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False-positive and false-negative assignments of topological insulators in density functional theory and hybrids

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Density-functional theory (DFT) approaches have been used recently to judge the topological order of various materials despite DFT's well-known band-gap underestimation. Use of the more accurate quasi-particle GW approach reveals few cases where DFT identifications are false positive, which can possibly misguide experimental searches for materials that are topological insulators (TIs) in DFT but not expected to be TIs in reality. We also present the case of false positives due to the incorrect choice of crystal structures and address the relevance of choice of crystal structure with respect to the ground-state one and thermodynamical instability with respect to binary competing phases. We conclude that it is necessary to consider both the correct ground-state crystal structure and the correct Hamiltonian in order to predict new TIs.

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Three-dimensional (3D) bulk topological insulators (TIs) have a band inversion, i.e., the s-like conduction band below the (p,d)-like valence band at the time reversal invariant momentum such as Γ. This order of bands is defined through the inversion energy $\Delta_i = \varepsilon_s - \varepsilon_{p,d}$ being negative (see Fig. 1). Specifically, for normal insulators such as CdTe, Δ_i is positive, while for topological insulators such as HgTe, Δ_i is negative. The excitation gap defined as the energy difference between the highest occupied state and the lowest unoccupied state can be either zero [Fig. 1(b)] or positive [Fig. 1(c)] even in TIs. When one truncates a 3D bulk TI to create a two-dimensional (2D) surface or interface, new states will appear inside the 2D excitation band gap: These will have linear dispersion ("massless fermions") crossing each other ("gapless") within the 2D excitation gap and will maintain spin polarization without net charge current.

Interest in their exotic properties has motivated recent search and discovery efforts for materials that would be topological insulators.[1–8] Theory predicts interesting cases expected to be TIs, and pleas are then made to experimentalists to make and probe such materials in the laboratory. As exciting as such a close level of theory-experiment interaction is, there are two potential issues that can impede progress. First, most of these calculations rely on density functional theory (DFT) or variants of it,[1–8] yet these methods are known to systematically underestimate band gaps specifically by placing the conduction band too low and the valence band too high, thereby creating the potential for "false positives" that predict a material to be a TI in DFT when it is not in reality, to the detriment of experiment-theory interaction. Second, sometimes[1–8] theoretical predictions of negative inversion energy Δ_i are conducted on *assumed* crystal structures of given candidate materials; in some cases those assumed structures are energetically quite far from the ground-state structure. This results in predicting an exciting property (e.g., TI) in unrealizable structures: We present here a case where the assumed crystal structure makes the compound thermodynamically unstable with respect to dissociation in competing binary phases.

In this Rapid Communication, we revisit the topological order of several families of materials previously predicted to be TIs within DFT, but now we (i) use improved approximations for the electronic levels GW and (ii) insist on calculating topological order in structures that are ground states or very close to it. The group of materials we study are (a) binary compounds InAs and HgTe, (b) half-Heusler compounds ABX [A = (Y, Lu), B = (Pt, Pd), and X = (Sb, Bi)],[1,2] (c) antiperovskite nitride $(\mathrm{M})_3\mathrm{BiN}$ [(M = Ca, Sr, Ba)],[6] and (d) honeycomb-lattice chalcogenides LiAgSe and NaAgSe.[7] We first describe the method we used based on quasiparticle self-consistent GW. Then, we present a list of false-positive cases due to DFT and as false positives due to the wrong crystal structure. Finally, we assess the potential of the recently used[9] screened hybrid functional, namely HSE06,[10] with respect to both DFT and GW methods.

Methods. Contrary to DFT, quasi-particle (QP) energies can be compared directly with experimental results. Also, GW does not suffer from self-interaction error and is orbital dependent,[11] which are two factors essential for excitation-gap prediction. Out of the many flavors of GW available, we employ the fully self-consistent (sc) version of GW.[12] The need for self-consistence is obvious in the case of a topological insulator: Usually GW is employed within the so-called $\mathrm{G}_0\mathrm{W}_0$ approximation, which is a perturbative correction to energies obtained from a mean-field Hamiltonian (usually DFT). However, such approximation assumes implicitly that the mean-field Hamiltonian could describe the system of interest accurately enough so that its energies are considered to be good approximations of quasiparticle energies.[13] DFT's dramatic underestimation of band gaps could result in metallic band structure within DFT for narrow-band-gap semiconductors. Therefore, $\mathrm{G}_0\mathrm{W}_0$ is not effective in such cases, and one need to self-consistently update both QP energies and wave functions in the GW Hamiltonian. Furthermore, spin orbit splittings calculated using norm-conserving relativistic pseudopotentials[14] were added to the GW quasiparticle energies as a first-order perturbation. All GW calculations were performed using the crystal structure relaxed within generalized gradient approximation (GGA).

False-positive predictions of topological characteristics due to DFT. Calculated DFT and sc-GW inversion energies

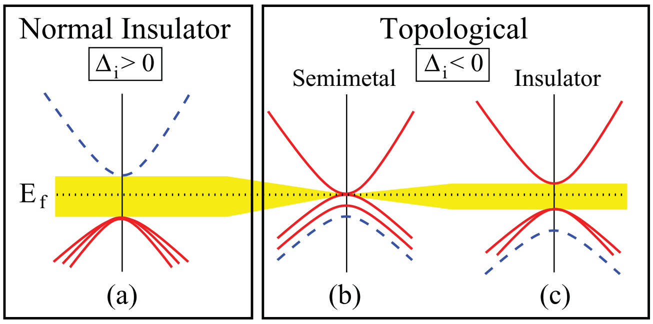

FIG. 1. (Color online) Schematic of the band ordering at the vicinity of Fermi level for (a) normal insulator, (b) topological semimetal insulator, and (c) topological insulator. Red solid lines represent p,d-like bands while blue dashed line represents s-like band.

for previously proposed TI materials are given in Table I, together with their topological designation.

InAs and HgTe. InAs is a narrow-excitation-gap normal semiconductor with $\Delta_i^{\text{Expt.}} = 0.43$ eV. Sc-GW reproduces it well (see Table I), while DFT predicts a negative inversion energy and consequently identify it incorrectly as a TI. Therefore, the assignment of topological order to InAs within DFT is considered a *false positive* and is due to the strong underestimation of the band gap in DFT. In the case of HgTe, both $\Delta_i^{\text{sc-GW}}$ and Δ_i^{DFT} are negative, making HgTe a topological insulator, which is in agreement with experimental findings. Only sc-GW is able to qualitatively and quantitatively reproduce experimental inversion energy and excitation gap for both HgTe and InAs.

The filled tetrahedral structures (FTSs). ABX with A = (Y, Lu); B = (Pd, Pt), and X = (Sb, Bi) crystallize in a structure based on the zinc-blend lattice, which has a fourfold coordinated cation at position $T_1 = (0,0,0)$ and a fourfold coordinated anion at $T_2 = (\frac{1}{4},\frac{1}{4},\frac{1}{4})$. Whereas in the zinc-blende lattice, the two tetrahedral intersitial sites—IT_1 at $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ coordinated by four T_2 anions, and IT_2 at $(\frac{3}{4},\frac{3}{4},\frac{3}{4})$ coordinated by four T_1 cations—are empty, the FTSs are based on stuffing an additional atom either at IT_1 (called α-type FTSs[15,16]) or at IT_2 (β-type FTSs[15,16]). We study both types. We found twice as many false positives in the α type as in the β type. Such difference can be attributed to the localization of the valence band maximum (VBM) wave function: in the α type, VBM is formed by nonbonding states, highly localized around atoms, while in the β type, VBM is formed by more delocalized bonding states. As a result, α-type FTSs suffer more from DFT-induced self-interaction error.[17] VBM is predicted to lie too high in energy within DFT, closing the band gap and in some extreme cases inverting the order of the bands around the Fermi level and therefore incorrectly assigning it to be a TI.

TABLE I. Calculated DFT and GW inversion energies Δ_i, and topological class (T, topological; N, normal) for InAs, HgTe, (α-,β-) (Y, Lu) (Pd, Pt) (Sb, Bi), (Li, Na) AgSe in the assumed ZrBeSi-type structure and their ground-state structure.

	Inversion energy (eV)		Topological status	
Material (structure)	DFT	sc-GW	DFT	sc-GW
InAs (zb)	−0.6	0.65	T	N
HgTe (zb)	−1.1	−0.26	T	T
LuPtSb (β-FTS)[a]	−0.21	1.04	T	N
YPdBi (β-FTS)[a]	−0.09	0.5	T	N
LuPtSb (α-FTS)	−0.65	0.45	T	N
LuPdBi (α-FTS)	−0.27	0.52	T	N
YPtSb (α-FTS)	−0.5	0.45	T	N
YPdBi (α-FTS)	−0.1	0.45	T	N
LiAgSe [Fig. 2(a)][b]	−0.17	1.3	T	N
LiAgSe [Fig. 2(b)][a]	0.4	1.9	N	N
NaAgSe [Fig. 2(a)][c]	−0.23	0.8	T	N
NaAgSe [Fig. 2(c)][a]	∼ 0.0	0.75	N	N

[a] Calculated ground-state structure.
[b] Excited-state structure 0.085 eV/atom higher.
[c] Excited-state structure 0.05 eV/atom higher.

Strained antiperovskite nitrides M_3BiN (M = Ca, Sr, and Ba). The materials belonging to this family are said to be topological insulators under strain (but not when strain free). According to DFT calculations, unstrained M_3BiN (M = Ca, Sr, and Ba) antiperovskites have a small energy gap between low-lying unoccupied s states of Bi and occupied p states of Bi (defined as the inversion energy Δ_i), prompting the suggestion[6] that application of external strain can drive such small-gap systems to have TI-like negative inversion energy. Band gaps obtained within sc-GW for unstrained bulk are in good agreement with experimental data when available.[18] Such a GW calculation for M_3BiN (M = Ca, Sr, and Ba) showed that the energy separation between p-like valence states and s-like conduction states significantly increases from $\Delta_i^{\text{DFT}} = 0.65$ eV to $\Delta_i^{\text{sc-GW}} = 1.85$ eV for Ca_3BiN, from $\Delta_i^{\text{DFT}} = 0.26$ eV to $\Delta_i^{\text{sc-GW}} = 1.55$ eV for Sr_3BiN, and from $\Delta_i^{\text{DFT}} = 1.08$ eV to $\Delta_i^{\text{sc-GW}} = 1.79$ eV for Ba_3BiN, making gap closure by strain extremely unlikely. Therefore, strained $(Ca,Sr,Ba)_3BiN$ is probably *false positive*.

False positive due to the wrong choice of crystal structure. LiAgSe and NaAgSe in the assumed honeycomb-lattice [ZrBeSi-type structure; see Fig. 2(a)] are one of the few DFT-predicted TI materials with light elements ($Z < 50$). The VBM is formed by p-d hybridized states from Se and Ag, while the conduction band minimum (CBM) is exclusively s-like. Within DFT, LiAgSe in the ZrBeSi structure has a negative inversion energy at Γ while NaAgSe in the same structure presents an odd number of negative inversion energies at Γ, A, and L, which makes both of them TIs[7] within such

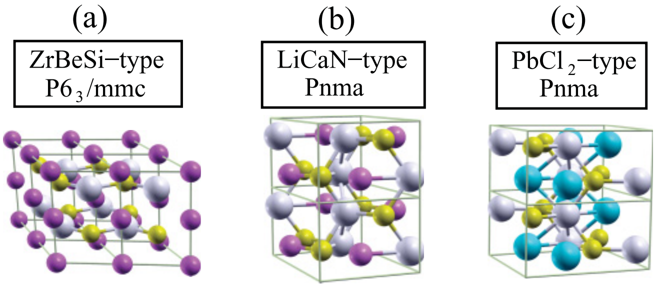

FIG. 2. (Color online) Structure type for (a) ZrBeSi type, (b) LiCaN type, and (c) $PbCl_2$ type.

TABLE II. Calculated DFT, HSE06, and GW inversion energies Δ_i and topological class (T, topological; N, normal) for CuTl(S,Se)$_2$. CH stands for chalcopyrite.

	Inversion energy (eV)			Topological status		
Material (structure)	DFT	HSE06	sc-GW	DFT	HSE06	sc-GW
CuTlS$_2$ (CH)	−0.77	0.06	−0.41	T	N	T
CuTlSe$_2$ (CH)	−1.0	−0.4	−0.85	T	T	T

crystal structure and DFT. Within sc-GW, none of the negative inversion energies are observed, leading to the conclusion that NaAgSe and LiAgSe are normal insulators in the ZrBeSi structure (see Table I for values of inversion energy at Γ). This is similar to the false positive due to DFT presented in the previous section.

Unfortunately, the ZrBeSi-type structure assumed for (Li,Na)AgSe in Ref. 7 is not the ground-state structure. According to our total energy calculations performed on more than 50 potential crystal structures, LiAgSe crystallizes in a LiCaN structure [Fig. 2(b)] (0.085 eV/atom lower than the ZrBeSi type), and NaAgSe crystallizes in the PbCl$_2$-type structure [Fig. 2(c)] (0.05 eV/atom lower than ZrBeSi type). Moreover, LiAgSe in the ZrBeSi-type structure is unstable with respect to dissociation into Li$_2$Se and Ag$_2$Se. Interestingly, both DFT and sc-GW predict a positive inversion energy for (Li,Na)AgSe in their respective ground-state structure at any **k** point in the Brillouin zone. Therefore, we discover a very special case of *false positive* due to the incorrect choice of ground-state structure, independent of the type of methods used to predict the inversion energies.

Is HSE06 the answer? Recently, Chen *et al.*[9] determined new topological insulators based on screened hybrid functional HSE06,[10] which is known to improve band gaps of solids with respect to DFT.[19] We performed HSE06 calculations for all the materials in Table I, and CuTl(S,Se)$_2$[20] was recently predicted to be a TI.[8] For most compounds, HSE06 gives qualitatively and quantitatively very similar results compared to sc-GW, with a 20% deviation for Δ_i with respect to sc-GW results. However, two problematic cases appear where HSE06 is in qualitative disagreement with both DFT and sc-GW: HgTe, where $\Delta_i^{\mathrm{HSE06}} \approx 0$ and the determination of topological order is then uncertain, and CuTlS$_2$, where $\Delta_i^{\mathrm{HSE06}} > 0$ (see Table II) yet $\Delta_i^{\mathrm{sc-GW}} < 0$. Such *false-negative* cases occur because of the dependence of HSE06 on a fixed mixing parameter for exchange, $a_x = \frac{1}{4}$. The mixing parameter a_x could be linked to inverse dielectric constant in the long-range limit $a_x \approx \frac{1}{\epsilon_\infty}$.[21–23] In the case of HSE06 and HgTe, $a_x = \frac{1}{4}$ and $\epsilon_\infty^{\mathrm{HgTe}} \approx 20.0$.

Conclusion. In conclusion, we revisited some of the numerous theoretical predictions of TI and found that many of them are *false-positive* and *false-negative* cases due to an inadequate use of *ab initio* methods or assumed structure. We use a robust method based on GW in order to avoid false-positive and false-negative results. We address the importance of using both the ground-state structure and the correct Hamiltonian in order to search for new TIs. The failure to do so could result in false predictions and might mislead experimentalists in their effort to grow new TIs.

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[1] S. Chadov, X. Qi, J. Kübler, G. Fecher, C. Felser, and S. Zhang, Nat. Mater. **9**, 541 (2010).

[2] H. Lin, L. Wray, Y. Xia, S. Xu, S. Jia, R. Cava, A. Bansil, and M. Hasan, Nat. Mater. **9**, 546 (2010).

[3] D. Xiao, Y. Yao, W. Feng, J. Wen, W. Zhu, X.-Q. Chen, G. M. Stocks, and Z. Zhang, Phys. Rev. Lett. **105**, 096404 (2010).

[4] W. Feng, D. Xiao, Y. Zhang, and Y. Yao, Phys. Rev. B **82**, 235121 (2010).

[5] W. Al Sawai, H. Lin, R. S. Markiewicz, L. A. Wray, Y. Xia, S.-Y. Xu, M. Z. Hasan, and A. Bansil, Phys. Rev. B **82**, 125208 (2010).

[6] Y. Sun, X.-Q. Chen, S. Yunoki, D. Li, and Y. Li, Phys. Rev. Lett. **105**, 216406 (2010).

[7] H.-J. Zhang, S. Chadov, L. Müchler, B. Yan, X.-L. Qi, J. Kübler, S.-C. Zhang, and C. Felser, Phys. Rev. Lett. **106**, 156402 (2011).

[8] W. Feng, D. Xiao, J. Ding, and Y. Yao, Phys. Rev. Lett. **106**, 016402 (2011).

[9] S. Chen, X. G. Gong, C.-G. Duan, Z.-Q. Zhu, J.-H. Chu, A. Walsh, Y.-G. Yao, J. Ma, and S.-H. Wei, Phys. Rev. B **83**, 245202 (2011).

[10] J. Heyd, G. E. Scuseria, and M. Ernzerhof, J. Chem. Phys. **124**, 219906 (2006).

[11] G. Onida, L. Reining, and A. Rubio, Rev. Mod. Phys. **74**, 601 (2002).

[12] M. van Schilfgaarde, T. Kotani, and S. Faleev, Phys. Rev. Lett. **96**, 226402 (2006).

[13] F. Bruneval, N. Vast, and L. Reining, Phys. Rev. B **74**, 045102 (2006).

[14] C. Hartwigsen, S. Goedecker, and J. Hutter, Phys. Rev. B **58**, 3641 (1998).

[15] D. M. Wood, A. Zunger, and R. de Groot, Phys. Rev. B **31**, 2570 (1985).

[16] S.-H. Wei and A. Zunger, Phys. Rev. Lett. **56**, 528 (1986).

[17] J. P. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981).

[18] M. Chern, D. Vennos, and F. DiSalvo, J. Solid State Chem. **96**, 415 (1992).

[19] J. Paier, M. Marsman, K. Hummer, G. Kresse, I. Gerber, and J. Ángyán, J. Chem. Phys. **124**, 154709 (2006).

[20] Both CuTl(S, Se)$_2$ were found to be TI within sc-GW. However, in order to obtain a qualitative estimation of the inversion energy, we used an HSE06 + G_0W_0 approach, which is known to be equivalent to sc-GW[24] and allows us to treat the metallicity of the band structure.

[21] E. Maksimov, I. Maxin, S. Savrasov, and Y. Uspenski, J. Phys. Condens. Matter **1**, 2493 (1989).

[22] J. Vidal, S. Botti, P. Olsson, J.-F. Guillemoles, and L. Reining, Phys. Rev. Lett. **104**, 056401 (2010).

[23] M. A. L. Marques, J. Vidal, M. J. T. Oliveira, L. Reining, and S. Botti, Phys. Rev. B **83**, 035119 (2011).

[24] F. Fuchs, J. Furthmüller, F. Bechstedt, M. Shishkin, and G. Kresse, Phys. Rev. B **76**, 115109 (2007).