A complementary screening for quantum spin Hall insulators in 2D exfoliable materials

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Quantum spin Hall insulators are a class of topological materials that has been extensively studied during the past decade. One of their distinctive features is the presence of a finite band gap in the bulk and gapless, topologically protected edge states that are spin-momentum locked. These materials are characterized by a $Z_2$ topological order where, in the 2D case, a single topological invariant can be even or odd for a trivial or a topological material, respectively. Thanks to their interesting properties, such as the realization of dissipationless spin currents, spin pumping and spin filtering, they are of great interest in the field of electronics, spintronics and quantum computing. In this paper we perform an high-throughput screening of quantum spin Hall insulators starting from a set of 783 two-dimensional exfoliable materials, recently identified from a systematic screening of the ICSD, COD, and MPDS databases. We find a new $Z_2$ topological insulator (Hg$_4$N$_4$S$_4$) as well as 3 already known ones and 7 direct gap metals that have the potential of becoming quantum spin Hall insulators under a reasonable external perturbation.

I. INTRODUCTION

Topological states of matter$^1$ have been one of the main subject of studies for condensed matter physicists in the past decade. One of the driving aspects lies in the robustness of many properties of topological materials, whose existence can be directly related to a specific set of topological invariant.$^{2-4}$ In the case of insulators, the ground state of a topologically trivial material can be connected to the one of an atomic insulator or vacuum by a smooth adiabatic deformation of its Hamiltonian, while for a topologically non-trivial material, this cannot happen without closing a gap in its band structure. Among the possible classifications of topological insulators, quantum spin Hall insulators (QSHIs) represent a class of materials protected by time-reversal (TR) symmetry where the quantum spin Hall effect (QSHE) can be realized. This is made possible by the presence of a finite bulk gap and spin-polarized gapless helical hedge states$^5$ that can sustain dissipationless spin currents,$^6$ thanks to the absence of backscattering forbidden by TR. Other interesting properties arise from spin-momentum locking$^7$, which allows for the possibility to realize spin filtering$^8$, injection, detection$^9$ and pumping$^{10}$, all of which make QSHIs of great interest for the realization of spintronic devices. It has also been shown that magnetic confinement can be used in order to realize qubits on the surface of a QSHI$^{11}$, making these materials promising for applications in quantum computing.

QSHIs can be identified through a $Z_2$ invariant which can be either even (0) or odd (1), as first proposed by Kane and Mele, that showed that a Dirac cone, with a gap opened by spin-orbit coupling (SOC) can lead to a topologically non-trivial order.$^{12,13}$ This concept has later been extended as, in general, a QSHI can be obtained whenever a band inversion takes place, as in the paradigmatic cases of, e.g., HgTe quantum dots$^{14,15}$ and Bi$_{1-x}$Sb$_x$. A non-trivial $Z_2$ invariant can emerge naturally due to the material intrinsic band structure, or can be induced by a perturbation, such as the application of strain or electric fields or the interaction with a substrate.$^{16}$ Hence, a trivial insulator can be driven into a topological insulator and vice-versa, leaving open the possibility to realize a topological transistor.$^{16}$ While for two-dimensional (2D) materials a single invariant is sufficient in order to describe their topology with respect to the QSHE, it has been shown that for three-dimensional (3D) materials a set of 4 invariants is required, leading to the possibility of weak or strong $Z_2$ topological insulator.$^{20}$ It has also been shown that the topology of a system can often be related to its symmetry.$^{21}$ For example, in the case of QSHIs with inversion symmetry, the $Z_2$ topological invariant can be computed easily by calculating the eigenvalues of the parity operator at the time-reversal invariant momenta (TRIM) points of the Brillouin zone (BZ)$^{21}$.

In this work we perform a complementary screening to that of Marrazzo et al.$^{22}$ by using a set of newly discovered 2D materials from Ref$^{23}$ in which 1205 new monolayers, exfoliable from their layered (typically van-der-Waals bonded) parents, have been added to the initial 2D portfolio$^{24}$ used in Ref$^{23}$. We set out with this, the aim of identifying all the 2D $Z_2$ topological insulators present in this set, analyzing all the materials with less than 40 atoms per unit cell, with the exception of lanthanides due to their typically complex, correlated electronic structure$^{25}$. We also identify direct gap metals (DGMs) which can serve as $Z_2$ candidates, by calculating the invariant for materials where the valence and conduction band manifolds are separated by a direct gap (DG), but where the indirect gap (IG) is negative.
II. METHODS

All the density-functional theory (DFT) calculations performed in this work use the Quantum ESPRESSO (QE)\textsuperscript{20,27} distribution. We perform fully relativistic calculations with SOC, using the Perdew, Burke and Ernzerhof (PBE) pseudopotential\textsuperscript{22} from the ONCVPS\textsuperscript{2} (v0.4) set\textsuperscript{22} contained in the PseudoDojo library\textsuperscript{22}. For every calculation we use a kinetic cutoff, high enough to ensure that the uncertainty on the energy eigenvalues is lower than 5 meV. In order to properly account for low-gap and metallic systems, a Fermi-Dirac smearing of 5 meV is used. For the initial self consistent calculations we use a k-point mesh of density $0.2\AA^{-1}$, which is refined to $0.1\AA^{-1}$ for QSHI. All the calculations have been performed assuming a non-magnetic ground state. Magnetism has been later checked for the selected candidates following the same approach used in Ref\textsuperscript{23}.

The topological invariant are computed either from an analysis of the band structures at the TRIM points or using the Z2Pack package\textsuperscript{31}, for which we set the maximum number of kpoints per line to 200, and the lowest acceptable distance between lines to $10^{-7}$. The threshold on the hybrid Wannier charge centers (HWCC)\textsuperscript{32} position variation per step on a line (pos\_tol) is set to 0.01, the threshold on the relative movement of the HWCCs position between neighboring (move\_tol) to 0.3 and the threshold for the distance between the middle of the largest gap in a line and the position of the neighboring HWCC (gap\_tol) to 0.3.

A. Screening procedure

The original set of material of which we explore the properties is derived from the ICSD\textsuperscript{33,34} and COD\textsuperscript{35} databases, by identifying 2D exfoliatable materials, starting from experimentally known bulk structures using vdW DF2-C09 DFT calculations\textsuperscript{24}. First we exclude all materials containing lanthanides, due to the inaccuracy of DFT pertaining calculations with these atoms caused by the presence of strongly correlated electrons\textsuperscript{25}. For the remaining 603 materials, compared to the 1306 structures studied in Ref\textsuperscript{22} by Marrazzo et al, we follow two strategies for the identification of QSHI in order to minimize the usage of computational resources. For the ones with inversion symmetry we use the formula given by Fu and Kane\textsuperscript{14}:

$$ (-1)^{\nu} = \prod \delta_i, \quad \delta_i = \prod_{m=1}^{N} \xi_{2m}(\Gamma_i) \quad (1) $$

where $\nu$ is the $\mathbb{Z}_2$ topological invariant, $\xi_{2m}$ is the eigenvalue of the parity operator calculated for a couple of TR-paired bands and $\Gamma_i$ are the TRIM points, of which there are 4 for a 2D material, defined as

$$ \Gamma_i = ^{-1}G + G \quad (2) $$

with $G$ being any reciprocal lattice vector. For a 2D material, 4 TRIM points can be found at the coordinates $(0,0)$, $(0,0.5)$, $(0.5,0)$ and $(0.5,0.5)$ expressed in units of the reciprocal lattice vector. Given the formula in eq. (1), the most computationally efficient route for materials that have inversion symmetry is to calculate first the band structure at the TRIM points to determine the topological invariants. Materials with $\nu = 0$ are discarded, while for those with $\nu = 1$ we proceed with a band structure calculation along the high-symmetry lines. The result can either be a material with finite DG on the entire k-point path, or with a zero DG. The latter is discarded as a metal-semimetal, while the former can either be a QSHI if the IG, defined as the difference between the minimum of the conduction band and the maximum of the valence band, is positive, or a DGM if the IG is negative. We discard materials that are DGM with an IG lower than -0.15 eV, as attempting to drive such a material to a topological phase would be hardly feasible.

If inversion symmetry is not present, we follow a different route, by determining the DG and IG first through a band structure calculation and discarding the metals and semimetals without a finite DG. We then use the Z2Pack package, which tracks the positions of one-dimensional HWCCs across half of the BZ, in order to compute the topological invariant\textsuperscript{31}. The package acts as an automation tool, which interfaces a DFT code (QE in our case) with Wannier90\textsuperscript{38} in order to calculate the HWCC positions on a progressively denser grid of k-points. If one of the convergence criteria of Z2Pack, with the parameters mentioned before, is not satisfied, then the material is discarded. If the results of the calculation is a non trivial topological invariant, the material is then classified as a QSHI or DGM following the same criteria mentioned for the inversion-symmetric cases.

Finally, for the selected candidates we assess the dynamical stability by computing the full phonon dispersion by means of density-functional perturbation theory\textsuperscript{29} and we check the non-magnetic ground state assumption comparing the energy of the non-magnetic ground state with different possible ferromagnetic, antiferromagnetic and ferrimagnetic configurations following the same procedure adopted in Ref\textsuperscript{24}. A flowchart describing the entire high-throughput calculation is shown in Fig. 1. The entire process has been automated using AiiDA\textsuperscript{22} to keep track of the provenance at every computational step. The data produced in this work, including both the results and the entire provenance tree, has been made available on the Materials Cloud as Ref. \textsuperscript{42}.

III. RESULTS AND DISCUSSIONS

We start our screening from a set of 783 2D exfoliatable structures taken from Ref\textsuperscript{23} which are reduced to 603 after removing materials containing lanthanides.
FIG. 1: Workflow adopted for the high-throughput screening of the QSHIs. Starting from 783 structures presented in Ref 23, we proceed to a study of the $Z_2$ topological invariant following two branches, depending on the presence of inversion symmetry in the material. The steps in both branches are organized as to limit the usage of resources, by performing the lowest cost screenings first in each branch. The set is further divided in two groups of 260/342 structures with/without inversion symmetry. For the inversion symmetric materials, we compute the eigenvalues of the parity operator $\xi_{2m}$, the calculation of which can sometimes fail due to limitations in the code to handle non-symmorphic space groups, or due to the accuracy threshold imposed for the calculation of the trace of the representation for each group of bands. 78 out of these 260 TRIM point calculation failed and were hence recalculated using Z2pack. Of the 182 successful calculations, 27 resulted in a non trivial topological invariant $\nu = 1$. We then performed a band structure calculations along the high-symmetry path, from which we excluded 22 metallic materials and identified 1 QSHI (Br$_2$Hf$_2$) and 4 direct gap metals (DGMs).

On the 343+78 remaining structures (the non-inversion symmetric ones and those with failed parity calculations), the band structure calculations show that 207 materials have a DG greater than 0: for them we proceed with Z2Pack calculations that identify, 3 QSHIs (Zr$_2$Te$_{10}$, Hf$_4$N$_8$S$_4$, Hf$_2$Te$_{10}$) and 3 DGMs. The summary of the data for every material is reported in Table I while a more detailed report is given in the supplementary materials, together with the crystal structure and band structure of the material identified and a plot of the HWCC for every Z2Pack calculation.

A summary for all the materials analyzed in the present work, together with those of the previous screening by Marrazzo et al (in absence of strain), is shown in Fig. 2, where the QSHIs are highlighted. In the figure, all materials with a negative IG have been put on the $y = 0$ axis in order to emphasize QSHIs and DGMs, especially with regard to the magnitude of the DG and IG, as these two parameters can be used to determine the range of temperatures at which a device could operate.

The interest in DGMs with a non trivial $\nu$ is twofold. First it is possible that, given the limitations of DFT-PBE calculations, the band gap of the material is being underestimated and, using more appropriate methods (such as many-body perturbation theory in the GW approximation), a material that was computed to be a DGM with DFT-PBE could actually result to be a QSHI. It is worth highlighting that the opposite could also be possible, where a material that is estimated to be a QSHI within DFT-PBE could end up being a trivial insulator in a GW calculation (as discussed for the case of TiNI in Ref 22). Second, a DGM could be driven into a $Z_2$ topological state through an external perturbation that could open a gap in the material without driving a band inversion. To this end, it is important to look at both the IG and DG of the material. The former is related to how strong a perturbation needs to be in order to drive the material in a semiconducting state, while the latter gives us an idea of how likely it is that a gap could be opened, without causing band inversion, or driving the material into a metallic state. Indeed, the higher the DG of a material, the more difficult it will be to close it. For this reason, DGMs with small negative IG and large DG are prime candidates for further studies; a visual summary of the direct and indirect gap of the DGMs is shown in Fig. 3. Among the various possible perturbations that could open the gap, the most interesting ones, from the standpoint of applications in a device, would be gating/electric fields, the interaction with a substrate, and/or the application of strain.

For all the materials found, we searched the current literature to determine which QSHIs were already known, and which one are novel to this study. We find that among the 4 QSHIs identified, 3 were already known, namely the two tellurides of hafnium/zirconium, and hafnium bromide. Br$_2$Hf$_2$ was already known both for being an easily exfoliable material and for its topological properties in its 2D and 3D forms. This material has a DG of 233 meV and an IG of 48 meV making it a good candidate for experiments and possible device realization. It should also be noted that this material be-
FIG. 2: Plot of the direct (color scale) and indirect (y-axis) band gaps in the presence of SOC for all the material screened in the current work (circles) and in the previous work of Marrazzo et al.\textsuperscript{22} (squares). Materials with negative IGs have been given a zero value. The DG for each material is given using the color scale on the right. QSHIs identified by the present screening effort and that of Ref.\textsuperscript{22} are highlighted using a blue contour to the circle/squares. Materials already known in the literature are also highlighted with a cross mark.

longs to a broader class of transition-metal halides MX (M=Zr,Hf X=Cl,Br) which has already been predicted to host topological properties. Furthermore, several class of similar honeycomb materials have also been predicted to host topological states such as transition metal carbides MC (M=Ti, Zr, Hf)\textsuperscript{60} and transition metal compounds MM’ (M=Ti, Zr, Hf) (M’=Bi, Sb)\textsuperscript{51}.

Hf\textsubscript{2}Te\textsubscript{10} (Zr\textsubscript{2}Te\textsubscript{10})\textsuperscript{52} are two pentatellurides both of which have large DGs of 300(281) meV and IGs of 171(220) meV making them both very good candidates for QSHIs applications at room temperature. Interestingly, the inversion in these materials has been shown to be due to the non-symmorphic space group and not to SOC, the effect of which is only to open a gap in a band structure that would be metallic in a non “fully-relativistic” calculation. These pentatellurides have also been proposed for the realization of the quantum anomalous Hall effect, when the transition metal Hf/Zr is substituted for a rare earth metal which could induce a magnetic ordering in the material, breaking time-reversal symmetry\textsuperscript{52,53}.

Hg\textsubscript{4}N\textsubscript{4}S\textsubscript{4} is a new compound which has not been discussed in the literature for its topological properties. Its direct and indirect gaps are both of 7 meV. Such low gap, in between that of silicene (1.4 meV) and germanene (23.8 meV) precludes room temperature applications. Nevertheless, at the gap, situated along the Γ – Y direction, the material shows a linear band dispersion akin to that of germanene at K when SOC is taken into account. The similarity between the two systems, opens the possibility for a plethora of studies, such as the effect of an electric field on the gap and band inversion\textsuperscript{16,17} or the possibilities for opto-electronic applications in THz devices\textsuperscript{54}.

Among the DGMs, the most promising ones are Fe\textsubscript{3}O\textsubscript{6} and Mo\textsubscript{2}O\textsubscript{17}Ta\textsubscript{3}, with small IGs of -21 and -36 meV respectively. The small negative IGs indicate that it could be feasible to force those from being DGM to a QSHI by acting via strain, electric field or other perturbations. There is also Cl\textsubscript{2}Hf\textsubscript{2} which, like Br\textsubscript{2}Hf\textsubscript{2}, is a transition
FIG. 3: Plot of the direct and indirect band gaps of the DGMs identified. The criteria used are that the material has to exhibit DG > 0 (which allows for the calculation of \( Z_2 \) on an isolated manifold) and a negative IG < 300 meV. These materials would become QSHIs in the presence of perturbations such as strain, substrate interactions or an electric field capable of opening the IG without causing a band inversion.

IV. CONCLUSIONS

We performed a systematic high-throughput study of 2D exfoliable materials in order identify novel QSHIs. Starting from a set of 783 materials we found 4 QSHIs and 7 DGMs that could be driven into a QSHI state by material engineering. Of the 4 QSHIs identified, the 3 with the largest gaps had already been explored in the literature. In particular, the two pentatellurides \( \text{Hf}_2\text{Te}_{10} \) and \( \text{Zr}_2\text{Te}_{10} \) exhibit both large direct and indirect gaps which makes them promising candidates for room-temperature applications. The remaining material, namely \( \text{Hg}_4\text{N}_4\text{S}_4 \), represents a newly identified QSHI with linear bands in proximity of its direct gap of 7 meV. The main feature of this material is the small gap and band linearity, akin to that of silicene or germanene. For this reason, \( \text{Hg}_4\text{N}_4\text{S}_4 \) could be a promising candidate for future electronic and photonic applications in the low energy regime.

All materials identified in this work are easily exfoliable, with a binding energy lower than 20 meV/\( \text{Å}^2 \) and for this reason they are prime candidates for possible experimental realization through exfoliation techniques starting from their experimentally known 3D bulk form.

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TABLE I: Table containing a collection of direct (DG) and indirect (IG) band gaps, binding energies ($E_B$) and previous literature references for the QSHIs and DGMs identified. In light gray, those in the previous work by Marrazzo et al.\cite{22} (in absence of strain).

| Formula   | DG (meV) | IG (meV) | $E_B$ (meV) | Ref. |
|-----------|----------|----------|-------------|------|
| Br$_2$Hf$_2$ | 233      | 48       | 15.8        | 48,49 |
| Hf$_2$Te$_{10}$ | 299     | 171      | 16.5        | 52   |
| Hg$_3$N$_4$S$_4$ | 7       | 7        | 19.4        |      |
| Zr$_2$Te$_{10}$ | 281     | 220      | 19.4        | 52   |
| Pt$_2$HgSe$_3$ | 178     | 142      | 60.2        | 55   |
| RhTa$_3$Te$_4$ | 67       | 67       | 26.4        | 56   |
| AsCuLi$_2$ | 65       | 58       | 62.7        |      |
| TiCu$_2$Te$_3$ | 6       | 5        | 44.0        |      |
| IrNbTe$_4$ | 40       | 37       | 27.1        |      |
| Bi          | 656      | 578      | 17.9        | 24   |
| TiNI        | 20       | 20       | 14.6        | 57   |
| In$_2$ZnS$_4$ | 7       | 5        | 36.1        |      |
| TaIrTe$_4$ | 15       | 15       | 25.8        | 56   |
| BaCr$_2$N$_2$O$_8$ | 19     | -124     | 11.0        |      |
| Br$_5$V$_2$ | 33       | -99      | 15.1        |      |
| C$_2$H$_6$Fe$_2$O$_8$P$_2$ | 11      | -58      | 18.8        |      |
| Cl$_2$Hf$_2$ | 264     | -166     | 14.8        | 55   |
| Fe$_4$O$_8$ | 17       | -21      | 6.4         |      |
| I$_4$Mo$_2$S$_4$ | 47     | -117     | 14.4        |      |
| Mo$_2$O$_{17}$Ta$_2$ | 17  | -36      | 10.0        |      |
| WTe$_2$     | 738      | 738      | 24.7        | 19,24 |
| MoTe$_2$    | 107      | -259     | 24.5        | 19,24 |
| ZrBr        | 45       | -19      | 15.6        | 58   |
| ZrCl        | 64       | -196     | 14.7        | 58   |