Correlated Topological Insulators with Mixed Valence

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We propose the local density approximation (LDA)+Gutzwiller method incorporating Green’s function scheme to study the topological physics of correlated materials from the first-principles. Applying this method to typical mixed valence materials SmB$_6$, we found its non-trivial $Z_2$ topology, indicating that SmB$_6$ is a strongly correlated topological insulator (TI). The unique feature of this compound is that its surface states contain three Dirac cones in contrast to most known TIs.

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Most of $Z_2$ topological insulators (TI)\cite{1,2} discovered up to now are semiconductors which are free of strong correlation effects and their topological nature can thus be predicted quite reliably by first principle calculations based on density functional theory (DFT)\cite{3}. The $Z_2$ classification of band insulators has been generalized to interacting systems by looking at its response to external electric magnetic field, namely the topological magneto-electric effect (TME)\cite{4}. A correlated insulator is a TI if the $\theta$-angle defines in TME is $\pi$. Given the TME theory and several simplifications\cite{5}, however, its application to realistic materials is still absent due to: (1) the lack of suitable compounds; (2) the difficulty to compute reliably correlated electronic structures from the first-principles. In this letter, we study a special class of materials, the mixed valence (MV) compounds, which contain rare-earth elements with non-integer chemical valence. By combining the Gutzwiller variational approach from the first-principles and the Green’s function method for the TME, we found SmB$_6$ is a 3D correlated TI. Interestingly, it has three Dirac cones on the surface, in contrast to most of the known TIs.

Classic MV compounds, such as SmB$_6$ and YbB$_{12}$\cite{6}, share the following common features. (i) The x-ray photoelectron spectroscopy (XPS) and X-ray absorption spectra (XAS) contain peaks from both divalent and trivalent multiplets with comparable spectral weight\cite{7,8}, indicating the valence of Sm or Yb to be close to 2.5. (ii) A small semiconducting gap opens at least in part of the Brillouin zone (BZ) at low temperature\cite{9}. Previous electronic structure studies indicate that the electrons transfer from Sm (or Yb) 4$f$ orbitals to 5$d$ orbitals, which leads to fractional occupation in 4$f$ orbitals\cite{10,11}. From the band structure point of view, the electron-transfer between 4$f$ and 5$d$ orbitals indicates possible band inversion between them, which is a crucial ingredient to realize TI (if it happens odd number of times in the entire BZ). At the mean while, SmB$_6$ has been recently suggested to be among the possible candidates of the interesting topological Kondo insulators \cite{12,13}. Although the analytical studies of MV compounds have been conducted by several groups, the reliable first-principle studies, which is crucial to identify the possible topological phases, is still lacking, due to the strong correlation nature of these materials\cite{14,15}. Here we report that the local density approximation (LDA)+Gutzwiller method, a newly developed first-principles tool for correlated electron systems, enables us to search for the topological phases in correlated matters. By taking the MV compound SmB$_6$ as an example, we will focus on two key issues: (i) how to compute $Z_2$ topological index with LDA+Gutzwiller; (ii) what’s the topological nature of SmB$_6$ with the strong correlation effects among the f electrons?

The LDA+Gutzwiller method combines the DFT within LDA with the Gutzwiller type trial wave function, which takes care of the strong atomic features in the ground state. Here we just sketch the most important aspects, and leaving details to reference \cite{16}. We start from the common Hamiltonian (used for most of the LDA++ schemes),

$$H_{Total} = H_{LDA} + H_{int} + H_{DC}$$

where $H_{LDA}$ is the single particle Hamiltonian obtained

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by LDA and $H_{\text{int}}$ is the local interaction term for the 4$f$ electrons described by the Slater integrals $F_0$, $F_2$, $F_4$, $F_6$. In the present study, for Sm atom we choose $F_0=5.8$ eV and $F_2 = 9.89$ eV, $F_4 = 7.08$ eV, $F_6 = 4.99$ eV to be their atomic values. $H_{\text{DC}}$ is the double counting energy representing the interaction energy already considered at the LDA level. In the present paper, we compute the double counting energy using the scheme described in references [26]. We then use the following Gutzwiller trial wave function, $|G\rangle = P_G|0\rangle = \prod_i P_i|0\rangle$, where $|0\rangle$ is a non-interacting state (obtained from LDA), $P_i = \sum_\Gamma \lambda_i^\prime |\Gamma_i\rangle \langle \Gamma_i|$ is the Gutzwiller projector at the $i$-th site with $|\Gamma_i\rangle$ being the atomic eigenstates and $\lambda_i^\prime$ being the variational parameters to be determined by minimizing the ground state total energy (under Gutzwiller approximation)\cite{27, 28}. The linear response theory for the coefficient of TME was developed and simplified by Z. Wang et al.\cite{29}.

The linear response theory for the coefficient of TME has been developed and simplified by Z. Wang et al.\cite{8}. For interacting systems, when the self-energy contains no singularity along the imaginary axis, the formula for the coefficient of TME has been derived:\cite{8}

$$\delta \lambda = \sum_{\mathbf{k}, \omega} \frac{\langle \Gamma | \Sigma | \Gamma \rangle}{\omega - \epsilon_{\Gamma} - \mu_{\Gamma} + i\eta},$$

where the second term describes the incoherent part of the Green’s function, which is ignorable for low frequency. Therefore by applying the Green’s function method described above, we reach the conclusion that the $Z_2$ invariance in LDA+Gutzwiller method is determined by the occupied eigenstates of the Gutzwiller effective Hamiltonian $H_{eff}$, which can be interpreted as the band structure of the “quasi-particles”.

The scheme preserves the nice aspect of variational, however, it is beyond LDA (and also LDA+$U$) because the total energy $E_G$ now relies on the balance between the renormalized kinetic energy of quasi-particle motion and the local interaction energy, which is configuration-dependent. We note that including the complete form of the Slater integrals \((\Gamma)\) in the local interaction is essential to obtain the correct electronic structure for these materials.

The band structure obtained by LDA is shown in Fig 2 (A and B), where we can find three major features. (i) The Sm-4$f$ orbitals, which split into the $j=5/2$ and $j=7/2$ manifolds due to the SOC, form narrow bands respectively with width around 0.5 eV near the Fermi level. (ii) The low energy band structure is semiconductor-like with a minimum gap about 15 meV along the $\Gamma$-$X$ direc-
The first two features of the LDA band structures are not consistent with the experimental observations. Firstly, the XPS measurements find quite strong 4f multiplet peaks, indicating strong atomic nature of 4f electrons in SmB$_6$ (in other words, most of the 4f electrons are not involved in the formation of energy bands). Secondly, both transport and optical measurements reveal the formation of a small gap only for temperature below 50 K. The above two features imply that the f electrons in SmB$_6$ have both localized and itinerant natures and the correct description of its electronic structure should include both of them. The qualititative physical picture can be ascribed to Kondo physics, which involves both itinerant and localized electronic states. At high temperature, these localized orbitals (4f states) are completely decoupled from the itinerant energy bands, forming atomic multiplet states. While in the low temperature, the coherent hybridization between localized and itinerant states is gradually developed leading to the formation of “heavy quasi-particle” bands. The insulating behavior appears when the chemical potential falls into the “hybridization gap” between the heavy quasi-particle and the conduction bands, which is mainly of the 5d orbital character in SmB$_6$.

Such Kondo picture can be nicely captured by our LDA+Gutzwiller calculations, which provide equal-footing descriptions of both the itinerant 5d bands and those heavy quasi-particle states formed by 4f orbitals. The quasi-particle band structures obtained by LDA+Gutzwiller is shown in Fig. 2 (C and D). Compared with the LDA results, there are three major differences induced by the strong correlation effects. (i) The 4f $j=5/2$ orbitals split into two $\Gamma_7^f$ and one $\Gamma_6^f$ bands. The $\Gamma_7^f$ bands cross and hybridize with another $\Gamma_7$ band formed by 5d orbitals. The band width of those “heavy quasi-particle” bands formed by 4f orbitals is the important consequence of the hybridization gap, which is around 10 meV now. We note that in contrast to the LDA results, the semiconductor gap obtained by LDA+Gutzwiller is indirect, which is quite consistent with the transport measurements.

We would emphasize that by LDA+Gutzwiller, we can only obtain the quasi-particle part in the spectral function, but not the Hubbard bands containing the atomic multiplet structure. While the Gutzwiller type wave function can well capture the multiplet features in the ground state. The Gutzwiller variational parameter $\lambda_F$ determines nothing but the probability of each atomic configuration $\Gamma$ in the ground state (which is defined as $\langle G(\Gamma)|\Gamma(\Gamma)\rangle$). In Fig. 4, we plot the corresponding probabilities for SmB$_6$ obtained by LDA+Gutzwiller together with that obtained by LDA wave function ($\langle\Gamma(\Gamma)|\Gamma(\Gamma)\rangle$). The LDA ground state is dominated by the atomic configurations with the number of f-electrons $N_f=6$, on the other hand however, the distribution of the probability of atomic states obtained by LDA+Gutzwiller is almost equally concentrated on two atomic multiplet states with five and six f-electrons respectively, leading to approximately +2.5 valence of Sm.

Moreover, the Gutzwiller wave function provides correct description of the intermixing between $j=7/2$ and $j=5/2$ orbitals, which can not be captured by LDA only calculation and manifest itself in the average occupancy of the f orbitals. The occupancy of $j=5/2$ and $j=7/2$ orbitals are 5.31 and 0.22 respectively using the LDA type wave function ($\langle\Gamma\rangle$). While the f orbital occupancy is modified to be 3.64 for $j=5/2$ and 1.89 for $j=7/2$ orbitals using the Gutzwiller type wave function ($\langle\Gamma\rangle$). The dramatic increment of the occupancy for $j=7/2$ orbitals is the important consequence of the $F_2 - F_6$ terms in the atomic interactions, which can not
be expressed by a pure "density-density" form in any single particle basis and generate strong multi-configuration nature for the ground state wave function.

The band inversion feature around the $X$ points is well persitent in the LDA+Gutzwiller quasi-particle bands. As discussed in previous paragraphs, the topological nature of this interacting system is fully determined by the Gutzwiller effective Hamiltonian $H_{\text{eff}}$. Since the spacial inversion symmetry is present for SmB$_6$, we are now able to determine its topological nature by simply counting the parities of those occupied quasi-particle states at 8 TRIM points. As listed in Table I, the parities are all positive except the $X$ points. Because there are totally three equivalent $X$ points in the whole BZ, the $Z_2$ topological index for SmB$_6$ has to be odd, resulting in a strongly correlated topological insulators with topological indices (1;111).

To see the topological surface states, we construct a tight binding model using the projected Wannier functions, which can reproduce the LDA band dispersion quite precisely. The surface states (SS) of the (001) surface are then obtained by combining the above tight binding Hamiltonian and the same rotational invariant Gutzwiller approach on a 40-layers slab. The obtained quasi-particle bands of the slab are plotted in Fig. 5. It is clearly seen that the surface states contain three Dirac cones: one cone is located at $\bar{\Gamma}$ and the other two are at two $X$ points of the surface BZ. The interesting multi-Dirac-cones behavior is quite unique among the existing TIs and is a natural consequence of the band inversion at the bulk $X$ points, which are projected onto to $\bar{\Gamma}$ and two $X$ points of the (001) surface BZ. The multiple Dirac cones on the surface of SmB$_6$ may generate interesting physical phenomenas, such as the unique quasi-particle interference pattern in scanning tunneling microscope (STM), which will be studied in our further publications.

In summary, we have developed the LDA+Gutzwiller method incorporating the Green’s function scheme to study the the topological phases of strongly correlated materials from the first-principles (beyond LDA and LDA+U). This method is systematically applicable to all correlated compounds as long as the quasi-particle weight is not reaching zero. Both quasi-particle bands and atomic multiplete structures can be well captured in the present technique. Applying this method onto typical mixed valence compound SmB$_6$, we demonstrate that it is a strongly correlated 3D TI with unique surface states containing three Dirac cones on the (001) surface. The strong interaction among the $f$ electrons reduces both the band width and the quasiparticle weight for almost one order, but the topological feature remains.

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