Topological insulators from the perspective of first-principles calculations

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1 Introduction

In two-dimensional electron systems at low temperature and strong magnetic field, the Hall conductance $\sigma_y$ takes quantized values [1], called quantum Hall (QH), which proved to have a fundamental topological meaning [2]. $\sigma_y$ can be expressed as an integral of the first Chern number over the magnetic Brillouin zone. Quantum anomalous Hall (QAH) is adiabatically equivalent to QH. Both QH and QAH systems are called Chern insulators due to the non-zero Chern number where the time-reversal symmetry (TRS) is broken. Recently a variety of topological insulators have been predicted by theories, and observed by experiments. First-principles calculations have been widely used to predict topological insulators with great success. In this review, we summarize the current progress in this field from the perspective of first-principles calculations. First of all, the basic concepts of topological insulators and the frequently-used techniques within first-principles calculations are briefly introduced. Secondly, we summarize general methodologies to search for new topological insulators. In the last part, based on the band inversion picture first introduced in the context of HgTe, we classify topological insulators into three types with s–p, p–p and d–f, and discuss some representative examples for each type.

Topological insulators are new quantum states with helical gapless edge or surface states inside the bulk band gap. These topological surface states are robust against weak time-reversal invariant perturbations without closing the bulk band gap, such as lattice distortions and non-magnetic impurities. Recently a variety of topological insulators have been predicted by theories, and observed by experiments. First-principles calculations have been widely used to predict topological insulators with great success. In this review, we summarize the current progress in this field from the perspective of first-principles calculations. First of all, the basic concepts of topological insulators and the frequently-used techniques within first-principles calculations are briefly introduced. Secondly, we summarize general methodologies to search for new topological insulators. In the last part, based on the band inversion picture first introduced in the context of HgTe, we classify topological insulators into three types with s–p, p–p and d–f, and discuss some representative examples for each type.

Surface states of topological insulator Bi$_2$Se$_3$ consist of a single Dirac cone, as obtained from first-principles calculations.
focus on 3D topological insulators with TRS. In this field, an important task is to systematically search for all topological insulators. In this process, first-principles calculations played a crucial role. Up to now, most of topological insulators were predicted first by first-principles calculations, and observed subsequently by experiments.

2 Theories and methods
2.1 First-principles methods Density functional theory (DFT) is a formally exact theory based on the two Hohenberg–Kohn theorems (HK) [16], but the functional of the exchange and correlation interaction is unknown in Kohn–Sham (KS) equation [17]. In order to perform numerical calculations, the local-density approximation (LDA) [17] and Generalized Gradient Approximation (GGA) [18, 19] are usually used to approximate the exchange and correlation interaction in KS equation. Based on recent experiences, LDA and GGA work quite well for the study of topological insulators, because most topological insulators found to-date are weakly correlated electronic systems, such as, Bi2Se3 [20], TlBiSe2 [21–24] and etc.

As we know, the conventional LDA and GGA first-principles calculations tend to underestimate the band gap [25, 26]. However the band gap is directly related to the possibility of the band inversion which is the key topological property [3]. For example, sometimes LDA and GGA predict a negative band gap, whereas the band gap is positive in reality [27]. This can cause the serious problem to predict topological insulators. So it is necessary to improve the calculations of the energy gap. The most effective method to calculate the band gap is GW approximation [28]. Simply saying, GW approximation considers the Hartree–Fock self-energy interaction with the screening effect. Though the GW method has been used to study topological insulators, for example, Hg chalcogenides, half-Heusler compounds, antiperovskite nitride, honeycomb-lattice chalcogenides, Bi2Se3 and Bi2Te3 [29–31], this method is very expensive. Besides the GW method, the modified Becke-Johnson exchange potential together with LDA (MBJLDA), proposed by Tran and Blaha in 2009 [32], costs as much as LDA and GGA, but it allows a band gap with similar accuracy to GW. MBJLDA potential can also recover LDA for the electronic system with a constant charge density, and mimic the behavior of orbital-dependent potentials as well. MBJLDA was successfully used to predict topological insulators with the chalcopryte structure [33].

LDA + U [34], LDA + DMFT [35] and LDA + Gutzwiller [36] are employed to study strongly correlated electronic systems (d and f electrons), because LDA often fails for these systems. In strongly correlated electronic systems, the electrons are strongly localized, and have more features of atomic orbitals. This case requires proper treatment of atomic configurations and orbital dependence. Both LDA and GGA do not include the orbital dependence of the Coulomb and exchange interactions. This is why they fail to describe strongly correlated electronic systems. Based on this understanding, all of LDA + U, LDA + DMFT and LDA + Gutzwiller include the orbital-dependent feature in different ways. For example, the on-site interaction is treated in a static Hartree–Fock mean-field manner in LDA + U method which is the simplest and cheapest method. It is often used for strongly correlated systems, but it does not work well with intermediately correlated metallic systems. The self-energy of the LDA + DMFT method is obtained in a self-consistent way. Up to now LDA + DMFT is the most accurate and reliable method, but its computational costs are high. LDA + Gutzwiller based on Gutzwiller variational approach is recently developed. This method works well for intermediately correlated electronic systems, and it is cheaper than LDA + DMFT. Though it is still an open question how well these methods work on strongly correlated systems. It is true that these methods could reproduce some results of experiments, and that they can help to understand some novel results in strongly correlated electronic systems, for example, the LDA + DMFT study for topological insulator PuTe [37].
2.2 Spin–orbit coupling Generally SOC describes the interaction of a particle’s spin with its orbital motion. For example, in one atom, the interaction between one electron’s spin and the magnetic field produced by its orbit around the nucleus can cause shifts in the electron’s atomic energy levels, which is the typical SOC effect. SOC Hamiltonian is given as [38]

\[ H_{\text{soc}} = -\frac{\hbar}{4m_e c^2} \mathbf{\sigma} \cdot \mathbf{p} \times (\nabla V_0), \]  

(1)

where \( \hbar \) is Planck’s constant, \( m_e \) is the mass of a free electron, \( c \) is the velocity of light and \( \mathbf{\sigma} \) represents the Pauli spin matrices. \( H_{\text{soc}} \) couples the potential \( V_0 \) and the momentum operator \( \mathbf{p} \) together.

In the case of the single atomic system \( V_0 \) is spherically symmetric, \( H_{\text{soc}} \) can be simplified,

\[ H_{\text{soc}} = \lambda \mathbf{L} \cdot \mathbf{\sigma}, \]  

(2)

where \( \lambda \) is the strength of SOC interaction. \( \mathbf{L} \) represents the angular moment. But in solid systems, \( V_0 \) is the periodic potential which can be quite complex in form. For convenience, it is sufficient for SOC effect to employ a second-variational procedure with a radial symmetric average around the atoms. SOC interaction is the key to the band topology, so all first-principles calculations to study topological insulators should be carried out with SOC.

2.3 The criterion of topological insulators There are four \( Z_2 \) invariants \((v_0; \nu_1 \nu_2 \nu_3)\) for three-dimensional topological insulators, first proposed by Fu, Kane and Mele [8]. When \( v_0 = 1 \), materials are strong topological insulators which have topologically protected gapless surface states consisting of odd number of Dirac cones. These surface states are robust against time-reversal-invariant (TRI) weak disorders. If \( v_0 = 0 \) and at least one of \( \nu_{1,2,3} \) is non zero, the corresponding materials are weak topological insulators which have surface states with even number of Dirac cones on special surfaces. We can simply consider weak topological insulators to be stacked by layered two-dimensional QSH materials. In the presence of disorder, the surface states of weak topological insulators can be destroyed. When all \( \nu_{0,1,2,3} \) are zero, materials are conventional insulators.

2.3.1 With inversion symmetry The calculation of \( Z_2 \) invariants is very simple for the compounds with inversion symmetry. The formula of \( Z_2 \) can be just expressed with the parity values at the eight time-reversal-invariant moments (TRIMs) [39],

\[ (-1)^{v_0} = \prod_{i=1}^{8} \delta_i, \]  

(3)

and

\[ (-1)^{\nu} = \prod_{n_i=1, \nu_{1,2,3}=0} \delta_{n_i(n_{1,2,3})}, \]  

(4)

where

\[ \delta_i = \prod_{n=1}^{N} \xi_{2n}(K_i), \]  

(5)

\( N \) is half of the number of occupied bands, and \( \xi_{2n}(K_i) \) is the parity eigenvalue of the 2\textsuperscript{nd} occupied energy band at TRIM \( K_i(\nu_{1,2,3}) = \sum (n_i h_i + n_i h_i + n_i h_i) \) where \( h_{1,2,3} \) represent primitive reciprocal lattice vectors.

2.3.2 Without inversion symmetry For the compounds without inversion symmetry, several methods are proposed to calculate \( Z_2 \) invariants [40–43]. Considering the simplicity for first-principles calculations, here we briefly introduce the proposal of Fukui et al. [40]. Firstly, \( Z_2 \) formula of QSH state can be expressed with the Berry connection and the Berry curvature, shown by Fu and Kane,

\[ Z_2 = \frac{1}{2\pi} \int_{\mathbb{B}} A(k) - \oint F(k) \mod 2, \]  

(6)

with

\[ A(k) = i \sum_{n}(u_n(k) | \nabla_k u_n(k)) \]  

and \[ F(k) = \nabla_k \times A(k) \]  

(7)

where \( \mathbb{B} \) and \( \partial \mathbb{B} \) indicate half of two-dimensional (2D) tori and its boundary, respectively. In order to do numerical calculations, Eq. (6) can directly be rewritten to its lattice version. Secondly, for 3D case, we can define six 2D tori as \( Z_2(k_x, k_y, 0) \), \( Z_2(k_x, k_y, \pi) \), \( Y_0(k_x, 0, k_y) \), \( Y_0(k_x, \pi, k_y) \), \( X_0(0, k_x, k_y) \), and \( X_0(\pi, k_x, k_y) \). We can calculate the \( Z_2 \) based on Eq. (6) for each of these six tori, as \( z_0, z_1, z_2, z_3, z_4 \), and \( z_5 \). The four \( Z_2 \) invariants of topological insulators are obtained by \( v_0 = z_0, v_1 = x_0, v_2 = y_0 \), and \( v_3 = z_4 \). Xiao et al. first successfully using these formulas to evaluate the \( Z_2 \) invariants of half-Heusler compounds by first-principles calculations [44].

2.3.3 Adiabatic argument Sometimes it is not necessary to directly calculate \( Z_2 \) for the compounds without inversion symmetry. One can start from a respective compound with inversion symmetry, and then adiabatically change this compound to that without inversion symmetry. If the energy gap does not close in an adiabatic process, the topological property will not change. For example, the space group of \( \alpha \)-Sn is \( \text{Fd}3m \) (No. 227) and the inversion symmetry is held in this structure. We can easily know \( \alpha \)-Sn is topologically non-trivial from the parity calculations [39]. The band gap of \( \alpha \)-Sn defined by Eq. (9) is negative, which is the key for \( \alpha \)-Sn to be topologically non-trivial. Then we assume to adiabatically change \( \alpha \)-Sn to HgTe without closing this negative gap. Based on the adiabatic argument, one can conclude, HgTe is topologically non-trivial. Another example to understand this adiabatic argument is to take SOC strength as an adiabatic parameter [45]. The band gap of YBiTe\(_3\) stays open with adiabatically tuning SOC strength from 0 to 100\%, which
means YBiTe$_3$ with SOC has the same topological property as the non-SOC case. So one can conclude that YBiTe$_3$ is topologically trivial.

2.3.4 Surface states Gapless surface states of topological insulators must include the odd number of Dirac cones on one surface, and these surface states are robust against TRI weak disorders. So the calculation of surface states is another useful method to judge the band topology. The simplest way to calculate surface states is based on the free-standing structure. It is true that this is a very powerful method to calculate surface states, but only for the compounds with inversion symmetry and layered structure, such as, Bi, Sb, Bi$_2$Se$_3$ etc. For example, if the compounds do not have inversion symmetry, the polarization field might cause serious artificial effect, especially for the compounds with a small band gap. In addition, if the compounds are not layered structures, the dangling bonds on the surface might cause a number of complex topologically trivial chemical surface states which can mix with topologically non-trivial ones. The topological surface states originate from the topological property of the bulk electronic structure. Though the details of these surface states can be modified by the special dangling bonds and the reconstruction of the electronic structure on the surface, we address that the topological feature does not change, such as, the odd number of Dirac cones. The calculation of the free-standing model also costs a lot, because the vacuum layer and the material part both should be thick enough in order to avoid hybridization between the up and down surfaces.

Besides the free-standing model, maximally localized Wannier function (MLWF) methods [46, 47] can be used to calculate the surface states [20, 48]. Essentially the MLWF method is a tight-binding method, but the difference from the conventional tight-binding method is that MLWF method can exactly reproduce the band structure of first-principles calculations. But it is not easy to obtain MLWFs, because the transformation from Bloch functions to Wannier functions is not unique due to the phase ambiguity of the Bloch functions used in first-principles calculations. Marzari and Vanderbilt reported an effective method to obtain MLWF by minimizing the spread function $\sum |(\langle r^2 \rangle - \langle r \rangle^2)|$ [46]. In order to calculate surface states, first we carry out the first-principles calculations for 3D bulk structure and then transform Bloch functions to MLWFs. At the same time the hopping parameters $H_{\alpha\alpha}(\mathbf{R}) = \langle n\alpha \Gamma | H | n\alpha \Gamma \rangle$ between Wannier functions are obtained. At the next step, we use these hopping parameters to construct the hopping parameters of the corresponding semi-infinite structure, and then iterative method can be used to solve the surface Green’s function,

$$ G_{\alpha\alpha}^{\Gamma\Gamma}(\mathbf{k}_0, \epsilon + i\eta) , \quad (8) $$

where $\eta$ denotes the unit cell along the surface normal, and $\alpha$ is the Wannier orbital in the unit cell. The MLWF method can predict surface states well for layered compounds. For example, the calculated surface states of Bi$_2$Se$_3$ with MLWFs method agree well with the ones of angle resolved photoelectron spectroscopy (ARPES) [20, 49]. Usually we do not expect to predict the exact dispersion of surface states, because this method does not include all complex situations on the surface. On the other hand, the surface states obtained from the MLWF method originate from the topological property of the bulk electronic structure, so this is an ideal method to judge whether one compound is topologically non-trivial or not.

3 Three-dimensional topological insulators After the initial discovery of the 2D topological insulator HgTe [3, 4], a number of 3D topological insulators are found with the great effort of theorists and experimentalists [10, 12, 13]. In the following, we classify the topological insulators by the type of the band inversion, because the band inversion has a clear and general physical picture for most topological insulators. Up to now, there are three basic types of band inversions (s–p, p–p, d–f) in topological insulators discovered so far. In the following discussions, we will take some representative compounds as examples for each type of topological insulators.

3.1 s–p type The most important s–p topological insulator is HgTe [3, 4] which has the zinc-blende structure with space group F43m (No. 216). Before HgTe was found to be a topologically non-trivial compound, it had been widely studied experimentally and theoretically [50–52]. Unlike other zinc-blende compounds, HgTe is a semiconductor with symmetry-protected zero-energy band gap. The Hg has occupied shallow 5d levels which tends to be delocalized, so Hg has a large effective positive charge in its core. The Hg s level, which forms $\Gamma_6$ state in cubic symmetry, is pulled down below the Te p levels which split into $\Gamma_8$ and $\Gamma_7$, by this effective positive charge of Hg’s core. Finally the energy level sequence at $\Gamma$ point shows the $\Gamma_6$–$\Gamma_8$–$\Gamma_7$ order, which we call the s–p-type band inversion. If we define the energy gap $\Delta E$,

$$ \Delta E = E_{\Gamma_8} - E_{\Gamma_6} , $$

where the $E_{\Gamma_6}$ and $E_{\Gamma_8}$ are the energy levels for $\Gamma_6$ and $\Gamma_8$ at the $\Gamma$ point. HgTe has a negative $\Delta E$ because of the s–p-type band inversion, so it is well known as a negative gap semiconductor.

The normal LDA and GGA can predict the band inversion between $\Gamma_6$ and $\Gamma_8$, but the exact band sequence of $\Gamma_6$–$\Gamma_8$–$\Gamma_7$ cannot be obtained [52]. The LDA band structure with SOC shows the $\Gamma_6$–$\Gamma_7$–$\Gamma_8$ sequence, shown in Fig. 1(a). As we addressed above, MBJLDA method can correct the error of LDA band structure. The band structure with the MBJLDA method is shown in Fig. 1(b), which perfectly shows the correct $\Gamma_6$–$\Gamma_7$–$\Gamma_8$ sequence.

Bernevig, Hughes and Zhang first identified the band inversion in HgTe to be the key ingredient of its topologi-
Figure 1 (online colour at: www.pss-rapid.com) (a) and (b) Band structure of HgTe by LDA and MBJLDA methods, respectively. Γ, Γ, represent the symmetry of energy levels at Γ point. The solid red circles indicate the projection of the s orbital of Hg. The LDA band structure shows the Γ−Γ−Γ− sequence which is not correct, but MBJLDA can calculate the correct band sequence as Γ−Γ−Γ−.

cally non-trivial behavior [3]. Its topological invariant can also be obtained by an adiabatic argument [39]. As we know, if we replace Hg and Te by the same atom in the zinc-blende structure, the crystal structure will change to the diamond structure with the inversion symmetry. Luckily, in nature grey tin has the diamond structure with space group Fd3m, and it is also a semiconductor with a negative energy gap ΔE due to the s level below the p level. Because grey tin holds the inversion symmetry, its parity values at all TRIMs can be easily calculated. It is worth to note that though grey tin is a zero-band gap semiconductor, we still can define the topological property for all of its occupied bands. Based on the formulas proposed by Fu and Kane, its Z2 invariants are calculated to be (1,000) which indicate topologically non-trivial. Here the key is that the s and p at Γ point have opposite parity values. The occupied s state forms Γ, whereas p states form Γ and Γ. Taking grey tin as the starting point, we assume that we make a thought experiment to adiabatically change grey tin to HgTe. In this process, the negative gap (ΔE) is never closed, which means grey tin and HgTe have the same topological property. So HgTe proves to be topologically non-trivial with Z2 invariant (1,000). Besides this adiabatic argument, HgTe’s Z2 invariants can also be directly calculated by the numerical method addressed above.

Similar to HgTe, there are a big family of compounds known as half-Heusler materials (XYZ) [53] which include more than 250 semiconductors and semimetals. Half-Heusler compounds consist of face-centered cubic (fcc) sublattices sharing the same space group with HgTe. Y and Z form zinc-blende structure which is stuffed by X. Usually X and Y are transition metal or rare earth elements, and Z is a main group element. Usually the 18-electron half-Heusler compounds are candidates for topological insulators due to the requirement of semiconducting. The band structure of these half-Heusler compounds at Γ point near the Fermi level is almost the same with that of HgTe case. s state forms Γ, and p states split into Γ and Γ. Some of half-Heusler compounds, such as ScPtSb with the band sequence Γ−Γ−Γ− are topologically trivial and some others, such as LaPtBi, with the inverted band sequence Γ−Γ−Γ−, are topologically non-trivial. The interesting thing is that half-Heusler family were independ-
ently reported almost at the same time by three theory-
groups [44, 54, 55]. Besides the topological property, half-
Heusler compounds are a class of multifunctional materials
[56, 57], such as, superconductivity and magnetism, due to
transition metals and rare earth elements. So half-Heusler
compounds might be the best platform to study the Major-
rana fermion in topological superconductors [58], dynam-
ical axion field in topological anti-ferromagnetic phase
[59], and quantum anomalous Hall effect (QAH) in topo-
logical ferromagnetic phase [60]. Recently, some ARPES
and transport experiments already have been reported for
half-Heusler compounds [61–63].

Generally due to the cubic symmetry, many topologi-
cally non-trivial compounds (HgTe and half-Heusler com-
ounds) are zero-gap semiconductors with Fermi level
through Γ level at Γ point, and a uniaxial strain is usually
needed to break the cubic symmetry in order to open a fi-
nite energy gap [64]. Feng et al. reported that chalcopyrite
structure can naturally break the cubic symmetry [33].

The chalcopyrite structure (ABC 2) is the body-centered
tetragonal structure with space group I42d (No. 122),
which could be regarded as a superlattice of two cubic
zinc-blende unit cells, AC and BC, seen in Fig. 2(a). In es-
sence, the unit cell of chalcopyrite is the double unit cell of
HgTe with naturally breaking the cubic symmetry, and we
expect that these two class compounds might share the
same topological property. Feng et al. found that it is true
that some materials with chalcopyrite structure are topo-
logical insulators, shown in Fig. 2(b).

Besides the compounds talked about above, there are a
lot of other s–p-type topological insulators, such as, β-
Ag2Te [65], KHgSb family [66, 67], Na3Bi [68],
CsPbCl3 family [69] and so on.

3.2 p–p type Due to the simple surface states consist-
ing of a single Dirac cone, Bi2Se3, Bi2Te3 and Sb2Te3 com-
ounds [20, 49, 72–75] quickly became topological insula-
tors extensively studied worldwide. Especially Bi2Se3 has a
big energy gap of 0.3 eV which is much larger than the en-
ergy scale at room temperature. These compounds share
the layered structure with a five-atom layer, called the quin-
tuple layer (QL), as the unit cell with the space group
R3m (No. 166). Two equivalent Se atoms, two equivalent
Bi atoms and a third Se atom are in each QL. The coupling
is the chemical bonding between neighboring atomic layers
within one QL, but the van der Waals type, which is much
weaker, between two QLs. It is worth to note that the in-
version symmetry is held in the crystal structure.

In the following, we briefly introduce the basic elec-
tronic structure of this family compounds by taking Bi2Se3
as an example. First of all, the band structure without SOC
shows Bi2Se3 to be a narrow band gap insulator. Both the
bottom of conduction band and the top of valence band are
at Γ point, seen in Fig. 3(a). After SOC is turned on, the
bottom of conduction band is pulled down below the top of
valence band, and an interaction gap opens at the crossing
of valence and conduction bands, seen in Fig. 3(b). Based
on the parity calculations, Z2 invariants of Bi2Se3 are cal-
culated to be (1;1000) which mean topologically non-trivial.
The key for Bi2Se3 to be the topological insulator is the
band inversion at Γ between the conduction and valence
bands with opposite parity values. The schematic of the
band sequence at Γ point clearly tells the band evolution
starting from atomic levels with three stages, shown in
Fig. 3(c). Because the s levels are much lower than p levels,
we just start from the atomic p levels of Bi (6s26p3) and Se
(4s24p4). At the stage (I), the bonding and anti-bonding ef-
fact between Bi and Se atoms are considered. All the
atomic orbitals are recombined into \( P_0 \), \( P_1 \), \( P_2 \),
where ‘0’ represents the third Se, and ‘1’, ‘2’ repre-
sent Bi and the other two Se, respectively. ‘±’ represents
the parity values. Because the third Se is exactly at the in-
version center, it is different from the two other Se atoms
which together can be classified by the parity. We use \( P_0 \)
to indicate the third Se. At the stage (II), after the crystal field is turned on, $p_{yz}$ levels will split into $p_{yz}$ and $p_{x}$. The levels of $P_1^{+}$ and $P_2^{-}$ are nearest to the Fermi level. At the stage (III), SOC effect is further introduced. $P_1^{+}$ becomes two degeneracy levels ($P_1^{+1}$) and $P_2^{-}$ becomes two degeneracy levels ($P_2^{-1}$) due to the time-reversal symmetry. Though the $\langle p_{yz} | H_{\text{soc}} | p_{yz} \rangle$ is zero, $\langle p_{x} | H_{\text{soc}} | p_{x} \rangle$ is not zero which acts like the level repulsion between $p_{yz}$ and $p_{x}$ orbitals, so SOC effect pulls $P_1^{+1}$ down and pushes $P_2^{-1}$ up. Finally, if SOC is strong enough, the $p-p$-type band inversion will happen between $P_1^{+1}$ and $P_2^{-1}$.

Due to the layered structure with inversion symmetry, both the free-standing model and the tight-binding model based on MLWFs can be used to calculate surface states. Figure 4(a) shows the clear surface states of Bi$_2$Se$_3$ with a single Dirac cone at $\Gamma$ calculated by the MLWFs tight-binding model. Almost at the same time of Zhang et al.’s theory prediction [20], the Hasan group reported the topologically non-trivial surface states of Bi$_2$Se$_3$ by the ARPES experiment [49], shown in Fig. 4(b). Comparing the theory and experimental results, we have to agree that first-principles calculations can successfully predict topological insulators, including the details of surface states. Recently a lot of experimental studies of topological insulators are focusing on these compounds, because these compounds are easily to be grown by all kinds of experiments.

The topological insulator Bi$_{1-x}$Sb$_x$ (0.07 $< x <$ 0.22) alloy also belongs to the $p-p$ type [39]. Bulk Bi and Sb share a rhombohedral $R\bar{3}m$ structure which holds the inversion symmetry, and they both are semimetals with some tiny Fermi pockets around the TRIM L and T points, but there is a direct gap at every $\mathbf{k}$ point through the whole Brillouin zone (BZ). So we can define an imaginary Fermi surface in the direct gap. Based on the parity calculations, we confirm that Bi is topologically trivial with $Z_2(0;000)$, and that Sb is topologically non-trivial with $Z_2(1;111)$. The key difference of Bi and Sb is the band sequence of the conduction and valence bands at three L points. For example, the conduction band of Bi is $L_{s}$, and the valence band is $L_{a}$ where ‘$a$’ indicates the $-/+_{+}$ parity. Differently, these two bands switched with each other in Sb. After carefully comparing the band structure between Bi and Sb, Fu and Kane predicted that the insulate phase of Bi$_{1-x}$Sb$_x$ (0.07 $< x <$ 0.22) alloy must be a topological insulator. Subsequently, the Hasan group observed the topologically non-trivial property of Bi$_{1-x}$Sb$_x$ by the ARPES experiment [71]. But the details of surface states do not agree with the
ones of tight-binding [70] and first-principles calculations [48]. The schematics of the difference among these results are shown in Fig. 5. We can see that the ARPES result indicates three surface states $\Sigma_{1,2,3}$, but two surface states $\Sigma_{4,5}$ are only found by tight-binding and first-principles calculations. Zhang et al. argued that the extra surface state $\Sigma_{5}$ might come from the imperfect surface, but this still is an open question up to now.

Following Bi$_2$Se$_3$ family, a number of other p–p Bi-based topological insulators are predicted by theories and observed by experiments, such as, TlBiSe$_2$ family [21–24], SnBi$_4$Te$_4$ and SnBi$_4$Te$_7$ family [76], and so on.

### 3.3 d–f type

There is no clear evidence for the limit ($>0.3$ eV) of the energy gap size for topological insulators. How could we find new topological insulators with bigger energy gap? One possible way to enhance the SOC energy gap is to consider the cooperation of the SOC interaction and other effects, such as, the electron–electron correlation. In this idea, topological Kondo insulators were proposed, and SmB$_6$ as an example was predicted to be a topological Kondo insulator [78]. Though due to 4f orbitals SmB$_6$ is a strong correlated system. It only has a tiny energy gap. Recently Zhang et al. predicted AmN and PuTe family compounds are d and f topological insulators with strong interaction [77]. All AmN and PuTe family compounds have rock-salt crystal structure with space group Fm$\overline{3}$m (No. 225), and the inversion symmetry is also held in this structure. All these compounds have been well studied by theories and experiments, known as mixed valence materials. Here we take AmN as an example to understand the band structure. The configuration of actinide Am is $5f^77s^6d^6$. The SOC interaction is stronger than Hund’s rule, so the f orbitals split into high energy $J = 7/2$ and low energy $J = 5/2$ states. Approximately, in AmN, Am forms $Am^{3+}$ with the configuration $5f^77s^6d^6$, the states of $J = 5/2$ should be fully occupied, and $J = 7/2$ states are unoccupied. But due to the delocalization of 5f in Am, 5f states partly hybridize with 6d states with neighbor Am atoms.

In the fcc crystal field, d orbitals first split into $t_{2g}$ and $e_g$ states, and $t_{2g}$ level goes down to cross 5f below the Fermi level along $\Gamma$–X direction, shown in Fig. 6. The band inversion happens at three X points. If only LDA calculations are used, the full energy gap cannot open through the whole BZ. After the electron correlation is introduced with LDA + U method, a band gap can open up with proper correlation parameter $U$. We have to address that the electron correlation $U$ is found to enhance the SOC in these compounds. Because there are three TRIM X points in BZ, $Z_2$ invariants of AmN must be topologically non-trivial. Furthermore, our conclusion suggests that all the mix-valence compounds with rock-salt structure must be topologically non-trivial. Especially, transport experiments showed, PuTe [79] has a big energy gap around 0.2 eV, and this gap can be enhanced to 0.4 eV with pressure. Many of these f compounds host all kinds of magnetic phases, so they might open the opportunity to study QAH effect and dynamic Axion field.

### 4 Summary and outlook

In this review, we first introduced widely-used techniques within first-principles calculations including LDA and GGA, GW and MBJLDA, LDA + U, LDA + DMFT and LDA + Gutzwiller methods, because they play a crucial role on the field of topological insulators. Then the basic concepts of topological insulators and some useful methods to confirm the topological property are summarized. We classify topological insulators found to-date into three types as s–p, p–p and d–f based on the clear band inversion picture. For each type of topological insulators, we take several typical compounds as examples with talking about the electronic structure and the topological property.

Though many topological insulators have been discovered, it is still important to find more with desired properties. First of all, a big band gap is important for the application of surface states of topological insulators. Up to now the biggest band gap is around 0.3 eV in Bi$_2$Se$_3$ compound. Secondly, the transport experiments to detect surface states are still very challenging [80–82]. One reason is that the quality of samples is not good enough with a low mobility. Another reason is that Dirac cone always coexists with some bulk carriers. In order to overcome this barrier, on the one hand, experimentalists are trying to improve the quality of samples. On the other hand, it is important to
find other new topological insulators with functional properties. In addition, it is interesting to study the cooperation of the topological property with other phases, such as, superconductivity, magnetism and so on. We hope that this review can provide some guidance in the search.

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