First Principle Simulations of Heavy Fermion Cerium Compounds Based on the Kondo Lattice

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We propose a new framework for first-principle calculations of heavy-fermion materials. These are described in terms of the Kondo lattice Hamiltonian with the parameters extracted from a realistic density functional based calculation which is then solved using continuous-time quantum Monte Carlo method and dynamical mean field theory. As an example, we show our results for the Néel temperatures of Cerium-122 compounds (CeXSi₂ with X=Ru, Rh, Pd, Cu, Ag, and Au) where the general trend around the magnetic quantum critical point is successfully reproduced. Our results are organized on a universal Doniach phase diagram in a semi-quantitative way.

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First-principle description of heavy-fermion materials has been a challenging problem for a long time. The difficulty arises from the dual nature of the electrons between the localized and itinerant electrons due to the large Coulomb repulsion energy $U$ at each site of the lattice. Here the relatively well-localized $f$-electrons interact with the itinerant $s,p,d$-electrons that form the conduction band. The heavy-fermion systems are generally described as the Anderson impurity model in the dilute limit [1] or the Anderson lattice model (ALM) in the dense limit, and the first-principle description offthem has been done by several authors [2,3,4,5]. With the development of dynamical mean field theory (DMFT) [6] and novel continuous-time quantum Monte Carlo (CT-QMC) solvers for the Kondo lattice [7,8,9], the ALM description has become quite successful except for a very low temperature range. The numerically exact treatment of the Anderson impurity model is still very expensive if the temperature range of $O(1)$ $K$ is to be reached. Thus, the first-principle description of strongly-correlated materials around the quantum critical point (QCP) [10], which has recently been attracting a lot of research interest is yet to be solved.

Here we attack the problem using the Kondo lattice model (KLM) [11] trying to focus on the low-energy physics of the ALM. We show how this new approach works for a archetypical family of so called Cerium 122 compounds, CeX₂Si₂ (X=Ru, Rh, Pd, Cu, Ag, and Au), which has been one of the most extensively studied strongly-correlated materials since the discovery of heavy-fermion superconductor CeCu₂Si₂ [12]. Strictly speaking, we deal with the Coqblin–Schrieffer model [12] with full 14 fold degenerate $f$-shell but effectively the degeneracy is lowered due to the spin–orbit and crystal-field splittings. With the localized Kondo–impurity picture we can save the amount of the degrees of freedom in our model by eliminating charge fluctuations, and we can reach much lower temperature range as compared to the ALM simulations. The conduction band in the model is given by the hybridization function between the localized $4f$ orbitals and the $s,p,d$–conduction bands calculated by the first–principle structure calculation based on the local–density approximation (LDA) with Hubbard I [13] type of the self-energy for the $f$ electrons. Then the Kondo coupling is defined via the Schrieffer–Wolff transformation [14], and the KLM is solved with the new efficient CT–QMC Kondo impurity solver [15] combined with DMFT.

Now we define the realistic KLM Hamiltonian for a given Cerium compound. The general Coqblin–Schrieffer Hamiltonian is the following.

$$\mathcal{H} = \sum_k \epsilon_k c_k^\dagger c_k + J_K \sum_{\alpha} f_{\alpha}^\dagger f_{\alpha} c_{\alpha}^\dagger c_{\alpha} + \sum_{\alpha} \Delta_{\alpha}^{\text{splitting}} f_{\alpha}^\dagger f_{\alpha},$$

(1)

Here $\epsilon_k$ is the conduction band, $J_K$ is the Kondo coupling, $\Delta_{\alpha}^{\text{splitting}}$ is the crystal and spin–orbital field, $c_k$ and $f_{\alpha}$ are the annihilation operators for the conduction and $4f$ electrons, respectively, with the orbital $\alpha$ on the lattice site $i$. To solve this Hamiltonian we first need to define $J_K$ and the conduction electron Green function. For this we perform the first principle DFT calculation within the local density approximation for $s,p,d$ electrons plus the Hubbard I approximation for the $f$ electrons based on the full-potential linearized muffin–tin orbitals (LMTO) method [13] and calculate the hybridization function $2 \Im(\Delta(\epsilon) – \pi \sum_k |V_{\alpha k}|^2 \delta(\epsilon - \epsilon_k) \simeq \pi |V_{\alpha k}|^2 \rho(\epsilon))$ where $V_{\alpha k}$ is the hybridization matrix element and $\rho(\epsilon)$ is the density of states of the conduction electrons at energy $\epsilon$ which we measure from the Fermi energy. We use experimental lattice parameters for all materials that we study.

The calculated $\text{Tr} \Im(\Delta(\epsilon)/(\pi N_F)) \equiv |1/(\pi N_F)| \sum_{\alpha=1}^{N_{\alpha}} \Im(\Delta_{\alpha}(\epsilon))$ is shown in Fig. 4 for several representative CeX₂Si₂ materials with X=Ru, Rh, Pd, and Ag. Here $N_F = 14$ is the total number of degeneracy and the trace of $\Im \Delta$ is taken over all of $N_F$ states. We note that $\Im \Delta$ shows strong frequency dependence therefore in order to define $J_K$ an averaging over some frequency intervals needs to be performed.
FIG. 1: (Color online) The hybridization function Tr$\mathcal{H}_0$/(1/14 between the conduction band and the 4f–electrons calculated by LDA + Hubbard I for CeX$_2$Si$_2$ with X=Ru, Rh, Pd, and Ag. The origin of the energy is set to be the Fermi level.

The Kondo coupling $J_K$ is defined by the Schrieffer–Wolff transformation \[ \frac{1}{\pi} \int_{-\Delta_{\text{cutoff}}}^{\Delta_{\text{cutoff}}} e^{-\delta \Delta_{\text{cutoff}}} d\epsilon \left( \frac{1}{|\epsilon|} + \frac{1}{(\epsilon + U_{\text{eff}})} \right) \] as follows

Here $\epsilon_0$ is the location of the energy level of 4f orbital, and $U_{\text{eff}} = U - J_{\text{Hund}}$ is the effective on–site Coulomb repulsion taking into account an effective Hund coupling $J_{\text{Hund}}$ that works in the virtual $f^2$ state. We set $\epsilon_0 = -2.5$[eV] and $U = 5$[eV] which is a typical value for Cerium compounds. The Hund coupling $J_{\text{Hund}}$ is explored around a realistic value 1 eV as is explained below. In the present formulation, $U_{\text{eff}}$ incorporates all of the possible multiplet effects in the virtual $f^2$ states and some systematic error comes in from the setting of this value, but it is small enough to see the general trend between the materials in the realistic Doniach phase diagram that is obtained in Fig. 4 in the end. Here we have a band cutoff $D_{\text{cutoff}}$ set to be 5 [eV] which is large enough to make a universal description of the low–energy physics.

The portion of the conduction electron Green function $G_{\alpha}(\epsilon)$ which has non–zero hybridization with the f–electrons is also proportional to $\Delta_{\alpha}(\epsilon)$. We define the normalized and Hilbert–transformed $G_{\alpha}(i\omega)$ as follows

$$G_{\alpha}(i\omega) = \int_{-\Delta_{\text{cutoff}}}^{\Delta_{\text{cutoff}}} d\epsilon \frac{\partial \Delta_{\alpha}(\epsilon)}{i\omega - \epsilon} / \int_{-\Delta_{\text{cutoff}}}^{\Delta_{\text{cutoff}}} d\epsilon \partial \Delta_{\alpha}(\epsilon).$$

The Eqs. provide necessary inputs which are plugged into the CT–QMC and solved with DMFT self–consistency loop. The details of the CT–QMC algorithm for the Coqblin–Schrieffer model are given in . These definitions for the realistic model are designed in such a way that it becomes exact in the limit of constant hybridization with the relevant quantity $N_F J_K \rho(0)$ that determines the behavior of the KLM.

The LDA results for $N_F J_K \rho(0)$ for the target materials are given in Table I. The level splittings $\Delta_{\alpha}$ appeared in are implemented as the difference of the positions of $\epsilon_{\alpha}$ which are used in the update probability as is described in Ref. . These level splittings are taken from the literature and summarized in Table I. We checked that our results for the Néel temperatures are robust against small changes of factor of $O(1)$ on the level splittings. Thus $\Delta_{\alpha}$ reduce the effective degeneracy close to $N_F = 2$ 18. Thus we call our model “realistic Kondo” lattice instead of the Coqblin–Schrieffer lattice even though we are actually doing the multi–orbital model.

We apply the above framework for the KLM description of CeX$_2$Si$_2$ with X=Ru, Rh, Pd, Cu, Au, Ag. We do the following analyses with several settings of $U_{\text{eff}} = U - J_{\text{Hund}}$ for $0 \leq J_{\text{Hund}} \lesssim 1$ eV for each of the material. For a given material and given parameter set, we determine the Néel temperature by looking at the temperature dependence of staggered susceptibility and locating at which temperature it diverges. Here we follow the formalism of DMFT for the localized f–electron systems as given in 19 and use the same method as was utilized for model calculations in 20. Regarding the realistic input of the Green’s function as is depicted in Fig. 1, we make an approximation in the calculation of the staggered magnetic susceptibility for the 4f–electrons by decoupling the two–particle density of states $\rho(\epsilon_1, \epsilon_2) = \delta(\epsilon_1 + \epsilon_2) \rho(\epsilon_1)$ as if there is a nesting property which becomes exact when the 4f–electrons are on a hypercubic lattice. Thus the tendency to the antiferromagnetic order would be overestimated in addition to having the infinite–dimensional nature in the DMFT solution to the lattice problem. The data specific to CeRh$_2$Si$_2$ with which we determine the Néel temperatures for several settings of $J_{\text{Hund}}$ are shown in Fig. 2. In this way for each of the material we look at the magnetic phase transitions for several $J_K$’s by varying corresponding $J_{\text{Hund}}$’s.

As was first discussed by Doniach 21, 22 and subsequently by many authors, Kondo lattices have two representative energy scales, namely the magnetic ordering energy that is proportional to $(J_K/\sqrt{N_F})^2 \rho(0)$ and the Kondo screening energy which behaves like $\exp(-1/N_F J_K \rho(0))$. For small $J_K$’s the former wins but as $J_K$ becomes larger the exponential growth of the latter dominates at some point. Thus a given system can realize in either magnetically ordered phase or non–magnetic Kondo–screened phase. Between these two phases at zero temperature there is thought to be a QCP. We explore this Doniach phase diagram for each material and find the material–specific QCP. We take the data with the setting $J_{\text{Hund}} = 0.94$ eV as our realistic result for each material as this strength of the Hund coupling is close to the realistic value and also gives reasonable trend over all materials in the family. Thus obtained Doniach phase diagrams for
We note that the valence fluctuations which we ignored in our simulation could be important in the realization of material to its QCP as can be seen from Fig. 3. So our numerical result is consistent with the experimental result that CeCu$_2$Si$_2$ is a superconductor at ambient pressure and is thought to be close to the QCP.
The line is a guide for the eye. We plot CeCu$_2$Si$_2$ but that just reflects the result that CeCu$_2$Si$_2$ is marked to note as it apparently has a finite N´eel temperature but that just reflects the result that CeCu$_2$Si$_2$ is very close to QCP as can be seen in Fig. 3.

FIG. 4: (Color online) Universal Doniach phase diagram for the material family of CeX$_2$Si$_2$. The horizontal axis is defined as follows: $t \equiv [N_F K \rho(0) - N_V K \rho(0)]_{QCP}/[N_F K \rho(0)]_{QCP}$. The line is a guide to the eye. We plot CeCu$_2$Si$_2$ with an asterisk mark to note as it apparently has a finite N´eel temperature but that just reflects the result that CeCu$_2$Si$_2$ is very close to QCP as can be seen in Fig. 3.

the non–magnetic ground state. Indeed it is known that there are some valence fluctuations in CeCu$_2$Si$_2$ [24] and CeRu$_2$Si$_2$ [25]. This might make the possible systematic error relatively larger on the right–hand side of our phase diagram [26, 27]. Nevertheless at the present level of description we believe that the realistic KLM works because the number of 4f electrons in Cerium ion is still very close to one [24, 25]. At least for the impurity problem the convergence to the Kondo impurity picture in large $|\epsilon_1|/\rho(0)V^2$ limit of the Anderson model was discussed exactly [28]. Careful comparison between the Anderson lattice and the Kondo lattice regarding the valence fluctuation issue is interesting, especially for CeCu$_2$Si$_2$, and further work is ongoing in this direction.

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