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Quasiparticle effects in the bulk and surface-state bands of Bi_2Se_3 and Bi_2Te_3 topological insulators

Oleg V. Yazyev,[1,2,3] Emmanouil Kioupakis,[4] Joel E. Moore,[1,2] and Steven G. Louie[1,2]
[1]*Department of Physics, University of California, Berkeley, California 94720, USA*
[2]*Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, USA*
[3]*Institute of Theoretical Physics, Ecole Polytechnique Fédérale de Lausanne (EPFL), CH-1015 Lausanne, Switzerland*
[4]*Department of Materials Science and Engineering, University of Michigan, Ann Arbor, Michigan 48109, USA*
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We investigate the bulk band structures and the surface states of Bi_2Se_3 and Bi_2Te_3 topological insulators using first-principles many-body perturbation theory based on the GW approximation. The quasiparticle self-energy corrections introduce significant changes to the bulk band structures, surprisingly leading to a decrease in the direct band gaps in the band-inversion regime as opposed to the usual situation without band inversion. Parametrized "scissors operators" derived from the bulk studies are then used to investigate the electronic structure of slab models which exhibit topologically protected surface states. The introduction of self-energy corrections results in significant shifts of the surface-state Dirac point energies relative to the bulk bands and in enlarged gap openings from the interactions between the surface states across the thin slab, both in agreement with experimental data.

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The recently discovered bulk topological insulators (TIs), a unique class of semiconducting materials characterized by the presence of spin-helical surface states resulting from strong spin-orbit (SO) interactions, have quickly become a subject of intense research.[1] It is believed that TIs are actually not uncommon among the heavy-element materials. Owing to their extraordinary electronic properties, such as the suppression of backscattering and intrinsic spin polarization of the surface-state charge carriers, TIs are expected to find applications in the future, including information technology, spintronics, and quantum computing.

First-principles electronic structure calculations can play an important role in exploring the properties of known TIs as well as in guiding the search of previously unknown materials. The widely used density functional theory (DFT) within the Kohn-Sham formalism, a workhorse first-principles method of condensed-matter physics, has proved its value already in the discovery of "second-generation" bulk TIs, Bi_2Se_3 and Bi_2Te_3.[2,3] A large number of TIs has been predicted using this technique,[4] and some of these predictions have been confirmed experimentally.[5] However, it is broadly recognized that the Kohn-Sham eigenvalues of DFT fail to describe accurately quasiparticle energies and band gaps,[6] the critical properties of TIs. A recent work has highlighted the limitations of the standard DFT approach in describing the topological nature of several borderline compounds.[7] Many-body perturbation theory techniques, such as the GW approximation, greatly improve the accuracy of predicting these excited-state properties.[8,9]

In this Rapid Communication, we investigate the self-energy effects in the quasiparticle bulk band structures and the surface-state dispersion of the reference TIs, Bi_2Se_3 and Bi_2Te_3, by using the first-principles GW method.[9] We find that the effects of quasiparticle corrections on the band structures are substantial, and show unique features resulting from the interplay with SO interactions in the band-inversion regime. By introducing parametrized energy-dependent "scissors operators" based on the bulk calculations, we have extended our study to the electronic structure of slab models. Our application of the proposed technique to slab models which exhibit topologically protected surface states finds significant shifts of the Dirac point energies relative to the bulk bands and larger surface-state gap openings resulting from the interactions between surface states across the slab. The proposed simple corrections basically eliminate the DFT eigenvalue problems and yield agreement with experimental data.

The DFT calculations were performed within the local density approximation (LDA) employing the QUANTUM ESPRESSO package.[10] We used norm-conserving pseudopotentials[11] and a plane-wave kinetic energy cutoff of 35 Ry for the wave functions. The quasiparticle energies were evaluated within the G_0W_0 approximation to the electron self-energy starting from LDA results as a mean-field solution using the approach of Hybertsen and Louie.[9] The static dielectric function was calculated using a plane-wave cutoff of 10 Ry, unoccupied bands up to 5 Ry above the Fermi level, and extended to finite frequencies with the generalized plasmon-pole model. This first-principles GW methodology is implemented in the BERKELEYGW code.[12] Spin-orbit interactions were included on the final stage after the quasiparticle self-energy corrections have been applied to $\mathcal{H}_0(\mathbf{k})$. That is, the SO Hamiltonian matrix $\mathcal{H}_{\mathrm{SO}}(\mathbf{k})$ was evaluated employing an approach described in Ref. 13 in the basis of eigenfunctions of $\mathcal{H}_0(\mathbf{k})$. That is, in the full two-component Hamiltonian

$$\mathcal{H}(\mathbf{k}) = \mathcal{H}_0(\mathbf{k}) + \mathcal{H}_{\mathrm{SO}}(\mathbf{k}), \tag{1}$$

$\mathcal{H}_0(\mathbf{k})$ is a diagonal matrix with matrix elements being either LDA or GW eigenvalues in the absence of SO interactions, while $\mathcal{H}_{\mathrm{SO}}(\mathbf{k})$ introduces off-diagonal matrix elements. The band structures have been obtained by diagonalizing the full Hamiltonian $\mathcal{H}(\mathbf{k})$. Notably, we find that the results obtained using this method are in agreement with an explicit approach in which GW calculations are performed starting from two-component LDA wave functions after SO interactions were taken into account (and thus band inversion is present at the Γ point).[14] We used experimental lattice parameters for both the bulk crystal as well as (111) slab models of different thickness.

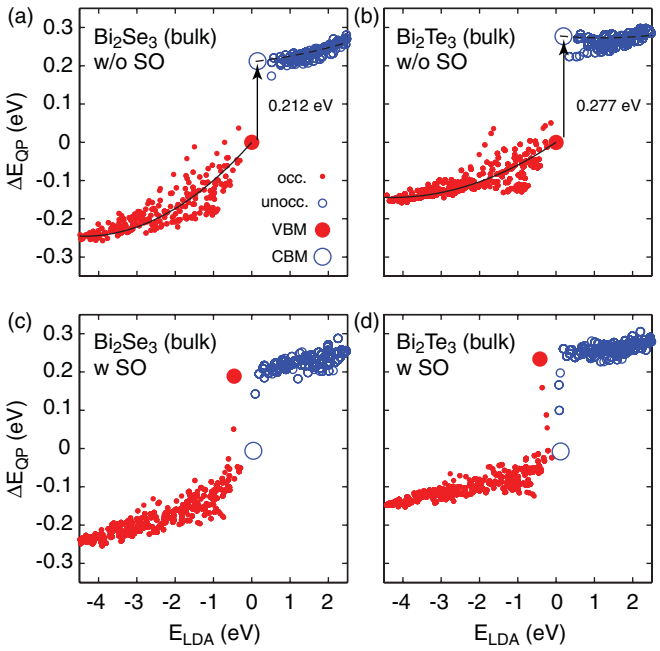

FIG. 1. (Color online) Quasiparticle self-energy corrections as a function of LDA energies for bulk (a) Bi_2Se_3 and (b) Bi_2Te_3 calculated without taking into account SO interactions. The positions of VBM and CBM are indicated by the larger solid and open circles, respectively. The lines correspond to the fitted "scissors operators." (c), (d) Same plots after the SO matrix elements were taken into account. Note the changes in GW corrections calculated for the states which correspond to VBM and CBM in (a) and (b).

We start our discussion by considering the GW quasiparticle energy corrections $\Delta E_{\rm QP}(n,\mathbf{k}) = E_{GW}(n,\mathbf{k}) - E_{\rm LDA}(n,\mathbf{k})$ for bulk Bi_2Se_3 and Bi_2Te_3. Figures 1(a) and 1(b) show $\Delta E_{\rm QP}(n,\mathbf{k})$ evaluated on a $6\times6\times6$ k-point grid as a function of LDA energy with no SO interactions taken into account. For convenience, we set the energies corresponding to the valence-band maximum (VBM) as a reference [i.e., $\Delta E_{\rm QP}({\rm VBM}) = E_{\rm LDA}({\rm VBM}) = 0$ for the case with no SO interactions included]. When SO interactions are neglected both materials are direct band-gap semiconductors with VBM and conduction-band minimum (CBM) located at the Γ point [dotted lines in Figs. 2(a) and 2(b)]. The inclusion of GW self-energy corrections increases the LDA direct gaps at Γ point (which are 0.151 and 0.188 eV for Bi_2Se_3 and Bi_2Te_3, respectively) by 0.212 and 0.277 eV, respectively. After SO interactions have been introduced in both LDA and GW calculations, the values of $\Delta E_{\rm QP}(n,\mathbf{k})$ barely change except for those which correspond to VBM and CBM in Figs. 1(a) and 1(b). These states, shown as large circles in Fig. 1, change their order in energy. The calculations performed using fully two-component implementation of GW (Ref. 14) quantitatively reproduce the overall quasiparticle shifts (≈0.2 eV for Bi_2Se_3) and the peculiar change of the order in energy of VBM and CBM.

The observed seemingly counterintuitive behavior is a direct consequence of band inversion due to SO interactions. It can be illustrated using the $k\cdot p$ Hamiltonian for Bi_2Se_3-type

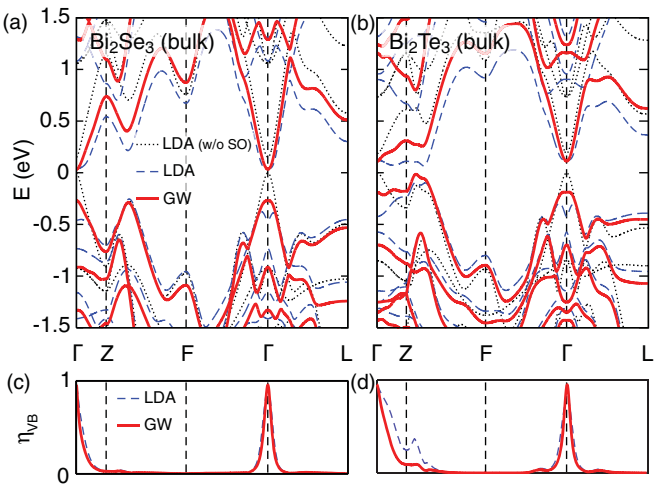

FIG. 2. (Color online) Band structures of bulk (a) Bi_2Se_3 and (b) Bi_2Te_3 calculated using the following theories: LDA with no SO (dotted lines), LDA with SO effects taken into account (dashed lines), and GW with SO interactions (solid lines). (c), (d) Degree of band inversion for the valence band [Eq. (3)] of Bi_2Se_3 and Bi_2Te_3, respectively, calculated along the same k path as in (a) and (b).

materials:[3]

$$\mathcal{H}_{k\cdot p}(k) = \begin{pmatrix} \mathcal{M}(\mathbf{k}) & A_z k_z & 0 & A_{xy}k_- \\ A_z k_z & -\mathcal{M}(\mathbf{k}) & A_{xy}k_- & 0 \\ 0 & A_{xy}k_+ & \mathcal{M}(\mathbf{k}) & -A_z k_z \\ A_{xy}k_+ & 0 & -A_z k_z & -\mathcal{M}(\mathbf{k}) \end{pmatrix} + \epsilon_0(k), \tag{2}$$

with $k_\pm = k_x \pm i k_y$ and $k = |\mathbf{k}|$. Without loss of generality we assume $\mathcal{M}(\mathbf{k}) = -\Delta_{\rm g}/2 - k^2/2m^*$ with a single m^* parametrizing both the valence and conduction bands, $\epsilon_0(k) = 0$, and $A_{xy} = A_z = A$. As the parameter $\Delta_{\rm g}$ decreases, a band inversion takes place around $k = 0$ for $\Delta_{\rm g} < 0$ and the band gap closes in the absence of off-diagonal matrix elements (dotted lines in Fig. 3). However, these off-diagonal SO matrix elements ensure nonzero band gap even in the band-inversion regime. For a small magnitude $\Delta_{\rm g} < 0$ the bands remain parabolic and the gap is $-\Delta_{\rm g}$. A further decrease of $\Delta_{\rm g}$ leads to the "camelback"-shaped bands and the band gap is

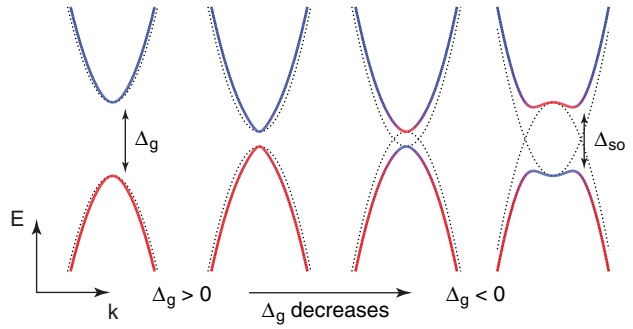

FIG. 3. (Color online) Evolution of the band structure (solid lines) calculated for the model Hamiltonian given by Eq. (2) upon the decrease of parameter $\Delta_{\rm g}$ (see text). Dotted lines represent the solution calculated in the absence of off-diagonal (SO) matrix elements.

$\Delta_{SO} \gtrsim 2Ak$. The "camelback" feature is clearly seen for the valence bands in the LDA band structures of both Bi_2Se_3 and Bi_2Te_3 [dashed lines in Figs. 2(a) and 2(b)]. The physical effect incorporated in the quasiparticle self-energy correction is the increase of Δ_g which is typically underestimated in DFT. Upon an increase of the value Δ_g in the $\Delta_g < 0$ regime, the energy of the valence band at $k = 0$ increases while the energy of the conduction band at $k = 0$ decreases. This behavior has been observed in other band-inversion semiconductors,[15] and is the opposite to the "normal" situation where no band inversion takes place. In other words, the quasiparticle self-energy corrections to the inverted bands reduce the direct Kohn-Sham DFT gap at Γ. This is exactly what is observed in Figs. 1(c) and 1(d) (large symbols) and in Figs. 2(a) and 2(b) at Γ.

The band structures of bulk Bi_2Se_3 and Bi_2Te_3 including both SO interactions and the GW quasiparticle self-energy corrections [solid lines in Figs. 2(a) and 2(b)] have been calculated using the Wannier interpolations technique.[16,17] Interestingly, the LDA band gap of bulk Bi_2Se_3 (0.29 eV) barely changes after the inclusion of GW corrections (0.30 eV). However, its character changes from indirect to direct in agreement with recent experiments.[18] The surprising accuracy of LDA in predicting the magnitude of minimum band gap is fortuitous. In Bi_2Te_3, the LDA and GW indirect band gaps are 0.09 and 0.17 eV,[19] with the latter being in good agreement with experiment.[20] One noticeable effect of the GW corrections on band dispersion is a considerable diminution of the dip in the valence bands at the Γ point. This behavior is also consistent with the discussed two-band model [Eq. (2); Fig. 3].

In order to gain further understanding of the effects of GW corrections we define the degree of band inversion for the valence band,

$$\eta_{VB}(\mathbf{k}) = \sum_{i=\mathrm{VB};\, j\in\mathrm{unocc.}} a^*_{ij}(\mathbf{k}) a_{ij}(\mathbf{k}), \qquad (3)$$

where the eigenfunctions $\psi_i(\mathbf{k}) = \sum_j a_{ij}(\mathbf{k})\phi_j(\mathbf{k})$ of Hamiltonian $\mathcal{H}(\mathbf{k}) = \mathcal{H}_0(\mathbf{k}) + \mathcal{H}_{SO}(\mathbf{k})$ are expressed in terms of $\phi_j(\mathbf{k})$, the eigenfunctions of $\mathcal{H}_0(\mathbf{k})$ which does not include SO interactions. The results for both LDA and GW methods are plotted in Figs. 2(c) and 2(d). For both Bi_2Se_3 and Bi_2Te_3 band inversion takes place only in a limited region of the Brillouin zone around the Γ point where η_{VB} achieves almost 100%. The introduction of GW shifts somewhat reduces the extension of this region of band inversion, but at the Γ point it is still complete. A very similar picture was obtained for the degree of band inversion of the conduction band (not shown).

The crux of our study is, of course, to investigate the effects of GW quasiparticle self-energy corrections on the topological surface states. Addressing this problem in a straightforward way would require performing GW calculations for two-dimensional slab models. At present, it is computationally too demanding to perform converged GW calculations on systems of this size. To overcome this difficulty, we parametrize the quasiparticle corrections ΔE_{QP} in terms of energy-dependent "scissors operators" $\Delta\tilde{E}_{QP} = aE^2_{LDA} + bE_{LDA} + c$ using the results of our GW calculations for bulk materials with no SO interactions included. Valence and conduction bands are fitted separately. Additionally, we require our "scissors operators" to reproduce exactly the quasiparticle shifts of the VBM and CBM, the critical components in our consideration. The fitted functions are shown in Figs. 1(a) an 1(b), and the corresponding parameters are given in Ref. 21.

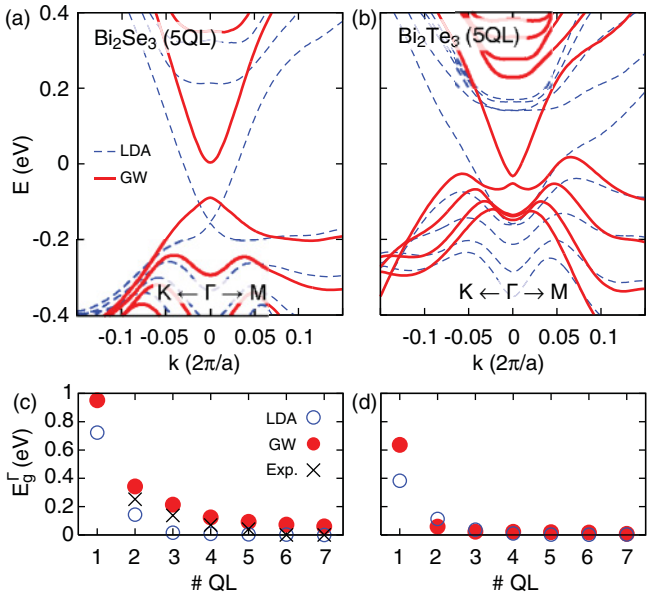

FIG. 4. (Color online) Band structures calculated for 5QL slabs of (a) Bi_2Se_3 and (b) Bi_2Te_3 using LDA and GW (SO interactions included in both cases). (c), (d) Band gaps at the Γ point as a function of slab thickness for Bi_2Se_3 and Bi_2Te_3, respectively. Experimental results are reproduced from Ref. 24. The zero of energy is set at E_{LDA}(VBM) with no SO.

Figures 4(a) and 4(b) show the band structures in the vicinity of the Γ point computed for (111) slabs of five-quintuple-layers (5QL) thickness using plain LDA and after applying the proposed generalized "scissors operator" technique. For the latter, we apply the "scissors operators" to the LDA Hamiltonian without SO interactions in the Bloch-state basis to obtain the quasiparticle Hamiltonian. The SO coupling terms are then added to it and the Hamiltonian is diagonalized to obtain the final quasiparticle energies. Both methods give rise to topologically protected surface states appearing as characteristic "Dirac cone" features at the Γ point but with a gap E_g^Γ owing to the hybridization of the surfaces states at the opposite surfaces of thin slabs.[22,23] The inclusion of quasiparticle corrections results in the following two important changes. First, the magnitudes of E_g^Γ are enlarged, especially in Bi_2Se_3 [Figs. 4(c) and 4(d)]. While LDA predicts essentially zero values of E_g^Γ for slabs thicker than 3QL, the dependence turns into a slow 1/width decay after the "scissors operator" was applied [Fig. 4(c)]. This behavior is actually consistent with the gaps measured in thin films of Bi_2Se_3 on SiC substrate.[24] The experimental magnitudes are somewhat smaller, which can be attributed to enhanced screening due to the presence of the substrate which is neglected in our calculations. The changes of band gaps are less systematic in the case of Bi_2Te_3. For a slab thickness larger than 4QL, the magnitudes of E_g^Γ are larger in the calculations including the quasiparticle corrections. Second, the positions of Dirac points relative to the bulk bands

change significantly. For both materials, the quasiparticle corrections "lift" the Dirac point from the bulk valence band. By extrapolating the results of our calculations on Bi_2Se_3 to the infinite slab thickness, we find that the incorporation of quasiparticle corrections via the "scissors operator" technique changes the position of Dirac point from 0.04 eV *below* the bulk valence band[23] to 0.07 eV *above* it. The latter value is in better agreement with experimental results of Analytis *et al.*: 0.205 eV below the bulk conduction band or 0.095 eV above the bulk valence band assuming a band gap of 0.30 eV.[25] For Bi_2Te_3, the quasiparticle corrections change the Dirac point energy from −0.20 to −0.10 eV relative to the bulk VBM. The experimentally observed value is −0.13 eV.[20] On the contrary, we find that some properties are not affected by the quasiparticle corrections. For instance, the degree of spin polarization of surface states investigated in Ref. 23 change very little.

In conclusion, while the Kohn-Sham DFT band structures are able to provide a qualitative description of the topologically nontrivial electronic structure of Bi_2Se_3 and Bi_2Te_3, a quantitative agreement with a number of experimentally measured properties is achieved only after including the GW quasiparticle self-energy corrections. We further propose an energy-dependent "scissors operator" technique which allows the introduction of parametrized quasiparticle corrections into standard DFT calculations before SO interactions are included, thus greatly enhancing their predictive power in describing systems based on the discussed topological insulators.

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[21] For Bi_2Se_3, valence bands: $a = 0.0128$ eV^{-1}, $b = 0.112$, $c = 0$ eV; conduction bands: $a = 0.0037$ eV^{-1}, $b = 0.011$, $c = 0.233$ eV. For Bi_2Te_3, valence bands: $a = 0.0079$ eV^{-1}, $b = 0.067$, $c = 0$ eV; conduction bands: $a = 0.0039$ eV^{-1}, $b = -0.009$, $c = 0.314$ eV. We recall that $\Delta\tilde{E}_{\rm QP}(\text{VBM}) = \Delta E_{\rm QP}(\text{VBM}) = E_{\rm LDA}(\text{VBM}) = 0$ and $\Delta\tilde{E}_{\rm QP}(\text{CBM}) = \Delta E_{\rm QP}(\text{CBM})$ by convention. Constant energy shifts c are the leading corrections.

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