation, we systematically derive the low-energy effective Hamiltonian and tight-binding Hamiltonian involving spin–orbit coupling (SOC) for silicene. This model Hamiltonian is very general because it applies not only to silicene itself but also to the low-buckled

germanene and stanene, as well as to graphene when the structure returns to the planar geometry [59].

Around the valley K and K' , the low-energy subspace reads as follows

$$\begin{aligned}\phi_1 &= u_{11}p_z^A + u_{21}s^A + u_{31}\left[\frac{1}{\sqrt{2}}(\tau_z p_x^B - ip_y^B)\right], \\ \phi_4 &= u_{11}p_z^B - u_{21}s^B + u_{31}\left[-\frac{1}{\sqrt{2}}(\tau_z p_x^A + ip_y^A)\right].\end{aligned}\quad (34)$$

In the representation of $\{\phi_1, \phi_4\} \otimes \{\uparrow, \downarrow\}$, the low-energy effective Hamiltonian reads

$$H_K^{\text{eff}}(\theta) = v_F(\theta)(k_x\sigma_x - k_y\tau_z\sigma_y) + h(\theta)\tau_z\sigma_z, \quad (35)$$

with

$$h(\theta) \equiv -\lambda_{so}(\theta)s_z - a\lambda_R(\theta)(k_ys_x - k_xs_y).$$

The Pauli matrix σ, s and τ act on the spaces of basis, spin and valley, respectively. $v_F(\theta)$ is Fermi velocity. a and θ are the lattice constant and buckled angle. The SOC parameter $h(\theta)$, which is a function of the buckled angle θ , contains a total new intrinsic Rashba SOC term and a first order next-nearest neighbor SOC term. It is the first order SOC that results in the larger QSH gap in the low-buckled silicene, germanene and stanene [59].

Finally, we introduce a second nearest neighbor tight-binding model

$$\begin{aligned}H &= -t\sum_{\langle ij \rangle\alpha} c_{i\alpha}^\dagger c_{j\alpha} + it_2\sum_{\langle\langle ij \rangle\rangle\alpha\beta} v_{ij}c_{i\alpha}^\dagger s_{\alpha\beta}^z c_{j\beta} \\ &\quad - it_1\sum_{\langle\langle ij \rangle\rangle\alpha\beta} \mu_{ij}c_{i\alpha}^\dagger (\mathbf{s} \times \mathbf{d}_{ij}^0)_{\alpha\beta}^z c_{j\beta}.\end{aligned}\quad (36)$$

The first term is the usual nearest neighbor hopping term. The second and third terms are effective SOC and intrinsic Rashba SOC. The three parameters t, t_2, t_1 are given explicit expression forms

$$t = \frac{2\sqrt{3}v_F}{3a}, \quad t_2 = \frac{\lambda_{so}}{3\sqrt{3}}, \quad t_1 = \frac{2}{3}\lambda_R. \quad (37)$$

Although stanene was first predicted to be a QSH insulator by us in 2011 [59], it has been experimentally synthesized very recently [60]. On the theoretical aspects, there are some works which extend our results to other 2D low-buckled materials with nontrivial topological properties, such as the QSHE in decorated stanene by adsorbing chemical functional group on Sn film in 2013 [61] and QSHE in dumbbell stanene with another kind of 2D structure of Sn film in 2014 [62].

4.1.3. X-hydride/halide ($X = \text{N–Bi}$) monolayers

Using FP method, we have recently demonstrated that the QSH effect can be realized in the 2D hydrogenated and halogenated group-V honeycomb monolayers family, with a huge gap opened at the Dirac points due to on-site SOC [63,64]. Their structures are similar to that of a hydrogenated silicene (silicane), as shown in Fig. 12(a). Note that two sets of sublattice in the honeycomb group X are not coplanar (a buckled structure). These monolayers is alternatively hydrogenated or halogenated on both sides.

In the absence of SOC, their band structures show linear energy crossing at the Fermi level around K and K' points of the hexagonal Brillouin zone. Taking BiH for example, it is a QSH insulator with a record bulk band gap larger than 1 eV, as shown in Fig. 12(c). The band edges mainly come from p_x and p_y orbitals from the Bi atoms of both sublattices. Fig. 12(d) plots the energy spectrum for the semi-infinite zigzag BiH monolayer. There are two helical edges states in the bulk gap, indicating the QSH phase. The X-hydride/halide ($X = \text{N–Bi}$) monolayers material family, being the first real

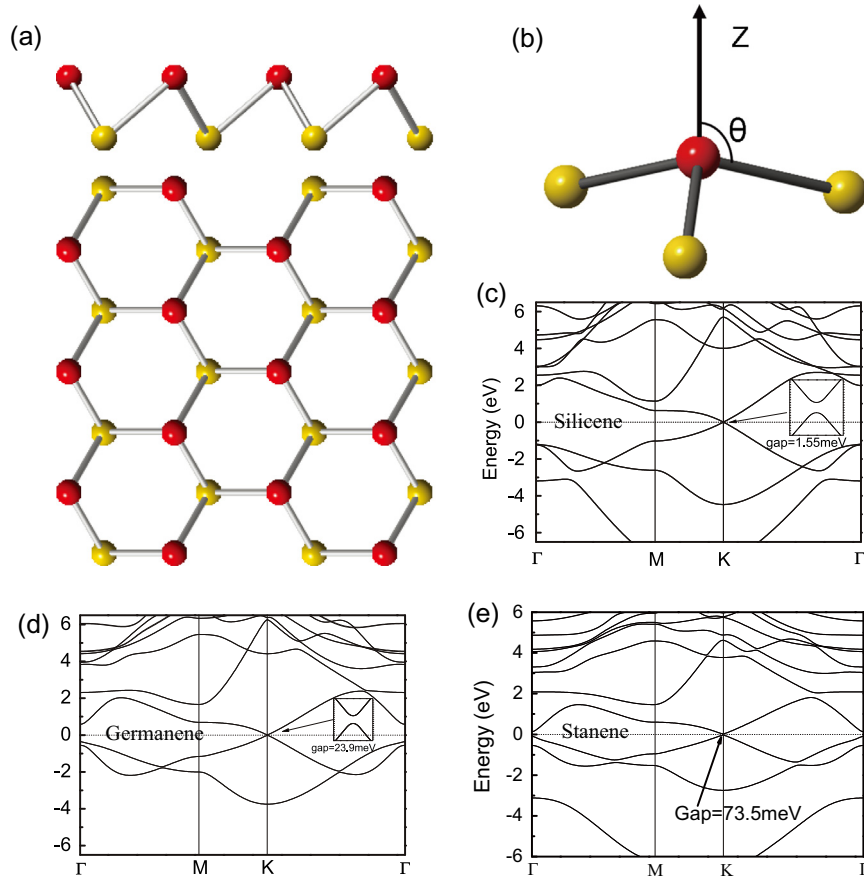


Fig. 11. The lattice geometries and relativistic band structures for the QSH insulators silicene, germanene and stanene. (a) The lattice geometry from the side view and top view, respectively. Note that the A sublattice (red or gray) and B sublattice (yellow or light gray) are not coplanar. (b) Definition of the angle as between the bond and the z direction normal to the plane. (c)–(d) The relativistic band structures of low-buckled silicene, germanene and stanene. Inset: Zoom of the energy dispersion near the K point and the gap induced by SOC. Partly adapted from Ref. [58]. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

condensed matter systems in which the low-energy physics is associated with p_x and p_y orbitals, are therefore expected to exhibit rich and interesting physical phenomena.

In the vicinity of K and K' , the low-energy Hilbert subspace for X-hydride reads as follows

$$\begin{aligned}\phi_1 &= u_{11}^\alpha \left[-\frac{1}{\sqrt{2}} (p_x^A + i\tau_z p_y^A) \right] + u_{21}^\alpha \tau_z s^B, \\ \phi_5 &= u_{11}^\alpha \left[\frac{1}{\sqrt{2}} (p_x^B - i\tau_z p_y^B) \right] - u_{21}^\alpha \tau_z s^A,\end{aligned}\quad (38)$$

In the representation of $\{\phi_1, \phi_5\} \otimes \{\uparrow, \downarrow\}$, the low-energy effective Hamiltonian reads

$$H_{\text{eff}} = v_F (k_x \sigma_x + \tau_z k_y \sigma_y) + \lambda_{so} \tau_z \sigma_z s_z, \quad (39)$$

where the analytical expressions and numerical values for Fermi velocity v_F and magnitude of intrinsic effective SOC λ_{so} are given in Ref. [64]. The Pauli matrix σ, s and τ act on the spaces of basis and spin and valley, respectively. $v_F(\theta)$ is Fermi velocity. For the X-halide ($X = \text{N–Bi}$) monolayers, the low-energy effective Hamiltonian is the same as the one of X-hydride. In the low-energy Hilbert subspace mainly consisted of p_x and p_y orbitals for X atoms, the SOC term is first order on-site SOC term. It is the first order on-site SOC that results in the huge QSH gap in X-hydride/halide ($X = \text{N–Bi}$) monolayers family. For the purpose of studying the topological properties of the honeycomb X-hydride/halide ($X = \text{N–Bi}$) monolayers family, as well as their edge states, we also give a simple spinful

lattice Hamiltonian for the family [64]. Similarly, large SOC gap also occurs on Bi adsorbed H-Si surface [65].

4.1.4. Monolayer Bi_4Br_4

We have also found that the monolayer of Bi_4Br_4 is a new QSH insulator with large band gap of about 0.18 eV [66], adequate for room-temperature applications. Bi_4Br_4 single crystal is a layered semiconductor with a trivial band gap. However, its monolayer structure, as shown in Fig. 13(a), has a nontrivial band gap (see Fig. 13(b)). The nontrivial band topology is originated from the band inversion between $\text{Bi-}p_x$ orbitals induced by SOC [66]. The external uniaxial strains along a -axis and b -axis could affect the inter-chain bonding and intra-chain bonding respectively. Hence, they might alter the nontrivial band gap of monolayer Bi_4Br_4 . Our result shows the uniaxial strains along different axes have opposite effect on the band gap, as shown in Fig. 13(c). Nevertheless, the QSH phase of monolayer Bi_4Br_4 survives in a relatively large range of strains.

Except for the large band gap and robustness of QSH phase against external strains, another advantage of this material is that it holds great promise for experimental fabrication. The interlayer coupling in Bi_4Br_4 single crystal is of weak van der Waals-type. The calculated interlayer binding energy is comparable to that of graphite, and is slightly smaller than that of MoS_2 . Therefore, the fabrication of monolayer Bi_4Br_4 becomes possible utilizing the “scotch tape” method similar to the fabrication of graphene and MoS_2 . Our further investigation on the electronic structure of

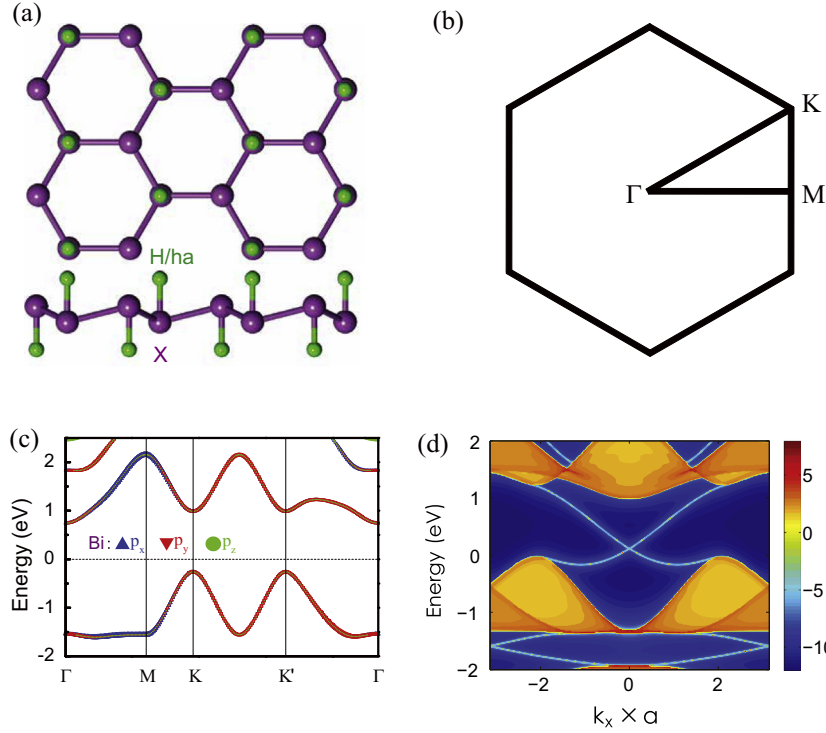


Fig. 12. (a) The lattice geometry for 2D X-hydride/halide (X = N–Bi) monolayer from the side view (top) and top view (bottom). (b) The first Brillouin zone and its points of high symmetry. (c and d) The projection bulk band structures and edge states for the BiH monolayer. Adapted from Ref. [64,76].

multilayer Bi_4Br_4 reveals that the interlayer coupling has very small effect on the band gap and low-energy electronic structure [67]. This result indicates that we can use the surface of bulk Bi_4Br_4 as the intrinsic insulating substrate for the monolayer Bi_4Br_4 , thus the preparation of freestanding monolayer Bi_4Br_4 is not necessary. The stair-stepped edge (see Fig. 13(e)) prepared by nano-fabrication on the cleaved surface of Bi_4Br_4 is adequate. From the calculated electronic structure of this geometry shown in Fig. 13(d), we can see that the topological edge states are preserved well inside the bulk band gap [67]. In addition, because of the special 1D molecular chain structure in Bi_4Br_4 , it is easy to form clean and atomically sharp edges, which could serve as ideal 1D wires for dissipationless transport.

4.2. 2D Chern TIs

4.2.1. Transition-metal atoms adsorbed graphene

Quantum anomalous Hall (QAH) phase is characterized by a finite Chern number and chiral edge states in the bulk band gap, and maintains robust stability against disorder and other perturbations [68]. Although the first proposal appeared over twenty years ago [68], not until recently was the experimental evidence for QAH phase reported in Cr-doped $(\text{Bi,Sb})_2\text{Te}_3$ at extremely low temperatures [69,70]. We have proposed some strategies to achieve QAH effects at high temperatures in honeycomb materials such as by transition-metal atoms adaption on graphene [16,71,72], heterostructure of graphene on an antiferromagnetic insulator [73], introduction of exchange field in silicene [74,75], and surface functionalization on hydrogenated monolayer honeycomb Bi (BiH) [76].

We predict that the quantum anomalous Hall effect can be realized in graphene by introducing Rashba SOC and an exchange field [16,71]. The tight-binding Hamiltonian for the graphene in the presence of Rashba SOC and exchange field can be written as

$$H = -t \sum_{\langle i,j \rangle \alpha} c_{i\alpha}^\dagger c_{j\alpha} + it_R \sum_{\langle i,j \rangle \alpha \beta} \vec{e}_z \cdot (\vec{\sigma}_{\alpha\beta} \times \vec{d}_{ij}) c_{i\alpha}^\dagger c_{j\beta} + \lambda \sum_{i\alpha} c_{i\alpha}^\dagger c_{i\alpha} \sigma_z, \quad (40)$$

where $c_i^\dagger (c_i)$ is the electron creation (annihilation) operator on site i , and σ are the Pauli matrices. The angular bracket $\langle i,j \rangle$ stands for nearest-neighboring sites. The first term is the usual nearest-neighbor hopping term. The second term is the Rashba SOC, and $\vec{d}_{ij}$ represents a unit vector pointing from j to site i . The third term corresponds to a uniform exchange field.

Fig. 14 presents the evolution of the band structures with Rashba SOC t_{SO} and exchange field λ . Fig. 14(a) plots the band structure of the pristine graphene with Dirac cones centered at K and K' points in the reciprocal space. Due to spin degeneracy, K and K' points are fourfold degenerate while other points are doubly degenerate. When only the exchange field is applied, the spin-up (spin-down) bands are pushed upward (downward) as shown in Fig. 14(b). When only Rashba SOC is turned on, spin-up and spin-down states are mixed around the band crossing points and spin degeneracy is lifted. A bulk gap is opened when both Rashba SOC and exchange field are present, and the four bands become completely nondegenerate. As shown in panel (d), the spin texture around K forms a Skyrmion: spins point down in the central region but point up in the outside region. And the spin texture around K' is similar to the one around K . Since each Skyrmion contributes to a Chern number $C = 1$, Skyrmions at K and K' points give rise to a total Chern number $C = 2$ in our model.

We also consider a concrete example with transition-metal atoms (e.g., Fe) adsorbed on top of graphene, as shown in Fig. 15. The resulting broken structural symmetry gives rise to a Rashba-type SOC whereas the hybridization between the carbon π state and the $3d$ -shell states of magnetic atoms produces a macroscopic exchange field. From first-principles calculations, the Hall conductivity is found to be $\sigma_{yx} = 2e^2/h$ when the Fermi level lies in the bulk gap, and we find that a bulk gap 5.5 meV can be opened by

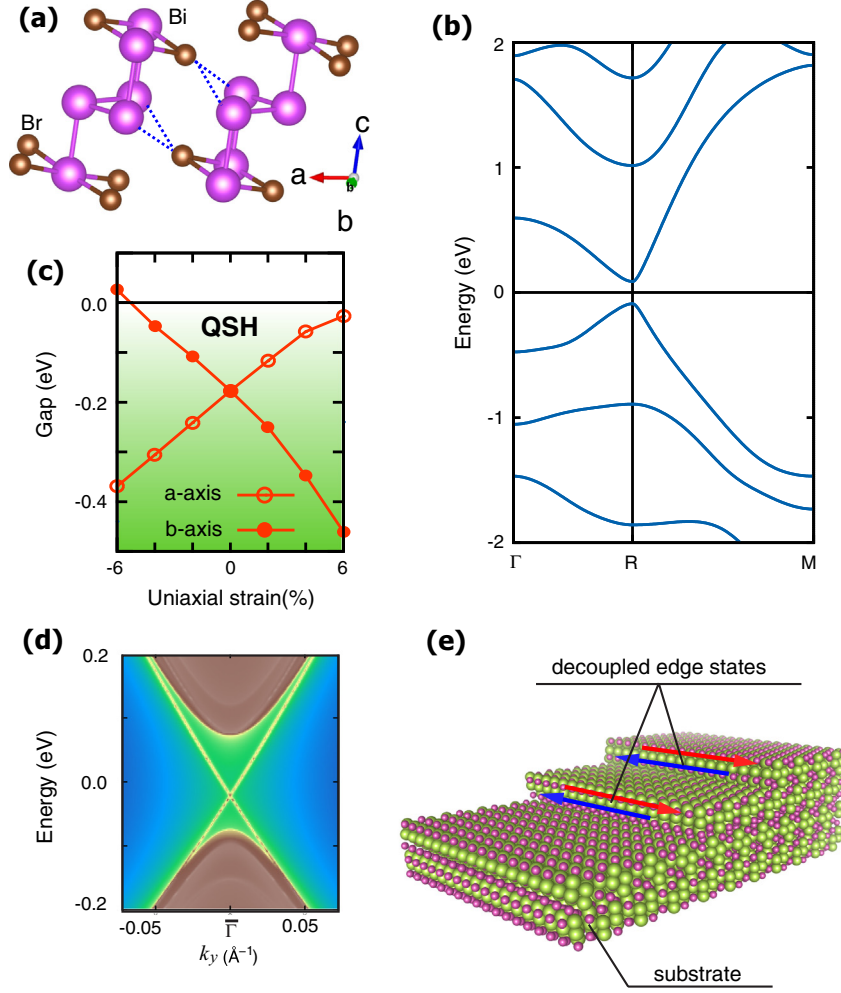


Fig. 13. (a) Crystal structure of monolayer Bi_4Br_4 . (b) Band structure along high-symmetry points. (c) Band gap as a function of uniaxial strain. (d) Electronic structure of the stair-stepped structure shown in (e). (e) The stair-stepped edge supported by bulk Bi_4Br_4 surface. Adapted from Ref. [66,67].

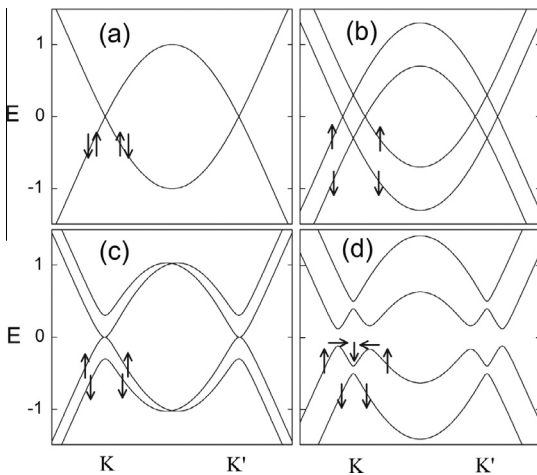


Fig. 14. Evolution of band structures of bulk graphene along the profile of $k_y = 0$. Arrows represent the spin directions. Adapted from Ref. [16].

adsorbing Fe atoms on top of graphene, which is readily accessible under current experimental conditions.

4.2.2. Silicene

Through tuning the Rashba spin–orbit coupling in silicene, we numerically find a new topological phase, the valley-polarized

quantum anomalous Hall (VP-QAH) state. Different from the conventional quantum anomalous Hall state, the new topological phase has not only a quantized Chern number $C = 1$, but also a nonzero valley Chern number $C_v = 3$. Therefore, it possesses the properties of both the quantum anomalous Hall effect and the quantum valley Hall effect, and can be considered as a good candidate for designing dissipationless valleytronics [74,75].

In the tight-binding approximation, the Hamiltonian for silicene in the presence of spin–orbit couplings and exchange field can be written as

$$H = -t \sum_{\langle ij \rangle \alpha} c_{i\alpha}^\dagger c_{j\alpha} + it_0 \sum_{\langle\langle ij \rangle\rangle \alpha\beta} v_{ij} c_{i\alpha}^\dagger \sigma_{\alpha\beta}^z c_{j\beta} - it_{SO} \sum_{\langle\langle ij \rangle\rangle \alpha\beta} \mu_{ij} c_{i\alpha}^\dagger (\vec{\sigma} \times \hat{d}_{ij})_{\alpha\beta}^z c_{j\beta} + it_R \sum_{\langle ij \rangle \alpha\beta} c_{i\alpha}^\dagger (\vec{\sigma} \times \hat{d}_{ij})_{\alpha\beta}^z c_{j\beta} + M \sum_{i\alpha} c_{i\alpha}^\dagger \sigma_{i\alpha}^z c_{i\alpha}, \quad (41)$$

where $c_{i\alpha}^\dagger$ ($c_{i\alpha}$) is a creation (annihilation) operator for an electron with spin α on site i . The first term represents the nearest neighbor hopping term with hopping energy t . The second term is the effective spin–orbit coupling involving the next-nearest neighbor hopping with amplitude t_0 . $v_{ij} = \vec{d}_i \times \vec{d}_j / |\vec{d}_i \times \vec{d}_j|$, where $\vec{d}_i$ and $\vec{d}_j$ are two nearest bonds connecting the next-nearest neighbor sites. The summation over $\langle\langle \dots \rangle\rangle$ ($\langle\langle \dots \rangle\rangle$) runs over all the nearest (next-nearest) neighbor sites. The third and fourth terms are respectively the intrinsic and Rashba spin–orbit couplings with t_{SO} and t_R the corresponding spin–orbit coupling strengths. $\hat{d}_{ij} = \vec{d}_{ij} / |\vec{d}_{ij}|$, where

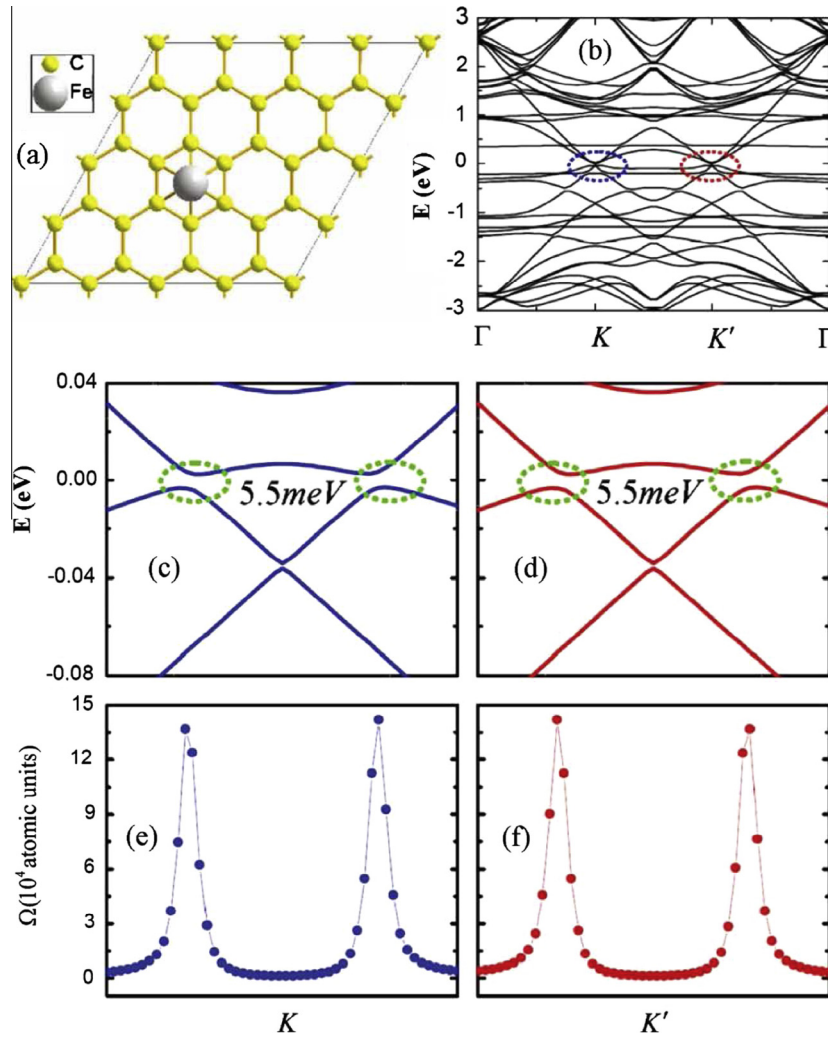


Fig. 15. (a) Typical structure of a Fe atom at the hollow site of a 4×4 supercell of graphene. (b) Relevatistic bulk band structure. The Fermi level is set to zero and exactly located in the gap. (c and d) Zooming in of the band structure at K and K' points. A gap about 5.5 meV circled by the green dotted curves is opened. (e and f) Berry curvature distribution of the valence bands near K and K' points. Adapted from Ref. [16].

$\vec{d}_{ij}$ represents a vector from site j to i and $\mu_{ij} = \pm 1$ for A or B site. The last term is an exchange field M , which arises from the interaction with a magnetic substrate.

Fig. 16(a) and (b) shows the contour of the Berry curvature distribution. One can find that the Berry curvatures are mainly localized around the valley points, and obviously the Berry curvature density near valley K is different from that near valley K' . This is a direct consequence of the inequality of the Chern number carried by valley K and K' . Through studying the wave function distribution of the gapless edge states inside the bulk band gap shown in Fig. 16(c) and from the energy dispersion, we find that the edge modes of the valley-polarized QAHE have the form plotted in Fig. 16(d). Finally, we give a phase diagram in the (t_{50}, t_R) plane.

4.2.3. Half-hydrogenated Bi honeycomb monolayers

We report the theoretical finding of novel VP-QAH topological phases, where QVH and QAH effects coexist in a half-hydrogenated (H-H) Bi honeycomb monolayer, as shown in Fig. 17. The bands around Fermi level mainly consist of the p_z orbital from the dehydrogenated Bi atoms of the A sublattice (Fig. 17(b)). From the Berry curvature distribution in Fig. 17(c), one can find an obvious dip around the valley K and an imbalance between valley K and K' . After integration of the Berry curvature throughout the whole Brillouin zone as well as around each individual valley,

we obtain the Chern number $C = 1$ as well as $C_K \simeq -1$ and $C_{K'} \simeq 0$ ($C_v = -1$), demonstrating its nontrivial topological features of simultaneously possessing both QAH and QVH phases. Fig. 17(d) clearly presents the K valley polarized chiral edge state with only a left mover, hence is a VP-QAH phase.

Moreover, we find topological phase transitions in a H-H Bi honeycomb monolayer via tuning the orientation of the spontaneous magnetization [76]. Depending on the orientation of the magnetization, there are four different phases, i.e. VP-QAH1, VP-QAH2, FM-Insulator, and FM-Metal. The mechanism for the nontrivial topological phase is given and a low-energy effective Hamiltonian is provided to capture the essential physics. Further, the low buckled geometry prominently increases the size of the gap by several times. Fully valley-polarized chiral edge states can be utilized as dissipationless conducting wires and chiral interconnects for the lower power-consumption devices in electronics and valleytronics. These make the hydrogenated Bi honeycomb monolayers an ideal platform to investigate SOC relevant physics, novel topological states and the related phase transitions, and indicate great potential for the practical applications in a controllable manner.

4.3. Topological superconductivity

The chiral superconductivity (SC) is a special kind of topological SC (TSC) characterized by time reversal symmetry breaking. The TR

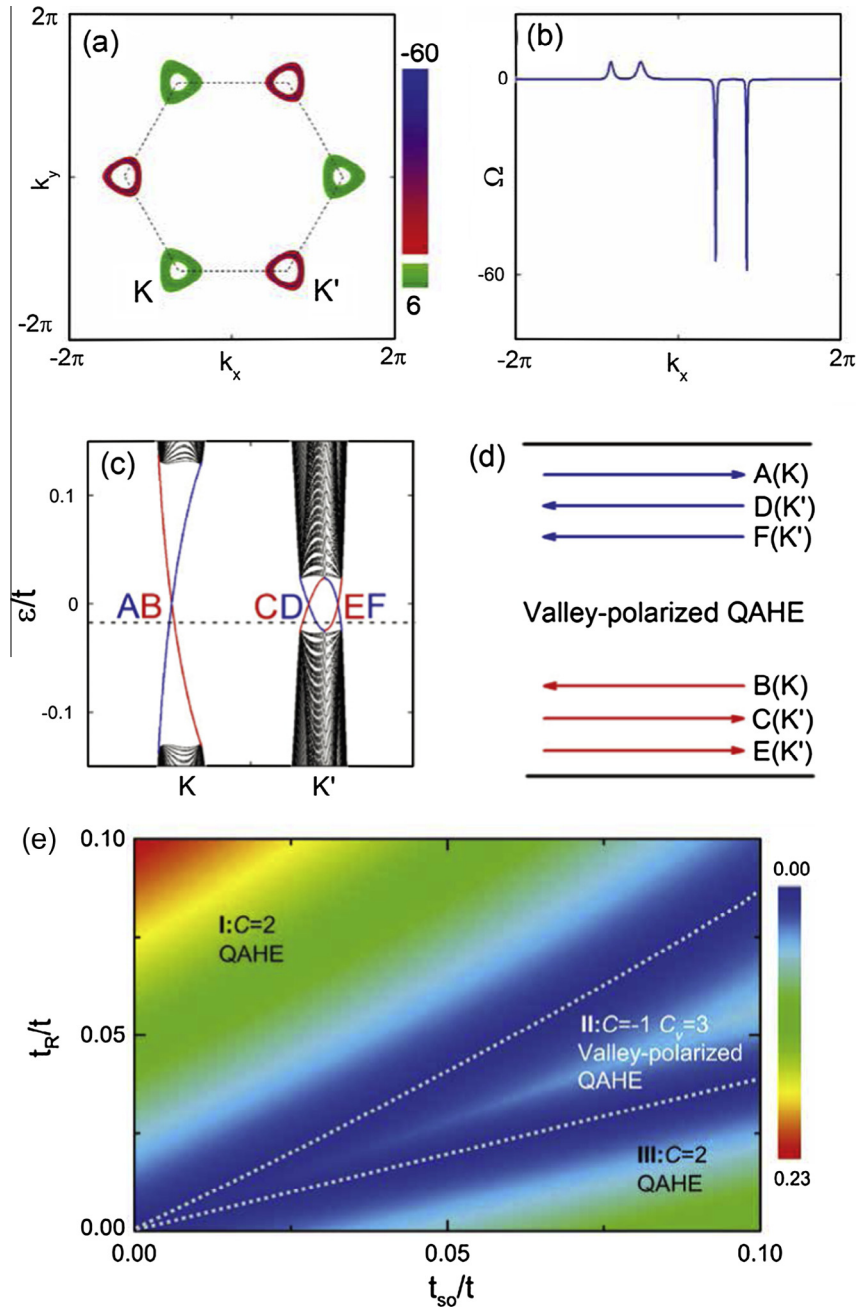


Fig. 16. (a) Contour of Berry curvature distribution in (k_x, k_y) plane for the VP-QAHE. (b) Berry curvature distribution as a function of k_x at fixed $k_y = 2\pi/\sqrt{3}$. (c) The band structure of zigzag-terminated silicene exhibiting the VP-QAHE, where colors are used to label the edge modes localized at opposite boundaries. (d) Valley-associated edge modes for the VP-QAHE. (e) Phase diagram. The dotted lines separate three topological phases for the single layer silicene, and colors are used to indicate the size of the bulk band gap. Adapted from Ref. [74]. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

breaking topological superconductors have also attracted a lot of interest recently, because of their relation with non-Abelian statistics and their potential application to topological quantum computation. On the other hand, the time-reversal symmetry invariant (TRI) helical TSC also have a full pairing gap in the bulk, gapless counterpropagating Majorana states at the boundary. Now the challenge is to find candidate materials for these new topological phases of matter. Here we predict two systems to realize the kinds of TSC, one in silicene, the other in *n*-doped BiH.

4.3.1. Chiral topological superconductivity in silicene

We have performed a FP calculation on the Bilayer Silicene (BLS). Through energy optimization and phonon dispersion, we

identified a stable D_{3d} symmetric stacking structure for the system. The band structure corresponding to this crystal structure was intrinsically metallic, with Fermi pockets around each K point whose areas were tunable via strain. Further RPA-based studies predicted a chiral $d + id'$ superconducting ground state of the system for realistic electron–electron interactions. The superconducting critical temperature of this spin-fluctuation mediated SC was well tunable via strain, which could be high when the SDW critical interaction strength was tuned near that of the real one. The realization of the chiral $d + id'$ SC in the BLS predicted here will not only provide a new playground for the study of the topological SC, but also bring a new epoch to the familiar Si industry [77].

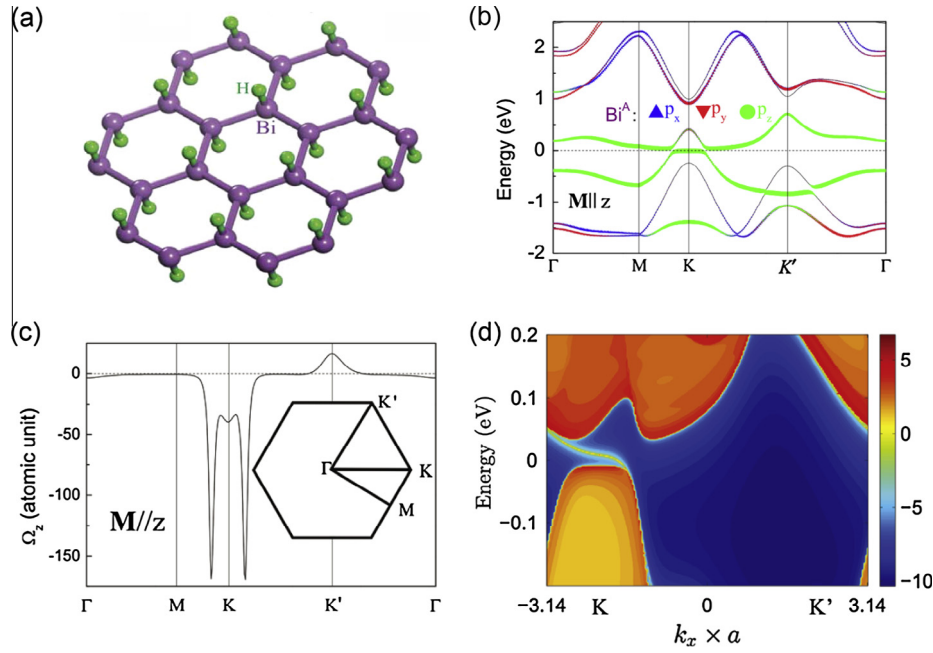


Fig. 17. (a) Lattice geometry for the H-H Bi honeycomb monolayers. Large purple and small green spheres represent the Bi and hydrogen atoms, respectively. A and B label the two sublattices. (b) The projection relativistic band structures for the H-H Bi monolayer with the magnetization along the + z axis. (c) The Berry curvature distribution along the line with high symmetry for the summation of all the valence bands. Inset: The first Brillouin zone and its points of high symmetry. (d) The energy spectrum for the semi-infinite zigzag H-H Bi monolayer with the magnetization along the + z axis. Adapted from Ref. [76]. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

For the doped monolayer silicene, when considering electron–electron interactions, we find that a perpendicular external electric field can induce an interesting quantum phase transition (QPT) from the singlet chiral $d + id'$ -wave SC phase to the triplet f -wave one. The emergence of the f -wave pairing results from the sublattice-symmetry-breaking caused by the electric field and the ferromagnetic-like intra-sublattice spin correlations at low doping. Due to the enhanced density of states, the superconducting critical temperature of the system is enhanced by the electric field remarkably. Furthermore, we design a particular dc SQUID experiment to detect the quantum phase transition predicted here. Our study will open up a new era to utilize the familiar Si-based material as a tunable platform to study the competition and QPT among different types of exotic unconventional SCs [78].

In addition, when considering electron–phonon mechanism, we predict that electron-doped monolayer silicene may be a good 2D electron–phonon mediated superconductor under biaxial tensile strain by first-principles calculations within the rigid-band approximation. Superconductivity transition temperature of electron-doped silicene can be increased up to above 10 K under suitable tensile strain. Band structures, phonon dispersive relations, and Eliashberg functions are calculated for detailed analysis. The strong interaction between acoustic phonon modes normal to the silicene plane and the increasing electronic states around the Fermi level induced by tensile strain is mainly responsible for the enhanced critical temperature [79].

4.3.2. $(p \pm ip')_{\uparrow\downarrow}$ helical topological superconductivity in a doped BiH

We present the theoretical evidence that the n-type doped single bilayer BiH is a TRI topological superconductor. We begin our analysis from a tight-binding model of the band structure of BiH. The tight binding parameters are chosen to reproduce the band dispersion of earlier first-principles calculations [63,64]. In particular, in the absence of doping, it yields a QSH insulator with a large indirect band gap. We model the electron correlation by the intra and inter-orbital Coulomb repulsion U, V and the Hund's rule

coupling J_H . These parameters are obtained from constraint density functional theory calculations. Upon electron doping, we perform a mean-field pairing instability analysis which predicts the dominant pairing channel as $(p + ip')_{\uparrow\uparrow}, (p - ip')_{\downarrow\downarrow}$ and hence leads to a TRI topological superconducting state. We stress that although the analysis in this paper is done for BiH, we believe similar physics should hold in other Bi-Hydride/Halide materials [80].

5. Three-dimensional topological materials

Three-dimensional topological insulators (3D TIs) in strongly spin–orbit coupling materials with time-reversal symmetry has garnered great interest in the fields of condensed matter physics and materials science [81,82]. In this section, several classes of 3D TIs predicted by us using first-principles calculations are introduced, including half-Heusler [83,84], chalcopyrite [85], β -Ag₂Te [86], strained InSb [87], core-hole affected Ge and InSb [88], Bi₂Te₃/Bi₂Te heterostructure [89], magnetic doping in Bi₂Se₃ family [90–92] and AuTlS₂ [93]. For more details of host materials of 3D TIs, one can refer to our recent review paper and references therein [94].

5.1. Half-Heusler

Half-Heusler is a kind of ternary compounds with the chemical formula XYZ, where X and Y are transition or rare earth metals and Z is a heavy element. Fig. 18(b) shows the crystal structure of half-Heusler, where the spatial inversion symmetry is broken. Half-Heusler are usually expected to be semiconductors due to 18 valence electrons in a primitive unit cell. However, some exceptions exist like semimetallic behavior, such as LaPtBi. Similar to the case of HgTe, the twofold degenerate γ_6 states sites below the fourfold degenerate γ_8 states. This is an indication of band inversion, which may presents a topologically nontrivial state. To remove the semimetallic behavior, a uniaxial strain along the

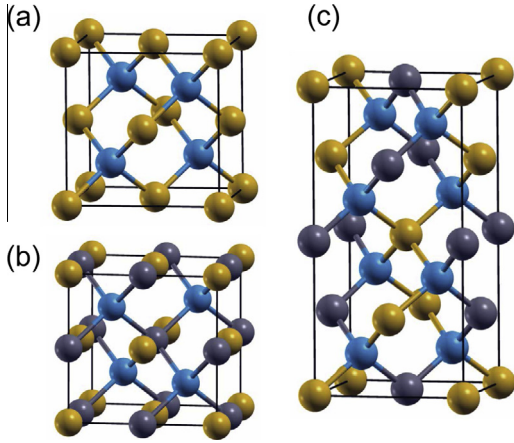


Fig. 18. The crystal structures of binary compound InSb (a), ternary compounds half-Heusler (b) and chalcopyrite (c).

[001] direction is needed to break the fourfold degeneracy of the Γ_8 states. The resulting band structure is shown in Fig. 19(a), in which one can clearly see a band gap opened at Γ point but the band inversion keeps unchanged. The band inversion is only an intuitive picture not a direct evidence for 3D TI. The calculated Z_2 topological invariants $1; (000)$, as shown in Fig. 19(b), definitively confirms LaPtBi is a 3D STI.

As mentioned above, the electronic structure of half-Heusler is very similar to that of well-known HgTe. In particular, the low-energy electron dynamics is dominated by energy bands at the Γ point. Therefore, the band topology of half-Heuslers can also be characterized by the so-called band inversion strength, $\Delta E = E_{\Gamma_6} - E_{\Gamma_8}$. The materials with positive ΔE are topological trivial while those with negative ΔE are topological nontrivial. Using both exchange–correlation potentials of generalized gradient approximation (GGA) and modified Becke–Johnson exchange potential plus the local density approximation correlation potential (MBJLDA), we studied the band inversion strength for a numbers of half-Heusler compounds, as shown in Fig. 20. Our results show that a large number of half-Heusler compounds are

candidates for 3D TIs and 3D topological metals. Furthermore, the conventional GGA potentials always underestimate the band gap and band order, and the MBJLDA potential are more suitably used to predict topological materials.

5.2. Chalcopyrite

The ternary chalcopyrite compounds with the chemical formula I-III-VI₂ or II-IV-V₂ are isoelectronic analogs of the II-VI or III-V binary semiconductors and their crystal lattices can be regarded as a superlattice of the zinc-blende structure with small structural distortions, as seen in Fig. 18 (c). Due to overall structural similarity between the ternary chalcopyrites and binary HgTe-like semiconductors, the electronic states of the former are expected to closely resemble those of the latter. We still first use the band-inversion strength ΔE to explore the topological nontrivial phases. Here, ΔE is defined as the energy difference between the s -orbital originated Γ_6 states and the valence band maximum at the Γ point. The band inversion strength for a numbers of chalcopyrite compounds, I-III-VI₂ (I = Cu, Ag, Au; III = In, Tl; VI = S, Se, Te) and II-IV-V₂ (II = Zn, Cd, Hg; IV = Ge, Sn; V = As, Sb), are calculated using MBJLDA potential, as seen in Fig. 21. One can find that $\Delta E > 0$ means topologically trivial materials and $\Delta E < 0$ are either topological insulators or topological metals. There are quite a few chalcopyrite topological insulators with a close lattice matching to several mainstream semiconductors, such as GaAs, InAs, InSb, which may has the potential to be integrated into current electronic industry. The excellent physical properties of chalcopyrite compounds, e.g., optical, electrical, structural, room-temperature ferromagnetism, make them appealing candidates for novel spintronics devices. We further extended our study of the topological materials in multinary compounds, such as quaternary I₂-II-IV-VI₄ chalcogenides, including Cu₂HgPbSe₄, Cu₂CdPbSe₄, Ag₂HgPbSe₄, and Ag₂CdPbTe₄ [95].

5.3. Strained InSb

InSb has the zinc blende crystal structure, as shown in Fig. 18 (a), which is the same as that of HgTe. However, it is a topological trivial insulator with a small band gap of 0.235 eV. Considering the

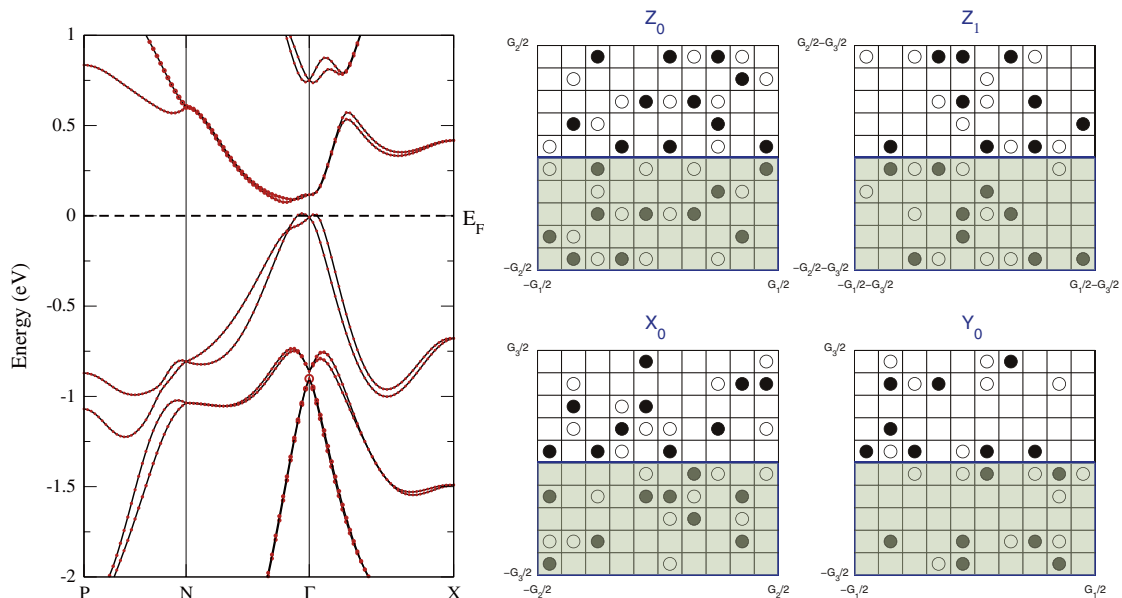


Fig. 19. (a) Band structure of LaPtBi under uniaxial strain along [001] direction ($c/a = 1.05$) but with constant volume. (b) The n -field configuration of LaPtBi under uniaxial strain. The four planes are $T(Z_0)$, $T(Z_1)$, $T(X_0)$ and $T(Y_0)$ with the shaded area indicating half of the area. The white and black circles denote $n = 1$ and -1 , respectively, while the blank denotes 0. The Z_2 invariant for each individual plane is obtained by summing the n -field over half of the plane. These read $z_0 = 1$, $z_1 = 0$, $x_0 = 1$, and $y_0 = 1$. The Z_2 invariants of the system are $1; (000)$. Adapted from Ref. [83].

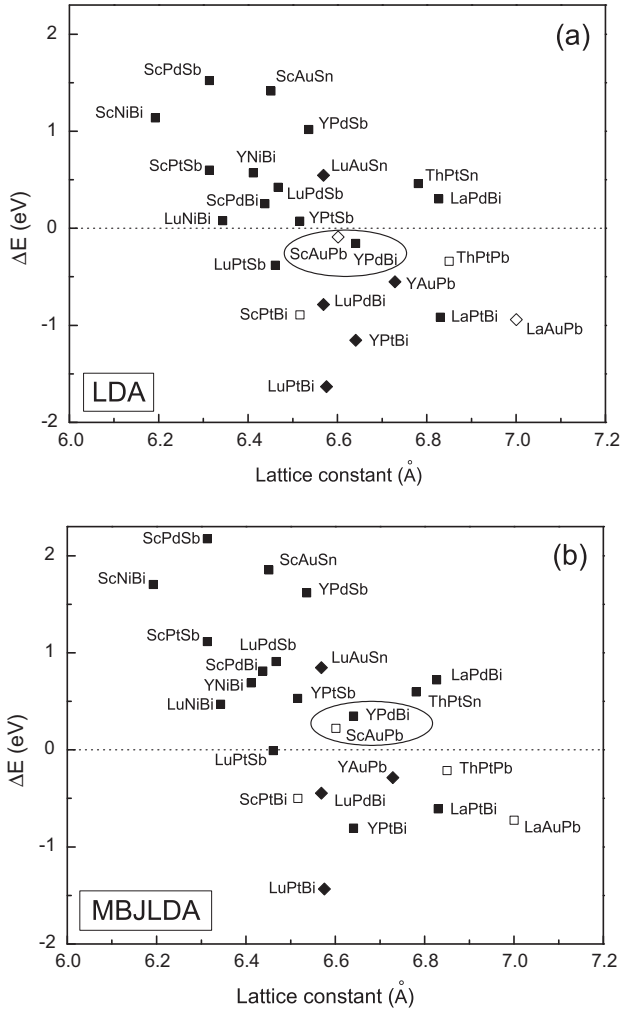


Fig. 20. Band inversion strength ΔE of half-Heusler compounds calculated by LDA (a) and MBJLDA (b) potentials. $\Delta E > 0$ and $\Delta E < 0$ indicate topological trivial and nontrivial phases, respectively. The diamonds mark metals; the squares mark insulators. The open symbols label the virtual materials which have not been experimentally reported. Adapted from Ref. [84].

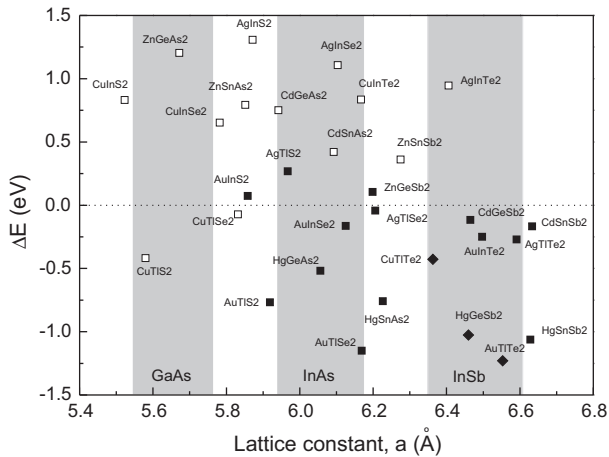


Fig. 21. Band inversion strength ΔE of chalcopyrite compounds calculated by MBJLDA potential. The open symbols label the virtual materials which have not been experimentally reported. $\Delta E > 0$ and $\Delta E < 0$ indicate topological trivial and nontrivial phases, respectively. The diamonds mark metals; the squares mark insulators. Shaded areas indicate materials that are expected to be closely ($\pm 2\%$) lattice matched to several mainstream semiconductors. Adapted from Ref. [85].

low-energy electronic properties around the Γ point, relevant states are the Γ_6 antibonding state of the s orbitals and the Γ_7 and Γ_8 bonding states of the p orbitals. HgTe is topological nontrivial with the so-called inverted band order, i.e., the Γ_6 state sites below the $\Gamma_{7,8}$ states. While InSb has the normal band order, i.e., the Γ_6 state locates above the $\Gamma_{7,8}$ states. From the analysis of tight-binding model, two parameters can be used to change the band order from normal to inverted: the SOC strength and neighbor hopping. The former one as an intrinsic property of materials is difficultly adjusted, while the latter one can be easily realized by external strains. With this in mind, we apply various strains on InSb and find that it can form the topological nontrivial phase in a 2–3% biaxial lattice expansion. This magnitude of strain is much realistic and may be realized by growing InSb on the top of a piezoelectric substrate. In this way, the topological order of the simple semiconductor, e.g., InSb, can be tuned by the electric field.

5.4. Core-hole affected Ge and InSb

Topologically nontrivial phases not only can exist in static systems, but also have been extended to dynamic systems. By shining the electromagnetic radiation, such as the X-ray, an initially topologically trivial system can be transformed into a nontrivial one. High-energy X-ray is a kind of core-level spectrum, such that the incident photons can excite the inner-shell electrons into the unoccupied electronic states or even out of the sample. As a result, a number of core holes are left in surface of bulk materials. The electronic states around the Fermi level can be remarkably affected by the number of core hole. First, we take simple element Ge as an example to discuss the detailed evolution of band structures induced by a 1s core hole. From Fig. 22, one can see that the inverted band order eventually emerge as the increase of the number of 1s core hole. Thus, an additional small uniaxial strain is needed to open the band gap at Γ point. There are similar results for binary compound InSb with zinc-blend structure. Our work makes clear the underlying relation between the core hole effect and the topological band order, and predict a kind of X-rayphotoinduced topologically nontrivial phases in simple cubic semiconductors.

5.5. $\text{Bi}_2\text{Te}_3/\text{BiTeI}$ heterostructure

BiTeI is a van der Waals layered semiconductor with giant bulk Rashba spin-splitting, but it is not a topological insulator. BiTeI can be converted to a topological insulator under compress strains. We proposed another way to realize the topological phase transition, by constructing heterostructures with another layered compounds Bi_2Te_3 . The underlying mechanism of topological nontrivial phase in $\text{Bi}_2\text{Te}_3/\text{BiTeI}$ heterostructure is as follows. From the orbital point of view, the conduction band minimum of quintuple layer of Bi_2Te_3 is dominated by $\text{Bi-}p_z^+$ orbital, which is lower than the conduction band minimum of triple layer of BiTeI dominated by $\text{Bi-}p_z$ orbital. The coupling between these p orbitals will decrease the conduction band minimum in the heterostructure. Similarly, the valence band maximum increase due to the orbital coupling between Bi_2Te_3 and BiTeI . Therefore, in the absence of SOC, the band gap of heterostructure turns to be significantly reduced compared to BiTeI . After SOC is switched on, the band inversion eventually appears.

An interesting point in this kind of heterostructure is that the giant Rashba spin-splitting will not be destroyed. Fig. 23 shows the surface energy spectra of Bi_3Te_4 ($[(\text{Bi}_2\text{Te}_3)_1(\text{BiTeI})_1]$) and Bi_4Te_5 ($[(\text{Bi}_2\text{Te}_3)_1(\text{BiTeI})_2]$), from which one can clearly see the Dirac cones, as the landmark of topological insulator. Due to the breaking of inversion symmetry, topological surface states have

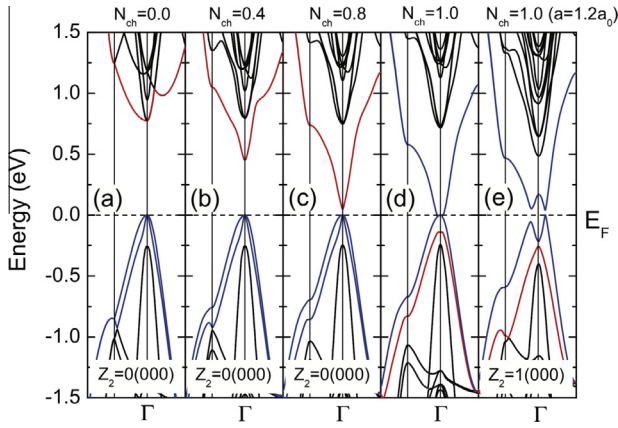


Fig. 22. The band structures of Ge with 1s core hole. The number of core hole is $N_{ch} = 0.0$ (a), $N_{ch} = 0.4$ (b), $N_{ch} = 0.8$ (c), and $N_{ch} = 1.0$ (d) in a $2 \times 2 \times 2$ supercell. (e) A 2% biaxial strain is applied when $N_{ch} = 1.0$. The red and blue colors indicate the s- and $p_{3/2}$ -orbitals dominated states around the Fermi level, respectively. Adapted from Ref. [88]. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

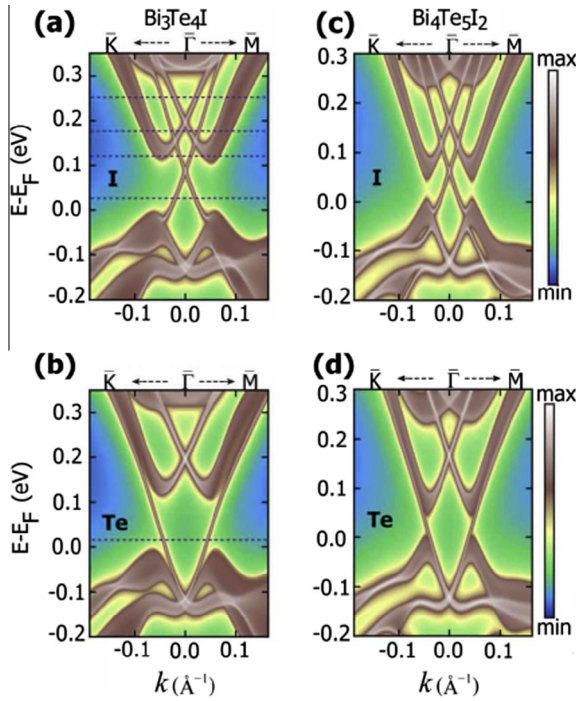


Fig. 23. The surface energy spectra of I-terminated surface of $\text{Bi}_3\text{Te}_4\text{I}$ (a) and $\text{Bi}_4\text{Te}_5\text{I}_2$ (c), and Te-terminated surface of $\text{Bi}_3\text{Te}_4\text{I}$ (b) and $\text{Bi}_4\text{Te}_5\text{I}_2$ (d). The Fermi level is set to the bulk valence band maximum. Adapted from Ref. [89].

different scenes for top and bottom surfaces. One can also see that giant Rashba states are the same for different surfaces because they are bulk states not the surface states. Our work provides a new avenue for designing topological spintronics devices based on heterostructures technique.

5.6. Magnetic doping in Bi_2Se_3 family and AuTlS_2

The interplay between topological order and ferromagnetic order is expected to give rise to a variety of unconventional quantum states that may lead to entirely new device paradigms, such as the long-sought quantum anomalous Hall effect. Bi_2Se_3 family are

famous 3D TIs with large band gaps up to 0.3 eV. A natural strategy to introduce magnetism in Bi_2Se_3 family is via magnetic doping. Using first-principles calculation, we investigate the feasibility of tailing Bi_2Se_3 , Bi_2Te_3 , and Sb_2Te_3 to ferromagnetic insulators via doping 3d transition metal elements, including V, Cr, Mn, and Fe. Fig. 24 shows an example of geometrical structure with a single dopant and formation energies of Bi_2Se_3 with the most stable configurations of single impurities as a function of the host element chemical potential. We find that for all these three TIs the cation-site substitutional doping is most energetically favorable with the anion-rich environment as the optimal growth condition. Detailed electronic structure analysis reveals that under the nominal doping concentration of 4%, Cr- and Fe-doped Bi_2Se_3 , Bi_2Te_3 , and Cr-doped Sb_2Te_3 remain as insulators, while all the V- and Mn-doped these three TIs, and Fe-doped Sb_2Te_3 become metals. The calculated magnetic coupling suggests that the magnetic interaction of Cr-doped Bi_2Se_3 tends to be ferromagnetic, while Fe-doped Bi_2Se_3 is likely to be weakly antiferromagnetic. Using Monte Carlo simulation, we estimated that the Curie temperature of 7.4% Cr-doped Bi_2Se_3 was about 76 K.

As described in Section 5.2, due to the good match of lattice constant with the mainstream semiconductors, many chalcopyrite TIs have the potential to be integrated with current semiconductor technology. Among the chalcopyrite TIs, AuTlS_2 with the largest band gap (0.14 eV) is expected to be a promising material. However, AuTlS_2 is a virtual material, which there is not any report about its experimental synthesis. Therefore, a theoretical guidance for optimal growth condition is urgently needed. Furthermore, the defect physics of AuTlS_2 is still unclear, which hampers the further study of the topological properties. Using first-principles calculation, we investigated the stabilities and electronic structures for all native point defects in AuTlS_2 . We find that intrinsic p-type conductivity is strongly preferred and the band gap can be tuned by the control of intrinsic defects. An optimal growth conditions for AuTlS_2 is also given, which may direct the further experiments.

6. Other spin-orbit coupling materials— MX_2 monolayers

The monolayers of group-VI dichalcogenides MX_2 are visible-frequency direct-gap semiconductors with X-M-X sandwich structure in trigonal prismatic coordination for the transition metal M atom. They exhibit fascinating electronic and optoelectronic properties, such as valley-dependent circularly polarized optical selection rules, strong valley-spin coupling, valley contrasting Berry curvature, valley Hall and spin Hall effects, etc. [96]. All these properties are intimately related to their hexagonal structure without inversion symmetry and strong SOC effects. To understand the low-energy physics of MX_2 monolayers, we have proposed a minimal $k \cdot p$ model which effectively describes the above mentioned features in the τK valley ($\tau = \pm 1$ is the valley index) [97]:

$$\hat{H} = at(\tau k_x \hat{\sigma}_x + k_y \hat{\sigma}_y) + \frac{\Delta}{2} \hat{\sigma}_z - \lambda \tau s_z \frac{\hat{\sigma}_z - 1}{2} \quad (42)$$

in which $\hat{\sigma}_{x/y/z}$ is the Pauli matrix in the bases of the conduction- and valence-band Bloch states at τK point, $s_z = \pm 1$ is the spin index, a is the lattice constant, and $k_{x/y}$ is the wave vector relative to τK . The effective hopping t , the band gap Δ , and the SOC splitting 2λ in the valence band are fitted from the first-principles bands.

It's known that $k \cdot p$ model is only valid in the neighborhood of specific k point (τK here), while tight-binding (TB) model can be used in the whole Brillouin zone in principle. To extend the scope of application, we further develop a three-band TB model based on symmetry, which better describes the low-energy physics of MX_2 monolayers [98]. Using this TB model together with the envelope function method, we study the intervalley coupling in MX_2

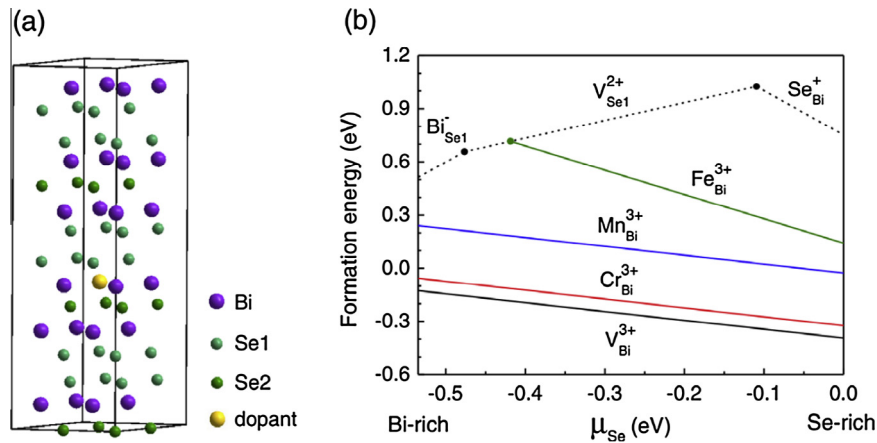


Fig. 24. (a) The $2 \times 2 \times 1$ supercell of Bi_2Se_3 contains a single dopant. (b) The formation energies of the most stable configurations of single V, Cr, Mn, and Fe impurities doped Bi_2Se_3 as a function of the host element chemical potentials. The values of intrinsic defects, selenium vacancies V_{Se1} , antisite defects Bi_{Se1} and Se_{Bi} , are shown in dashed lines. Adapted from Ref. [90].

monolayers with quantum-dot confinement potentials [99]. We find that the intervalley coupling is very small and hence the valley hybridization is well quenched by the much stronger valley-spin coupling. This means that the valley degree of freedom is still reasonable and available in MX_2 monolayers with quantum confinement. It's also found that the strength of intervalley coupling depends sensitively on the central position, the lateral size, the potential depth, and the smoothness of the confinement potentials, which make it possible to tune the intervalley coupling by various external controls.

We have also studied the effects of doping and strain modulations on the transport of MoS_2 monolayer [100]. We find that the electric resistance mainly comes from the intervalley scattering between the Q and K valleys through M momentum phonons and the strain in low-doping cases can effectively suppress this electron-phonon coupling and hence improve the mobility. These findings can be used to improve the electron transport of MoS_2 monolayer. We also investigated the strain effect on superconductivity of monolayer phosphorene and found that the electron-phonon coupling is more significantly enhanced by the biaxial strain than the uniaxial strains and the superconducting transition temperature T_c increases sharply from 3 to 16 K when the biaxial strain reaches 4.0% [101].

7. Summary and outlook

In recent years, our research group has made great efforts to the studies of the Berry phase effect in SOC materials. Firstly, we developed computational methods for the anomalous Hall, spin Hall, and anomalous Nernst conductivities, which have been used to exactly describe the transverse Hall transports. In the Fe, Co, Ni, $\text{CuCr}_2\text{Se}_{4-x}\text{Br}_x$, and Mn_5Ge_3 , we first demonstrated that the intrinsic mechanism is dominated in the AHE other than the extrinsic scattering ones at certain case. We first reported large SHC in the simple semiconductors (GaAs and Si) and metals (W and Au). Secondly, we developed a systematic method to calculate the Chern number and the Z_2 topological invariants without consideration of special symmetry. By taken advantage of these toolkits, we can discover efficiently new topological materials. In two-dimensional, we found that silicene, germanene, stanene, X-hydride/halide ($X = \text{N-Bi}$) monolayers, and Bi_4Br_4 are quantum spin Hall insulators; magnetic atoms adsorbed graphene and half-passivated BiX are quantum anomalous Hall insulators; silicene can be turned to a valley-polarized quantum anomalous Hall insulator in the presence of Rashba spin-orbit coupling and

exchange field; $d + id'$ chiral superconductivity presents in bilayer silicene and $p + ip'$ superconductivity presents in monolayer Bi-H. In three-dimensional, we found that half-Heusler, chalcopyrite, and strained InSb are topological insulators; X-ray photoinduced topological phase transition exists in simple cubic semiconductors (Ge, InSb); $\text{Bi}_2\text{Te}_3/\text{BiTeI}$ is a novel heterostructure containing both giant Rashba spin-splitting and topological nontrivial surface states; optimal growth conditions for magnetic doped Bi_2Se_3 family and chalcopyrite AuTlS_2 .

The Berry phase theory in solids is still young so far, and there are many fantastic phenomena to be fully explored. Condensed-matter physicists over the years have gradually recognized that the Berry curvature plays a crucial role in the electronic structure and electron dynamics of crystals. Here, we address some of the aspects which have greatly attracted us, especially in the first-principles framework. (1) Orbital magnetization. Magnetism in matter originates from two distinct sources, namely, the spin and the orbital degrees of freedom of the electrons. The spin contribution usually dominates in many bulk ferromagnets and can be numerically calculated very precisely. In contrast, the orbital magnetization is traditionally calculated from the integrating currents inside atom-centered muffin-tin spheres, which is somewhat arbitrarily due to a cutoff radius and thus neglects contributions from the interstitial regions. Although a modern theory of orbital magnetization has been proposed [102–106], the computational results from this new equation are still deviated from the experimental results within a certain level. This may need the endeavors from both analytical theory and computational technique. (2) Magnetoresistance. Magnetic transport properties, such as magnetoresistance, have been investigated intensively based on the Boltzmann equation for metals and semiconductors. Previously we have studied the magnetoresistance in MgB_2 by using first-principles Wannier interpolation without full consideration of spin-orbit coupling [107]. However, the exact evaluation of magnetoresistance in spin-orbit coupling system is very important in current research to obtain the satisfactory interpretations of the giant negative magnetoresistance and large unsaturated magnetoresistance. We need a reliable and efficient scheme to compute the magnetoresistance in first-principles framework. (3) Anomalous and spin Hall effects in topological metals. Transverse Hall transports have been a long-standing research issue during the development of spintronics. The main objects of study concerning the anomalous and spin Hall effects are conventional metals, such as transition-metals and their alloys or compounds. Topological metals, such as the Z_2 topological metals [84,85], Dirac topological (semi)

metals [108–110], and Weyl topological (semi) metals [111–113], are new states of quantum matter with characteristics (nontrivial band topology in the bulk and the Fermi arcs on the surface) sharply distinguishing them from regular metals. Study of anomalous and spin Hall effects in topological metals not only has the fundamental physics interest but also has great potential technological applications. Besides the issues mentioned above, the Berry phase effect is also valuably generalized to the regimes of non-Abelian statistics, many-body interaction, and light-matter interaction.

Acknowledgments

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