Isolated highly localized bands in YbI₂ monolayer caused by 4f orbitals

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Abstract
The novel electronic structures can induce unique physical properties in two-dimensional (2D) materials. In this work, we report isolated highly localized bands (HLB) in YbI₂ monolayer by the first-principle calculations within generalized gradient approximation (GGA) plus spin–orbit coupling (SOC). It is found that YbI₂ monolayer is an indirect-gap semiconductor using both GGA and GGA+SOC. The calculations reveal that Yb–4f orbitals constitute isolated HLB below the Fermi level at the absence of SOC, and the bands are split into the \( j = 7/2 \) and \( j = 5/2 \) states with SOC. The isolated HLB can lead to a very large Seebeck coefficient and very low electrical conductivity in p-type doping by producing very large effective mass of the carrier. It is proved that isolated HLB have very strong stability against strain, which is very important for practical application. When the onsite Coulomb interaction is added to the Yb–4f orbitals, isolated HLB persist, and only their relative positions in the gap change. These findings open a new window to search for novel electronic structures in 2D materials.

Keywords: monolayer, spin–orbit coupling, novel electronic structures

(Some figures may appear in colour only in the online journal)

1. Introduction

Since the discovery of graphene [1], 2D materials have attracted enormous research interest in electronic, optical, topological and thermal properties. A large amount of 2D materials have been predicted theoretically, or achieved experimentally, such as transition metal dichalcogenide (TMD), group-VA, group IV–VI and group-IV monolayers [2–7]. Graphene has a peculiar electronic structure with the dispersion relation being linear around the Fermi level, and the related electrons and holes need to be described by the Dirac equation [1]. Compared with the gapless graphene, MoS₂ as a representative semiconducting TMD monolayer has triggered a new wave of research in TMD monolayers due to potential application for novel ultrathin and flexible devices [8, 9]. Recently, Janus monolayer MoSSe has been experimentally synthesized by replacing the top S atomic layer of MoS₂ with Se atoms [10], which provides more possibilities for more extensive nanoelectronic and optoelectronic applications. Phosphorene, possessing novel high carrier mobility and intrinsically large fundamental direct band gap, has great prospective for its applications in field-effect transistors and photo-transistors [11, 12]. Experimentally, the 2D Dirac nodal line fermions has been reported in monolayer Cu₂Si, which provides a platform to study the novel physical properties in 2D Dirac materials [13]. Thermal transports of 2D materials have been widely investigated, including external perturbation like strain, substrate and clustering [14].

Searching for other peculiar electronic structures, like isolated HLB, would be of great significance to the design and development of nano-devices. Recently, the plentiful 2D materials are predicted from high-throughput computational
exfoliation of experimentally known compounds [15]. Among them, YbI$_2$ monolayer with 4$f$ electrons is predicted, which is interesting to investigate its electronic structure due to localized 4$f$ orbitals. In this work, the electronic structures of YbI$_2$ monolayer are studied by first-principles calculations. It is found that there are some isolated HLB with Yb-4$f$ character in a very large gap. The SOC can split the 4$f$ bands into $j = 7/2$ and $j = 5/2$ states, and the splitting gap is up to about 1.22 eV. In p-type doping, the very large Seebeck coefficient and very low electrical conductivity can be found due to very large effective mass of the p-type carrier caused by the isolated HLB. Calculated results show that isolated HLB are very stable against strain, and the electron correlation effects only change the relative positions of HLB in the gap.

2. Computational detail

Within the density functional theory (DFT) [16], we use a full-potential linearized augmented-plane-waves (FPLAPW) method to investigate electronic structures of YbI$_2$ monolayer, as implemented in the WIEN2k code [17], and the local orbitals (lo) is used to improve upon the linearization. By dividing the unit cell into non-overlapping atomic spheres and an interstitial region, a linear combination of radial functions times spherical harmonics is used inside atomic sphere, and an interstitial region, a linear combination of radial functions is used to improve upon the linearization. Local orbitals (lo) is used to improve upon the linearization.

By dividing the unit cell into non-overlapping atomic spheres and an interstitial region, a linear combination of radial functions times spherical harmonics is used inside atomic sphere, and a plane wave expansion is used in the interstitial region. The popular GGA of Perdew et al (GGA-PBE) [18] is used as the exchange-correlation potential, and the lattice parameters ($a = b$) and internal atomic positions are optimized with energy minimization and a force standard of 2 mRy a.u. The optimized lattice constants and radii, respectively, and we set $R_{\text{mt}} \times R_{\text{mt}} \times R_{\text{mt}} = 30$ maximum (VBM) is at $\Gamma$ point, and the conduction band minimum (CBM) at M point. The GGA and GGA + SOC gap is 0.916 eV and 0.390 eV, respectively, and the gap reduce caused by SOC is 0.526 eV. The bands from $-5.5$ to $-3.0$ eV are mainly composed of I-p character states, slightly hybridized with Yb-d/s ones. The hybridized Yb-d and I states are observed in the conduction bands. When considering SOC, it is found that both conduction bands and valence bands below localized states move toward lower energy compared with ones using GGA.

The electronic transport coefficients of TMD monolayers have been widely investigated in theory [27–29]. It is natural to ask what effects on transport coefficients can be induced by HLB. Based on CSTA Boltzmann theory, the Seebeck

Figure 1 shows the structure of the YbI$_2$ monolayer, containing three atomic sublayers with the Yb layer sandwiched I layers. The similar structure can also be found in TMD monolayer [25], such as ZrS$_2$ and PtSe$_2$ monolayers with 1T phase. However, it is different from the MoS$_2$ as a representative TMD monolayer with 2H phase. The unit cell of the YbI$_2$ monolayer is built with the vacuum region of more than 18 Å to avoid spurious interaction between neighboring layers. The optimized lattice constants $a (b)$ using GGA is 4.46 Å with Yb and I atoms occupying the (0, 0, 0) and (1/3, 2/3, 0.922) positions, respectively. The Yb-I bond length is 3.14 Å, and I-Yb-I bond angle for 89.26° (90.735°), and the thicknesses of the YbI$_2$ monolayer for 3.58 Å.

The calculated energy band structures of YbI$_2$ monolayer are shown in figure 2 with GGA and GGA + SOC, and the related density of states (DOS) are plotted in figure 3. Without SOC, fourteen HLB with Yb-4$f$ character are observed near the Fermi level, and the bandwidth is only 0.118 eV. When including SOC, the 4$f$ bands are split into the $j = 7/2$ and $j = 5/2$ states, producing a gap of 1.218 eV. Similar splitting can also be found in YbB$_6$ by SOC [26]. The $j = 7/2$ states are near the Fermi level with bandwidth 0.092 eV, and $j = 5/2$ states are $-1.309$ eV below the Fermi level with bandwidth 0.086 eV. Both using GGA and GGA + SOC, the valence band maximum (VBM) is at $\Gamma$ point, and the conduction band minimum (CBM) at M point. The GGA and GGA + SOC gap is 0.916 eV and 0.390 eV, respectively, and the gap reduce caused by SOC is 0.526 eV. The bands from $-5.5$ to $-3.0$ eV are mainly composed of I-p character states, slightly hybridized with Yb-d/s ones. The hybridized Yb-d and I states are observed in the conduction bands. When considering SOC, it is found that both conduction bands and valence bands below localized states move toward lower energy compared with ones using GGA.

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Figure 2. The energy band structures of the YbI$_2$ monolayer using GGA (Left) and GGA+SOC (Right).

Figure 3. (a)–(c) the total and projected DOS of the YbI$_2$ monolayer using GGA; (d) the total DOS using GGA and GGA+SOC.
coefficient $S$ and electrical conductivity $\sigma/\tau$ are performed within rigid band approach. It is noted that the calculated $\sigma/\tau$ depends on $\tau$, while $S$ is independent of $\tau$. The n(p)-type doping effects can be simulated by simply moving the Fermi level into conduction (valence) bands, namely electron (hole) doping. The room temperature $S$ and $\sigma/\tau$ of YbI$_2$ as a function of doping level ($N$) using GGA and GGA+SOC are plotted in figure 4. In low p-type doping, a detrimental influence on $S$ caused by SOC can be observed, while a neglectful effect on $S$ (absolute value) in n-type or high p-type doping can be found. For $\sigma/\tau$, the SOC has little effect in both n- and p-type doping. It is clearly seen that the p-type $S$ is larger than 300 $\mu$V K$^{-1}$ with doping level being up to 0.1 hole/per unit cell. However, for n-type doping, the $S$ can reach 300 $\mu$V K$^{-1}$, only below doping level of 0.008 electron/per unit cell. It is also found that the $\sigma/\tau$ is very close to zero in p-type doping. These results are because the $S$ is proportional to the effective mass of the carrier, while $\sigma$ is inversely proportional to one. Therefore, HLB can induce very large $S$ and very low $\sigma$ by producing very large effective mass of the carrier. A similar effect can be found in hole-doped PbTe or PbSe [30, 31], and the flat-band (localized bands) can be observed below their gaps.

During the fabrication process, 2D materials will commonly have residual strain. Next, we investigate the stability of HLB again biaxial strain. The strain effects on the energy band structures and transport properties of TMD monolayers have been widely investigated [28, 29, 32, 33]. The $\varepsilon = (a - a_0)/a_0$ is defined to simulate biaxial strain, in which $a_0$ is the unstrained lattice constant. The $\varepsilon < (>)0$ means compressive (tensile) strain. The related energy band structures of YbI$_2$ monolayer are shown in figure 5 using GGA+SOC, with strain from −6% to 6%. In considered strain range, compressive strain can reduce the numbers of conduction band extrema (CBE) from two to one, while tensile strain can change relative position of two CBE. For example, at 6% strain, the CBM changes from M to $\Gamma$ point, which means that tensile strain can induce conduction bands convergence between 4% and 6% strain, producing very large n-type $S$. Similar phenomenon caused by strain can also be found in TMD monolayers [28, 29, 33]. The energy band gap, the gap between the $j = 7/2$ and $j = 5/2$ states and the widths of the $j = 7/2$ and $j = 5/2$ states as a function of $\varepsilon$ are plotted in figure 6. With increasing strain, the energy band gap increases from −6% to 4% strain, and then slightly reduces at 6% strain. It is clearly seen that the gap between the $j = 7/2$ and $j = 5/2$ states and the widths of the $j = 7/2$ and $j = 5/2$ states have very minor changes from −4% to 6% strain, and the change is only 0.038 eV, 0.023 eV and 0.039 eV, respectively. So, the HLB have very strong stability against strain.

To account for 4f electron correlation effects, the onsite Coulomb interaction is included. In [26], the band structures of YbB$_6$ for $U = 0$ (small U region), $U = 5$ eV (middle U region) and $U = 8$ eV (large U region) have been shown. Here, the Coulomb potential $U_{\text{eff}}$ for the Yb-4f orbitals in YbI$_2$ is chosen to be 5 eV. In fact, the isolated HLB stay with $U_{\text{eff}} = 8$ eV. The DOS of YbI$_2$ using GGA+SOC, GGA+$U_{\text{eff}}$ +SOC, GGA and GGA+$U_{\text{eff}}$ are shown in figure 7. Calculated results show that the isolated HLB still exists, and only they move to lower energies, which leads to increased energy band gap. When including onsite Coulomb interaction, the GGA gap
changes from 0.92 eV to 2.53 eV, and GGA+SOC gap from 0.39 eV to 1.94 eV. However, the gap between the $j = 7/2$ and $j = 5/2$ states hardly changes. In fact, as $U$ is increased, HLB

Figure 5. The energy band structures of the YbI$_2$ monolayer with $\varepsilon$ changing from $-6\%$ to $6\%$ using GGA+SOC, and the $\varepsilon$ stands for strain.

Figure 6. The energy band gap (Gap), the gap between the $j = 7/2$ and $j = 5/2$ states ($f_{7/2}$-$f_{5/2}$) and the widths of the $j = 7/2$ and $j = 5/2$ states ($f_{7/2}$ and $f_{5/2}$) (unit: eV) as a function of $\varepsilon$, and the $\varepsilon$ stands for strain.

Figure 7. The DOS of the YbI$_2$ monolayer using GGA+SOC, GGA+U+SOC, GGA and GGA+U.
gradually move to lower energies. When $U$ is large enough, the $j = 5/2$ states firstly cross with $I$-$p$ states, and then the $j = 7/2$ states also cross.

4. Conclusion

In summary, we investigate electronic structures of YbI$_2$ monolayer, based mainly on the reliable first-principle calculations. Calculated results show that the YbI$_2$ monolayer is an indirect-gap semiconductor using GGA+SOC, GGA+$U$+SOC, GGA and GGA+$U$, and the isolated HLB with Yb-4$f$ character are observed in a very large gap of up to about 4 eV. With the inclusion of SOC, the 4$f$ bands are split into the $j = 5/2$ and $j = 7/2$ states. The isolated HLB can induce a very large Seebeck coefficient and very low electrical conductivity in p-type doping. Calculated results show that strain can tune the effective mass of the p-type carrier, and then leads to a very large Seebeck coefficient and very low electrical conductivity in p-type doping. Calculated results show that strain can tune the strength of conduction bands convergence by changing the in p-type doping. Calculated results show that strain can tune the Seebeck coefficient and very low electrical conductivity in p-type doping. Calculated results show that strain can tune the Seebeck coefficient and very low electrical conductivity in p-type doping.

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