Multi-orbital model reveals second-order topological insulator in 1H-transition metal dichalcogenide

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Recently, a new class of second-order topological insulators (SOTIs) characterized by an electronic dipole has been theoretically introduced and proposed to host topological corner states. As a novel topological state, it has been attracting great interest and experimentally realized in artificial systems of various fields of physics based on multi-sublattice models, e.g., breathing kagome lattice. In order to realize such kind of SOTI in natural materials, we proposed a symmetry-faithful multi-orbital model. Then, we reveal several familiar transition metal dichalcogenide (TMD) monolayers as a material family of two-dimensional SOTI with large bulk gaps. The topologically protected corner state with fractional charge is pinned at Fermi level due to the charge neutrality and filling anomaly. Additionally, we propose that the zero-energy corner state preserves in the heterostructure composed of a topological nontrivial flake embedded in a trivial material. The novel second-order corner states in familiar TMD materials hold promise for revealing unexpected quantum properties and applications.

Topological insulators are materials with gapped band structure characterized by quantized topological invariants that are defined with respect to the symmetries of their bulk Hamiltonian [1, 2]. In a d-dimensional (dD) topological insulator, a topologically non-trivial bulk band structure implies the existence of (d − 1)D boundary states. Instead, a dD second-order topological insulator (SOTI) exhibits (d − 2)D topological states [3–16]. For example, there are symmetry protected corner states with localized fractional charge in a 2D SOTI [4, 5, 7–11, 15, 16]. In 2017, the concept of higher-order topological insulators is introduced and characterized by quantized multipole [4]. SOTIs and their corner states are investigated in systems with electronic quadruples [8–10, 14–16]. Further in 2018, Ezawa further proposed that the electronic dipole could also induce second-order corner states in a breathing kagome model [5, 7, 17]. This new kind of second-order corner states have been experimentally realized via artificially designing metamaterials in various fields of physics [18–32].

It is charming to search SOTIs in natural and stable materials, especially the ones have been fabricated through mature technology of high-quality, for further study and application [33]. However, experimental demonstration of the existing single-orbital and multi-sublattice models, e.g., the breathing kagome model, in natural electronic materials is still lacking [24]. It is well known that the electronic bands of a material are usually contributed from multi-orbital, due to the degeneracy nature of the atomic orbitals and the hybridization between them. A multi-orbital model would provide a better guidance for realizing intriguing physics in natural materials [34].

Here, we construct a novel multi-orbital model to reveal several familiar transition metal dichalcogenides (TMDs) as a material family of 2D SOTI with a nontrivial bulk electronic dipole. The multi-orbital model proposed here shares similarity to the multi-sublattice breathing kagome model [5, 7] and has special advantages on materials realization. Our first-principles calculations and theoretical analysis show that the 1H-MX2 monolayers with M = (W, Mo) and X = (Te, Se, S) are 2D SOTIs with nontrivial electronic dipoles $\mathbf{P} = (\frac{1}{3}, \frac{2}{3})$ and large band gaps about 2 eV, while some other insulators, for example, 1H-TiS2, are topologically trivial. In the topologically nontrivial phase, the Wannier center of the occupied state locates on neither the M nor the X atom sites. The mismatch between the Wannier center of electron and the atom sites refers to an electronic dipole that is quantized and protected by the $C_3$ rotation symmetry. Using a topological nontrivial MoS2 flake as a typical example, our calculations and analysis demonstrate the in-gap corner state with localized fractional $-\frac{1}{3}|e|$ charges. Additionally, the zero-energy corner state can be protected from edge deformation and environmental impaction in the heterostructure composed of a MoS2 flake embedded in a trivial TiS2 monolayer.

Monolayers TMD-MX$_2$ with M = (W, Mo) and X = (Te, Se, S)-possess a variety of polytypic structures. The most-studied 1H structure has the $D_{3h}$ point-group symmetry and is a sandwich of three planes of 2D hexagonally packed atoms, X-M-X, as shown in Fig. 1(a). It has been known that the 1H structure in MX$_2$ is typically stable in free-standing conditions, which is the subject of our
FIG. 1. Atomic structure and electronic structure of a 1H-MX$_2$ monolayer. M stands for (W, Mo) and X stands for (Te, Se, S). a. Atomic structure of a 1H-MX$_2$ monolayer. The arrows $\mathbf{a}_1$ and $\mathbf{a}_2$ ($\mathbf{b}_1$ and $\mathbf{b}_2$) are the two (reciprocal) lattice vectors. One rhombic unit cell is colored in cyan. The black hexagon in the lower right corner is the first Brillouin zone. b. Orbital projected band structure of a 1H-MoS$_2$ monolayer. Colored circles represent contributions from different M-d-orbitals. The Fermi energy $E_F$ is set to be zero as a reference. c. Wilson loop of WCC of the highest valence band showing the calculated electronic dipole $\mathbf{P} = (1/2, \frac{3}{2})$.

FIG. 2. Schematic lattice diagram and phase diagram of the simplified multi-orbital model Eq. (1). In (a), the three ellipses in different colors represent three orbitals on the same site. The thicker and thinner lines present two different kinds of nearest neighbor hoppings. The dashed lines present the electronic dipole $\mathbf{P} = (1/2, \frac{3}{2})$. Topological phase diagrams of the multi-orbital model for the (b) $t_E = 0$ and (c) $t_{23} = 0$ cases.

The electronic structures of various 1H-MX$_2$ monolayers were obtained by first-principles calculations. Figure 1(b) shows a typical band structure of 1H-MX$_2$ using a 1H-MoS$_2$ monolayer as an example, and the results of the other five compounds are shown in Fig. S1. The 1H-MoS$_2$ is an insulator with a fundamental gap of about 2 eV. From early theoretical studies [36], we know that the Bloch states of a MoS$_2$ monolayer near the band edges for both conduction and valence bands mostly consist of Mo-d-orbitals with no hybridization between the $d_{x^2}$, $d_{xy}$, $d_{xz}$, and $d_{yz}$ orbitals, which is explicitly shown in Fig. 1(b). With respect to the symmetry consideration, it is reasonable to construct a multi-orbital tight-binding model of monolayer MX$_2$ using the minimal set of M-d$_{x^2}$, d$_{xy}$, and d$_{xz}$-y$_2$ orbitals as basis [36]. Here we construct a simplified while symmetry faithful Hamiltonian $\mathcal{H}_s$ as

$$
\mathcal{H}_s = \sum_{\mathbf{r},ij;jk} \frac{t_{23} + t_{32} \pm (t_{23} - t_{32})\epsilon_{ijk}}{2} d_{\mathbf{r},i}^\dagger d_{\mathbf{r} \pm \mathbf{a}_k,j} \epsilon_{ijk} + t_E \sum_{\mathbf{r},i} d_{\mathbf{r},i}^\dagger d_{\mathbf{r},j},
$$

(1)

where the hopping parameters for different 1H-MX$_2$ monolayers are listed in Table I. It notes that the indirect interaction mediated by the X atoms is reflected in the difference between $t_{23}$ and $t_{32}$, which breaks the inversion symmetry. Figure 2(a) is a schematic diagram of the above multi-orbital model, which shares similarity to the multi-sublattice breathing kagome model [5, 7]. See more details in the Supplemental Material.

The electronic dipole can be calculated as [37–39]

$$
P = \frac{1}{S} \int_{BZ} \text{Tr}(\mathbf{A}) d^2 \mathbf{k},
$$

(2)

where $\mathbf{A} = -i \langle \Psi | \partial_k | \Psi \rangle$ is the Berry connection for all the valence bands, $S$ is the area of the Brillouin zone, and the integration is over the first BZ. The two elements $P_1$ and $P_2$ are actually the average values of Wannier charge center (WCC) along the reciprocal lattice vectors $\mathbf{b}_2$ and $\mathbf{b}_1$, respectively, with the values module 1 confined in the range of $[0, 1]$ [37–39]. The location of Wannier center in real space is $P_1 \mathbf{a}_1 + P_2 \mathbf{a}_2$ [37–39]. For the multi-orbital model here, the electronic dipole $\mathbf{P}$ is determined by the WCC of the lowest band that is also the highest valence band and decoupled from other bands.

Since a 1H-MX$_2$ structure shown in Fig. 1(a) has the $D_{3h}$ point-group symmetry, the electronic dipole must be quantized as $\mathbf{P} = (0, 0)$, $(\frac{2}{3}, \frac{1}{3})$, or $(\frac{1}{3}, \frac{2}{3})$ [39], corresponding to a Wannier charge centered on the M site, X site, or hollow site, respectively. The calculated electronic dipole is $\mathbf{P} = (\frac{1}{3}, \frac{2}{3})$ for a 1H-MoS$_2$ monolayer corresponding to a Wannier charge located on the hollow.
rotation symmetry and the charge neutrality \([5, 7, 39]\). and the filling anomaly due to the coexistence of the C
produce the zero-energy boundary state at the corner This topologically nontrivial polarization is expected to
that the system is nontrivial with \(P\) though the calculated value \(P\) is perpendicular to the zigzag direction, metallic edge states are expected due to the charge accumulation at the zigzag edge. In contrast, no such charge accumulation and metallic states at the armchair edges that are parallel to \(P\). A flake with insulating armchair edges is a better choice for the observation of in-gap corner states.

The first-principles calculated electronic spectrum of the 1H-MoS\(_2\) flake is shown in Fig. 3. There are 6 corner states at the Fermi level with 3 corner states for each spin. In our calculations, both spin degeneracy and spin-orbit coupling are taken into consideration. It notes that the spin-orbit coupling does not split the spin degeneracy of the corner states since time-reversal symmetry preserves. As an example, the charge distribution of the corner state numbered as \(n = 808\) is shown in red color. The charge distribution of bulk state \(n = 760\), edge states \(n = 814\), and \(n = 869\) are presented in cyan color for comparison. For a corner state, one electron is equally distributed on the three corners with \(-\frac{1}{3}|e|\) charge on each corner.

To explicitly show the zero-energy corner state, a triangular flake of 1H-MoS\(_2\) with armchair edges is constructed, as shown in Fig. 3. There are 45 unit cells in the triangular 1H-MoS\(_2\) flake and the length of an edge is five hexagons. The triangular shape is chosen to keep the \(C_3\) rotation symmetry which is important for the degeneracy of the corner states. It notes that the appearance of the corner state is sensitive to the choice of the edge geometry for a topological system protected by spatial symmetry. Previous works have shown that a zigzag edge of MoS\(_2\) has metallic edge states while an armchair edge is insulating [40, 41]. It can be understood in terms of electronic polarization. Since polarization \(P\) is

site. The Wilson loop of WCC of the highest valence band along the two reciprocal lattice vectors is shown in Fig. 1(c). It is a kind of topologically nontrivial polarization when the Wannier charge dislocates from the M or X atom sites. It notes that the mismatch between the Wannier center and the atom site is gauge invariant, though the calculated value \(P\) depends on the choice of the unit cell [5, 37–39]. Figure 2(a) provides an intuitive diagram of the multi-orbital model showing the Wannier charge locates at the center of the thicker triangle formed by larger hoppings (\(t_{32}\)). In Fig. 2(b), we plot phase diagrams of the multi-orbital model of Eq. (1). It shows that the system is nontrivial with \(P = (\frac{1}{3}, \frac{2}{3})\) when the \(t_{32}\) has a negative value and its amplitude is larger than other hopping parameters. The first-principles calculations and combined theoretical analysis show that all the six 1H-MX\(_2\) monolayers with \(M = (\text{W, Mo})\) and \(X = (\text{Te, Se, S})\) are topologically nontrivial with \(P = (\frac{1}{3}, \frac{2}{3})\). This topologically nontrivial polarization is expected to produce the zero-energy boundary state at the corner and the filling anomaly due to the coexistence of the \(C_3\) rotation symmetry and the charge neutrality [5, 7, 39].

![Energy spectrum of a triangular MoS\(_2\) flake with armchair edges.](image)

**FIG. 3.** Energy spectrum of a triangular MoS\(_2\) flake with armchair edges. The red dots on the Fermi level represents the 6 in-gap corner states. Other bulk and edge states are colored in cyan. The atomic structure and the charge distribution of the corner states since time-reversal symmetry preserves. As an example, the charge distribution of the corner state numbered as \(n = 808\) is shown in red color. The charge distribution of bulk state \(n = 760\), edge states \(n = 814\), and \(n = 869\) are shown in the inset. For the corner state \(n = 808\), the electron is localized and equally distributed on the three corners with \(-\frac{1}{3}|e|\) charge on each corner.

| \(t_{32}\) | \(t_{33}\) | \(t_{34}\) | \(t_{35}\) | \(t_{36}\) | \(t_{31}\) |
|---|---|---|---|---|---|
| \(-0.353\) | \(-0.382\) | \(-0.412\) | \(-0.456\) | \(-0.499\) | \(-0.543\) |
| \(-0.922\) | \(-1.159\) | \(-0.987\) | \(-0.626\) | \(-0.772\) | \(-0.922\) |
| \(0.122\) | \(0.210\) | \(0.065\) | \(0.139\) | \(0.022\) | \(0.099\) |

**TABLE I.** Hopping parameters in unit of eV for the six 1H-MX\(_2\) monolayers and calculated electronic dipole \(P\).

To explicitly show the zero-energy corner state, a triangular flake of 1H-MoS\(_2\) with armchair edges is constructed, as shown in Fig. 3. There are 45 unit cells in the triangular 1H-MoS\(_2\) flake and the length of an edge is five hexagons. The triangular shape is chosen to keep the \(C_3\) rotation symmetry which is important for the degeneracy of the corner states. It notes that the appearance of the corner state is sensitive to the choice of the edge geometry for a topological system protected by spatial symmetry. Previous works have shown that a zigzag edge of MoS\(_2\) has metallic edge states while an armchair edge is insulating [40, 41]. It can be understood in terms of electronic polarization. Since polarization \(P\) is perpendicular to the zigzag direction, metallic edge states are expected due to the charge accumulation at the zigzag edge. In contrast, no such charge accumulation and metallic states at the armchair edges that are parallel to \(P\). A flake with insulating armchair edges is a better choice for the observation of in-gap corner states.

The first-principles calculated electronic spectrum of the 1H-MoS\(_2\) flake is shown in Fig. 3. There are 6 corner states at the Fermi level with 3 corner states for each spin. In our calculations, both spin degeneracy and spin-orbit coupling are taken into consideration. It notes that the spin-orbit coupling does not split the spin degeneracy of the corner states since time-reversal symmetry preserves. As an example, the charge distribution of the corner state numbered as \(n = 808\) is shown in red color. The charge distribution of bulk state \(n = 760\), edge states \(n = 814\), and \(n = 869\) are presented in cyan color for comparison. For a corner state, one electron is equally distributed on the three corners with \(-\frac{1}{3}|e|\) charges on each corner. By counting the number of electrons in a charge-neutral flake, the 6 corner states are occupied by 4 electrons at the Fermi level. When the corner states are unoccupied as a result of filling anomaly [7], there will be \(\frac{1}{3}|e|\) charges at each corner. See more detailed information in the Supplemental Material.

Though the corner state is symmetry protected, the degeneracy of the corner state and the fractional charge nature may deviate from the ideal case when the \(C_3\) rotation symmetry is destroyed via edge deformation or external influence [7, 18, 22–24]. It is expected that edges and corners can be protected via embedding the topological 1H-MoS\(_2\) flake in a trivial material as a heterostructure. Figure 4 shows a typical heterostructure of a triangular 1H-MoS\(_2\) flake in a 1H-TiS\(_2\) monolayer. It notes that the two materials share similar structures as well as lattice parameters. In contrast, the 1H-TiS\(_2\) monolayer is a topologically trivial insulator because it has two fewer valence electrons per unit cell less than that of the 1H-MoS\(_2\) monolayer [33, 35]. We further checked that the MoS\(_2\)/TiS\(_2\) lateral heterostructure is insulating at the armchair boundary. Thus, a 1H-TiS\(_2\) monolayer provides a perfect platform to protect a topological 1H-MoS\(_2\) flake and its in-gap corner states. As shown in Fig.
FIG. 4. Energy spectrum of a heterostructure composed of a triangular MoS$_2$ flake in a TiS$_2$ monolayer. In (a), the red dots on the Fermi level represent the 6 in-gap corner states. b. The charge distribution of corner state $n = 3160$. The electron is localized and equally distributed on the three corners with $-\frac{1}{3}|e|$ charges on each corner.

4, the 6 corner states and their fractional charge nature preserve in the heterostructure. The 6 corner states are occupied by 4 electrons at the Fermi level, which is the same to the freestanding flake case.

We reveal several familiar TMD monolayers as a realistic material family of 2D SOTIs. The topologically protected corner state is pinned at the Fermi level due to the charge neutrality and filling anomaly. A multi-orbital model is proposed to reveal these TMDs as SOTIs. Additionally, we propose that the zero-energy corner state of a topologically nontrivial flake can be further protected from edge deformation and environmental implication via embedding it in a trivial material using the MoS$_2$/TiS$_2$ heterostructure as a typical example. The novel second-order corner state in familiar TMD materials hold promise for revealing unexpected quantum properties and applications.

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