Chern insulators from heavy atoms on magnetic substrates

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We propose searching for Chern insulators by depositing atomic layers of elements with large spin-orbit coupling (e.g., Bi) on the surface of a magnetic insulator. We argue that such systems will typically have isolated surface bands with non-zero Chern numbers. If these overlap in energy, a metallic surface with large anomalous Hall conductivity (AHC) will result; if not, a Chern-insulator state will typically occur. Thus, our search strategy reduces to looking for examples having the Fermi level in a global gap extending across the entire Brillouin zone. We verify this search strategy and identify several candidate systems by using first-principles calculations to compute the Chern number and AHC of a large number of such systems on MnTe, MnSe, and EuS surfaces. Our search reveals several promising Chern insulators with gaps of up to 140 meV.

The discovery of the quantized conducting edge states characteristic of the integer quantum Hall effect (IQHE), and their explanation in terms of a bulk topological invariant known as the Chern number or TKNN invariant [1], initiated a new emphasis on topology in the theory of electronic structure. In recent years, this trend has accelerated enormously, extending also to materials with time-reversal (TR) symmetry and leading to important discoveries including two-dimensional (2D) quantum spin Hall (QSH) systems and three-dimensional (3D) topological insulators (TI) [2, 3].

Concerning systems with broken TR symmetry, it has been known since the work of Haldane [4] that it is possible in principle to have an insulating magnetic material exhibiting a non-zero Chern number, as in the IQHE, but in the absence of any applied magnetic field. These Chern insulators, or quantum anomalous Hall insulators, would display many of the same properties as IQHE systems, including robust edge states with quantized conductance, potentially at room temperature. Theoretically, it seems quite plausible that spin-orbit coupling (SOC), when combined with broken TR symmetry, could allow for a non-zero Chern number in an insulator just as it allows for non-zero anomalous Hall conductivity in metals [5–8]. While some aspects of the Chern-insulator state have been investigated theoretically [9, 10], there are currently no experimentally known examples of Chern insulators, and finding one remains a major challenge in condensed matter physics.

Motivated in part by the spectacular recent progress concerning other kinds of topological insulators, there has been a dramatic renewal of interest recently in the search for experimental realizations of the Chern-insulator state. Previous experimental and theoretical proposals for Chern insulators have typically involved starting with non-magnetic topological-insulator or Dirac-cone systems, such as HgTe quantum wells [11, 12], graphene [13], and Bi_2Se_3 [14–17], and doping them with magnetic ions in order to break TR symmetry in such a way as to generate a Chern-insulator state [18]. While these proposals are promising, there are serious challenges associated with this strategy, including the difficulties of magnetically doping these materials in a controlled fashion, understanding the role of the associated disorder, aligning the spins of the dopants, and keeping these small-gap materials insulating during the process. Further proposals have focused on avoiding doping by using thin layers of stoichiometric compounds like $GdBiTe_3$ [19] and $HgCr_2Se_4$ [20], but the band gaps remain small.

In this work, we propose an alternate search strategy for Chern insulators that overcomes many of the materials challenges of previous work, and we use first principles calculations to prove its viability. In addition, we suggest several candidate systems with non-zero Chern numbers, including several with significant gaps. Our proposal is to start with a known magnetically-ordered insulating substrate, choose a surface which breaks TR symmetry, and deposit a layer of heavy atoms (Pt-Bi) with large SOC (see Fig. 1). In other words, we directly combine the two key ingredients necessary to create a Chern insulator: broken TR symmetry and large SOC. By starting with a large-band-gap substrate with naturally aligned spins, we avoid the difficulties related to magnetic dopants and disorder. In addition, by including the heaviest possible atoms, we maximize the SOC and have the potential for band gaps over 0.5 eV.

As will be discussed shortly, our strategy *generically* gives rise to surface bands in the bulk band gap having two crucial properties: (i) they are isolated, in the sense that surface band N does not touch bands $N \pm 1$ anywhere in the 2D Brillouin zone (BZ); and (ii) these bands *typically carry non-zero Chern numbers*. Property (i) insures that the minimum direct gap between bands N and $N+1$ is generically positive. Property (ii) implies that if the indirect gap between these bands is also positive, so that a global gap exists, then a surface with N filled surface bands is likely to realize the Chern-insulator state.

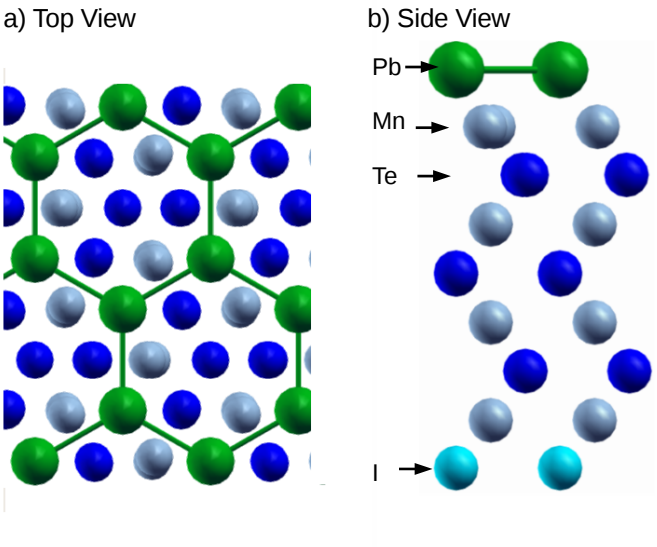

FIG. 1: a) Top view and b) side view of the tripled surface unit cell of MnTe with 2/3 ML Pb. Pb is in green, Mn in gray, Te is dark blue and I in cyan.

The essential challenge for our strategy, therefore, is to choose a magnetic substrate and a heavy-adatom surface decoration that can put the Fermi energy in a global gap of the 2D surface bandstructure. As we show below, this is not an insurmountable difficulty.

We give here a brief justification of properties (i) and (ii) above, although they are also amply illustrated by the results presented later. Regarding (i), it is well known that, in the absence of special symmetries, accidental degeneracies between bands in 2D generically do not occur. This fact can be understood by considering that the Hamiltonian near any potential crossing between two bands can be written as a linear combination of the three Pauli matrices; for the bands to cross, the coefficients of all three matrices must vanish. In the 2D (k_x, k_y) space of the BZ, this will not happen except by special tuning of some third parameter. Moreover, since we consider systems with a net magnetization at the surface in the presence of SOC, neither time reversal (TR) nor common crystallographic point symmetries (e.g., $3m'$ for most of the cases below) enforce degeneracies at any high-symmetry points in the BZ. Regarding property (ii), we find that if the SOC, magnetic exchange, and interatomic hoppings are all of comparable magnitude, then non-zero Chern numbers are typical. To illustrate this, we performed a numerical study of random tight-binding Hamiltonians consisting of between two and six orbitals on a square lattice with random complex hoppings to the four adjacent and four diagonal unit cells, and found that the Chern numbers of the resulting bands appear to be normally distributed around zero with a standard deviation of 1-2. In other words, non-zero Chern numbers are abundant in 2D in the absence of TR or other special symmetries.

In order to prove the viability of our proposal, we perform first-principles calculations on surfaces of three insulating magnetic substrates with a variety of monolayer or submonolayer heavy-atom coverages, searching for promising Chern-insulator systems. We consider the (001) surfaces of MnSe and MnTe in the NiAs structure ($P6_3/mmc$), and the (111) surface of EuS in the rock-salt structure ($Fm\bar{3}m$). These hexagonal surfaces are closely related, as the structures only differ by the stacking sequence of the hexagonal close-packed atomic layers. MnSe and MnTe are A-type antiferromagnets, with layers of ferromagnetically aligned spins lying in the xy plane, while EuS is ferromagnetic. For MnSe, we calculate that the spins can be aligned in the $\pm z$-direction by applying an epitaxial strain of -2%, so we adopt this strain state in what follows. These substrates were chosen for their large magnetizations, large band gaps, and simple structures.

Our computational supercells consist of slabs of four layers of the magnetic substrate, passivated by iodine atoms on the bottom surface and stacked with a vacuum separation of $\sim$12 Å, as illustrated in Fig. 1. The top surfaces of the substrates are terminated on the magnetic-atom layer (Mn or Eu) so that when the heavy atoms (Pt through Bi) are absorbed, the direct contact with the magnetic ions will maximizing the exchange splitting. We note that these terminations are all polar, with each 1×1 area donating one electron to the surface adatoms. This fact highlights the difficulty in combining heavy atoms directly with magnetic atoms in a thermodynamically stable way, as both types of atom typically prefer positive oxidation states. However, it may be possible to stabilize these surfaces as metastable states. Further theoretical work, combined with experimental investigations, will be necessary to identify which structures can be achieved in practice.

We begin our search by considering full monolayers of heavy atoms on MnTe surfaces. Promisingly, the bands show both large exchange splittings and strong SOC effects, but the bandwidths of the surface bands are about 3 eV, making it difficult to find systems with gaps. In order to reduce the dispersion of the surface bands to the same magnitude as the spin-orbit and exchange splittings, we consider tripled unit cells with only 1/3 or 2/3 ML of heavy atoms adsorbed. These structures, which produce flatter surface bands, are the focus of the remainder of this work.

In Figs. 2(a-b) we show the band structure of 2/3 ML of Pb of MnTe arranged in a honeycomb lattice (see Fig. 1) with the spins aligned along the $\pm z$ and $\pm x$ direction respectively. We label the Chern numbers of each gap, defined as the total Chern number of all bands below the gap; the Chern number of an isolated band is then just the difference between the gap Chern numbers above and below it. The system with spins in the $\pm z$ direction is a

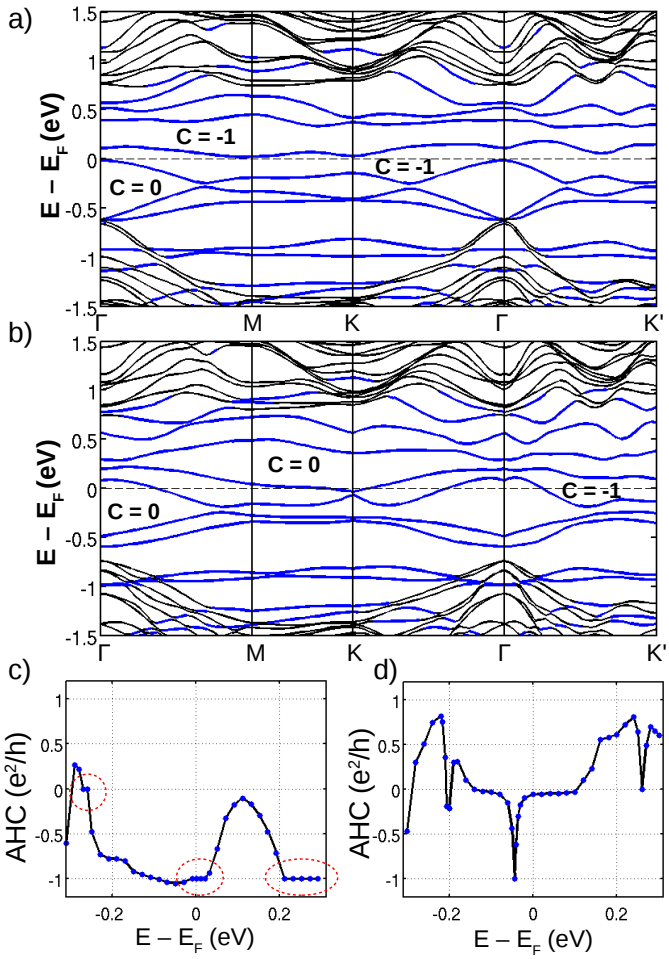

FIG. 2: (a-b) Band structure of 2/3 Pb on MnTe with spins in (a) the $\pm z$-direction, and (b) the $\pm x$-direction. Bands with the most Pb character are highlighted in thick (blue) lines; bulk-like MnTe bands are in thin (black) lines. Chern numbers of gaps near the Fermi level are labeled. (c-d) Anomalous Hall conductivity of band structures in (a-b), in units of e^2/h. Quantized plateaus are highlighted.

Chern insulator (C=−1) with a direct band gap of 126 meV and an indirect band gap of 36 meV, providing a proof of principle for our search method. The effect of the non-zero Chern numbers on the AHC can be seen for the insulating case of Fig. 2(c), which shows quantized Hall plateaus (circled). For the case of a semimetal, Fig. 2(d), the plateaus disappear but the AHC remains on the order of e^2/h, especially near avoided crossings. Incidentally, we find a similar behavior for the case of a honeycomb layer of Pb atoms at the same lattice constant in vacuum with a Zeeman field of about 0.5 eV representing the coupling to Mn; such a (hypothetical) system also produces similar flat bands with non-zero Chern numbers.

The Pb honeycomb structure has seven Pb p bands occupied in the tripled unit cell. We can change the doping of the system, modifying this number down to one and up to nine, by scanning through the (Au, Hg, Tl, Pb, Bi) series of heavy elements. We have carried out corresponding DFT calculations of all of these systems, and the results are summarized in Table I. We find that 2/3 ML Au on MnTe with spins along z also produces a Chern insulator with properties similar to that of Pb, except that the Chern number is now C=+1.

Substrate	Surface	Spin direction	C	E_g^{dir} (meV)	E_g^{indir} (meV)
MnTe	**AuAu**	z	1	141	36
MnTe	AuAu	x	m	m	m
MnTe	HgHg	z	0	31	−341
MnTe	TlTl	z	m	m	m
MnTe	**PbPb**	z	−1	126	36
MnTe	PbPb	x	−1	12	−156
MnTe	BiBi	z	m	m	m
MnSe	Pb	z	0	25	24
MnSe	AuAu	z	1	64	−731
MnSe	**PbPb**	z	−1	213	1
MnSe	PbPb	x	−1	12	−103
MnSe	PbBi	z	−2	31	−9
MnSe	**PbPbI**	z	−3	84	56
MnSe	**BiI**	z	1	302	41
MnSe	**BiBr**	z	1	213	142
MnSe	TlI	z	0	5	−53
MnSe	HgSe	z	−1	22	−23
EuS	PbPb	z	−1	91	−48
EuS	AuAu	z	0	188	−251

TABLE I: Chern number (C) and direct (E_g^{dir}) and indirect (E_g^{indir}) gaps for surface adatoms on four layers of magnetic insulator. Surfaces are labeled by number of adatoms per tripled unit cell (e.g., PbPbI consists of 2/3 ML Pb and 1/3 ML I). Chern insulators are in bold. Systems with E_g^{dir} < 2 meV are labeled m ("metallic").

While encouraging, our initial examples of Chern insulators on MnTe have two problems: (i) the band gaps are rather small, and (ii) experimentally the spins of bulk MnTe lie in the xy plane, which we find tends to close the gaps. We address these problems by searching though a variety of structures on EuS and strained MnSe surfaces, which have their spins in the z (surface-normal) direction. We consider tripled surface unit cells decorated with 1-2 heavy adatoms and 0-2 electron-accepting adatoms (S, Se, I, Br), thus allowing us to tune the filling of the surface bands towards potentially Chern-insulating combinations. We perform 51 calculations in our initial search by using slabs of magnetic insulator which are only two layers thick. We find that 30 of these are metallic, 6 because of a near-zero direct gap and 24 because of indirect overlap ($E_g^{indir} < 0$). Of the latter, the Chern number of the gap is non-zero for 14, of which 3 are nearly Chern insulators ($E_g^{indir} > -10$ meV). Of the remaining surfaces, 11 are trivial insulators and 9 are Chern insulators (4 of which, however, have $E_g^{indir} < 10$ meV). Then we

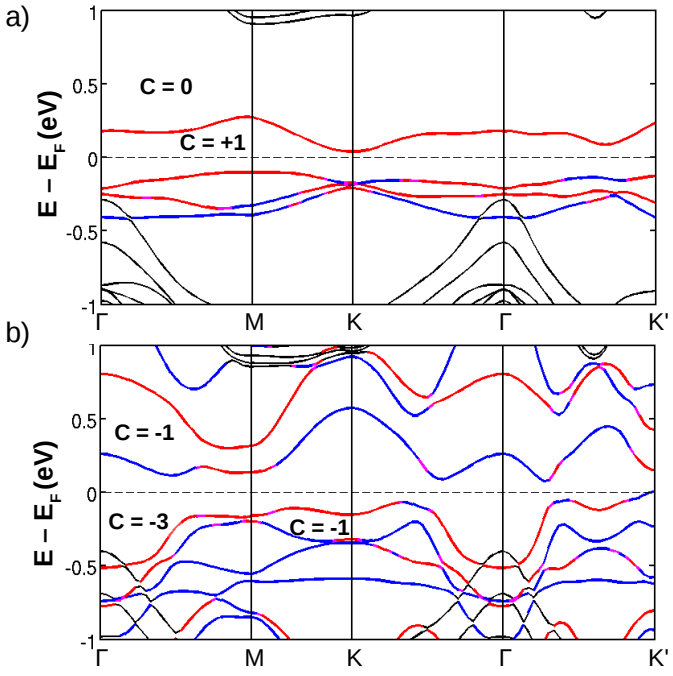

FIG. 3: Band structures of atoms on −2% epitaxially strained MnSe. Top: 1/3 ML Br, 1/3 ML Bi, Bottom: 2/3 ML Pb, 1/3 ML I. Majority spin-up surface bands are in red; majority spin-down surface bands are in blue; bulk-like bands are in thin black lines. Chern numbers near the Fermi level are labeled.

re-calculate several interesting candidate systems using four-layer slabs, usually finding similar surface bands but with modified gaps. The results for some representative cases are presented in Table I. In general, the systems with EuS and MnSe are similar, with both producing many non-zero Chern numbers. On the other hand, fewer of the EuS systems are insulating; we trace this to the reduced overlap between the very localized Eu $4f$-states and the surface adatoms, leading to reduced exchange splittings.

As shown in Table I, we find a variety of materials with non-trivial Chern numbers, including six Chern insulators with indirect gaps ranging from a minuscule 1 meV to a robust 142 meV (BiBr on MnSe). To our knowledge, this is the largest calculated band gap for a theoretically proposed Chern-insulator state. In addition, BiI on MnSe has a direct band gap which never falls below 302 meV, suggesting that there is no fundamental principle which prohibits this search method from producing gaps at least as large as those seen in Bi_2Se_3, the largest-gap topological insulator.

Fig. 3 shows the band structures of two of our largest-gap Chern insulators, 2/3 ML Pb plus 1/3 ML I (PbPbI) and 1/3 ML Bi plus 1/3 ML Br (BiBr) on strained MnSe. These two band structures are typical of these systems, except that these examples have unusually large gaps at the Fermi level. Systems with one heavy atom per tripled unit cell, like BiBr, frequently have flat bands with large gaps; however, many of these gaps are trivial. In contrast, systems with two heavy atoms, like PbPbI, have more non-zero Chern numbers but fewer large gaps; this results from the larger number of dispersive bands around the Fermi level, which leads to more avoided crossings.

While we have not addressed the kinetic or thermodynamic stability of these particular Chern-insulator surface systems under realistic experimental conditions, our strategy of putting heavy atoms on the surfaces of magnetic substrates produces so many non-trivial band structures that it is likely that suitable candidates can be achieved through future collaboration between theory and experiment. In addition, it should be possible to search this class of surfaces experimentally for candidates that are metallic but have a large AHC, on the order of e^2/h as in Fig. 2(d). Since this implies that strong SOC is already generating a non-trivial band structure, one could then attempt to tune these candidates via chemical additions or substitutions, strain, or spin-alignment engineering, in such a way as to arrive at a Chern-insulating state. Undoubtedly, a combined experimental and theoretical search will be the best strategy for arriving at the desired Chern-insulating surfaces.

In summary, we have proposed a search strategy for finding Chern insulators which avoids many of the materials-related difficulties of previous proposals. Our approach is to use magnetically insulating large-gap substrates and decorate their surfaces with elements having large spin-orbit coupling. We have demonstrated the viability of this approach with first-principles calculations, finding a number of Chern insulators with gaps on the order of 50-150 meV, and have discussed the possibilities for the experimental realization of this strategy.

METHODS

Our first-principles plane-wave calculations are carried out in the context of density functional theory (DFT) [21, 22] using the local-density approximation (LDA) [23, 24] and the PBE generalized-gradient approximation (GGA) [25] for calculations on Mn and Eu compounds respectively. We add Hubbard U (DFT+U) [26, 27] corrections to Mn and Eu using literature values (U=5 and 6 eV respectively) which which have been shown to be needed to describe the bulk materials as insulators [28, 29]. We have tested the sensitivity of our results to the choice of U; for variations of 1-2 eV the calculated Chern numbers are constant, but the magnitude of the gaps can change. The calculations are done with two codes: Quantum Espresso [30], using fully-relativistic norm-conserving non-local pseudopotentials from the OPIUM package [31, 32], as well as VASP [33, 34] using PAWs [35, 36] (we find very similar results

with both codes).

Results from both codes are used as input to construct maximally-localized Wannier functions (MLWF) using WANNIER90 [37, 38]. Chern numbers and band gaps are calculated using Wannier interpolation of the band structure; the Chern numbers are computed by sampling a dense k-point grid (from 32×32 to 128×128, if necessary for convergence) and adding up the Berry phases around the loops formed by each set of four adjacent k-points in the Brillouin zone. In addition, we calculate the anomalous Hall conductivity (AHC) for a few examples using a 128×128 k-point grid with the WANNIER90 postprocessing code [39–41].

Acknowledgments

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