Charge Kondo Effect and Superconductivity in the Falikov-Kimball model with the Pair Hopping

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We study the Falikov-Kimball model with the pair hopping between the conduction and localized bands to discuss how the charge Kondo effect is realized. By combining dynamical mean-field theory with the continuous time quantum Monte Carlo method, we clarify that the charge Kondo state survives even at zero temperature and this competes with the charge ordered and s-wave superconducting states. The role of the interorbital repulsion for the superconducting state is also addressed.

I. INTRODUCTION

Electron valence in the transition-metal and rare-earth ions has attracted interest in the strongly correlated electron systems. Typical examples are the valence skipping phenomena for bismuth and thallium ions in some compounds. In the ions, electron configurations prefer the closed shell structure in the s orbital and avoid the ionic state with a spin. This should lead to interesting low temperature properties such as colossal negative thermal expansion in La-doped BiNiO$_3$ [1–3] and superconductivity in K-doped BaBiO$_3$ [4, 5]. Moreover, in PbTe system with non-magnetic Tl impurities, Kondo-like behavior appears in the resistivity, which is known as the charge Kondo effect [6, 7]. The valence skipping phenomenon in d-electron systems has also been suggested [8, 9], which stimulates further theoretical investigations on the valence skipping and related phenomena [10–16].

In valence skipping ions, the effective degrees of freedom should be represented by the empty and doubly occupied states for the s orbital. There are two distinct models to describe the valence skip ions. (i) in most theoretical studies, an effective attractive interaction is introduced in the orbital of the ions to mimic the stability of closed shell configurations [10–17]. Low temperature properties have been discussed such as the valence transition in La-doped BiNiO$_3$ [15–17], charge ordering and superconductivity in K-doped BaBiO$_3$ [11], and charge Kondo effect in Tl-doped PbTe [13–14]. (ii) Another mechanism has recently been proposed, where the inter-band correlations are taken into account [17]. It has been suggested that the charge Kondo effect in the single impurity model is well reproduced by the introduction of the pair hopping between the impurity and conduction bands in addition to the repulsive interaction. On the other hand, as for the periodic system, the ground state remains unclear as well as the finite-temperature properties. In particular, it should be instructive to clarify in the periodic system the possibility of the superconductivity against the charge Kondo state as the pair hopping may induce the superconducting (SC) state, which is trivially realized in the system with the attractive interaction [18].

In this paper, we study the correlated electron system with conduction and localized bands. By considering Coulomb interaction and pair hopping between conduction and localized orbitals, we discuss how the valence skipping phenomena affect low temperature properties in the bulk system. Here, we use dynamical mean-field theory (DMFT) [19–21] combined with the continuous-time quantum Monte Carlo (CTQMC) method [22, 23]. Examining electron configurations, charge correlations, and order parameters, we discuss the stability of the charge Kondo state against spontaneously symmetry breaking states.

The paper is organized as follows. In Sec. II, we introduce the model Hamiltonian and briefly summarize our numerical method. In Sec. III, calculating various physical quantities, we discuss the role of interorbital repulsion and pair hopping in realizing the charge Kondo, charge ordered, and superconducting states. Then, we determine the phase diagram. A summary is given in the final section.

II. MODEL AND METHOD

We study low energy properties in strongly correlated electron systems with the localized valence skipping ions. To this end, we deal with the extended Falikov-Kimball model [24, 25], where conduction electrons interact with localized ones. This is the natural extension of the impurity model discussed in Ref. [17], and its Hamiltonian is given as,

\[ H = H_0 + H', \]

\[ H_0 = \sum_{ij\sigma} (t_{ij} c_{i\sigma}^\dagger c_{j\sigma} + \epsilon_d \delta_{ij} n_{i\sigma}^{d}), \]

\[ H' = U_{cd} \sum_{i\sigma} n_{i\sigma}^{c} n_{i\sigma}^{d} - J_{ph} \sum_i \left( c_{i\uparrow}^\dagger c_{i\downarrow}^\dagger d_{i\uparrow} d_{i\downarrow} + H.c. \right), \]

where \( c_{i\sigma} (d_{i\sigma}) \) is an annihilation operator of a conduction electron (localized electron) with spin \( \sigma (\uparrow, \downarrow) \). \( n_{i\sigma}^{c} (= c_{i\sigma}^\dagger c_{i\sigma}) \) and \( n_{i\sigma}^{d} (= d_{i\sigma}^\dagger d_{i\sigma}) \) are the number operators of the conduction and localized electrons at the \( i \)th site, respectively. \( t_{ij} (= -t\delta_{ij}) \) is the hopping integral...
of the conduction electrons between the nearest-neighbor sites and \( \epsilon_d \) is the energy level of the \( d \) orbitals. \( U_{cd}(J_{ph}) \) is the repulsive interaction (pair hopping) between the conduction and localized electrons.

When \( J_{ph} = 0 \), the system is reduced to the conventional Falikov-Kimball model [24]. In the infinite dimensions [25], the model is exactly solved, and ground state properties have been discussed in detail [26]. It is known that, in the presence of the particle-hole symmetry, the interorbital Coulomb interaction suppresses the single occupancy at each orbital and the charge ordered (CO) state is realized at zero temperature.

In the paper, we consider both the interorbital Coulomb interaction and pair hopping between the conduction and localized bands on an equal footing. In the atomic limit (\( t_{ij} = 0 \)) under the particle-hole symmetry, these interactions prefer the electronic configuration with one of two orbitals empty and the other doubly occupied, while no singly occupied states are realized in each orbital. Therefore, valence skip feature should be captured in our model. To provide more insight, we wish to introduce the pseudo spin operators for orbital band as,

\[
I^x_{\alpha} = \frac{1}{2} \left( \alpha^\dagger_{i\alpha} \alpha^\dagger_{i\uparrow} + \alpha_{i\uparrow} \alpha_{i\alpha} \right), \\
I^y_{\alpha} = \frac{1}{2i} \left( \alpha^\dagger_{i\alpha} \alpha_{i\downarrow} - \alpha_{i\downarrow} \alpha^\dagger_{i\alpha} \right), \\
I^z_{\alpha} = \frac{1}{2} (\rho^\dagger_{\alpha} - 1).
\]

Then, the interaction part of the original Hamiltonian can be rewritten as the following the Kondo lattice model with anisotropic interactions [27]:

\[
H' = 2 \sum_i \left[ 2U_{cd} I^x_{ic} I^x_{id} + J_{ph} (I^x_{ic} I^x_{id} + I^y_{ic} I^y_{id}) \right].
\]

We wish to note that \( U_{cd} \) and \( J_{ph} \) yield distinct low temperature properties. When \( |J_{ph}| \ll 2U_{cd} \), the diagonal Ising interactions make the pseudo-spins antiparallel in the \( z \) direction. If one considers the lattice model, the antiferro-type ordered state is realized with the staggered pseudo-spin moments \( \langle I^z_{\alpha} \rangle \sim (-1)^{i+\delta_\alpha} \), where \( \delta_\alpha = 0(1) \) for conduction (local) band. This implies the CO state is realized in the original model. The characteristic quantities are alternated electron densities \( \rho_c \) and \( \rho_d \), where \( \rho_\alpha = \sum \langle -1 \rangle \epsilon^\alpha_N / N \). In the opposite case with \( |J_{ph}| \gg 2U_{cd} \), the pseudo-spins are on the \( xy \) plane with the staggered configuration, e.g., \( \langle I^y_{\alpha} \rangle \sim (-1)^{i+\delta_\alpha} \) due to the inplane anisotropy in Eq. (7). Then the superconducting state is realized with the staggered pair potential \( \langle \alpha_{i\uparrow} \alpha_{i\downarrow} \rangle \sim (-1)^{i+\delta_\alpha} \). When the particle-hole transformation \( c_{i\alpha} \rightarrow (-1)^{\sigma} \tilde{\epsilon}_{i\alpha} \) is applied, \( H(t,U_{cd},J_{ph}) \) is transformed to \( H(t,U_{cd},-J_{ph}) \), and the superconducting order parameter is uniform in the model. Therefore, the sign of the pair hopping is essentially irrelevant, and the SC state can be regarded as a conventional \( s \)-wave SC state. When \( 2U_{cd} = J_{ph} \), the system is reduced to the isotropic Kondo lattice model. In the strong coupling case, the Kondo insulating state is realized with the pseudo-spin singlet \( \langle \mathbf{I}_c \cdot \mathbf{I}_d \rangle = -3/4 \). This implies the existence of the charge Kondo state in our model, which is mainly formed by empty and doubly occupied states.

To study the competition between the SC, CO, and charge Kondo states in the original model Eq. (3), we make use of DMFT [19, 21] in the Nambu formalism [28]. In the framework of DMFT, the lattice model is mapped to an effective impurity model, where local electron correlations are taken into account precisely. The Green function for the original lattice system is then obtained via self-consistency equations imposed on the impurity problem. The non-interacting Green function in the lattice system is represented as the two-by-two matrix,

\[
\hat{G}_{0\alpha}(\mathbf{k},i\omega_n) = \left[ i\omega_n \sigma_0 + (\mu - \epsilon_{\alpha\mathbf{k}}) \sigma_2 \right]^{-1},
\]

where \( \sigma_0 \) is the identity matrix, \( \sigma_2 \) is the \( z \) component of the Pauli matrix, \( \omega_n = (2n + 1)\pi T \) with integer \( n \) is the Matsubara frequency, \( T \) is the temperature, and \( \mu \) is the chemical potential. \( \epsilon_{\alpha\mathbf{k}} \) is the dispersion relation for the \( \alpha \)th band, namely, \( \epsilon_{\alpha\mathbf{k}} = \epsilon_k \) and \( \epsilon_{\alpha\mathbf{k}} = \epsilon_d \). Since there is no hybridization between conduction and localized bands, no interband elements appear in the Green’s function [29]. The lattice Green’s function is then given by the site-diagonal selfenergy as

\[
\hat{G}_{\alpha}(i\omega_n) = \int d\mathbf{k} \left[ \hat{G}_{0\alpha}(\mathbf{k},i\omega_n) - \hat{\Sigma}_\alpha(i\omega_n) \right]^{-1},
\]

where the Green’s functions and selfenergies are represented in the Nambu formalism.

In the following, we use the semicircular density of states \( \rho(x) = 2\sqrt{1-(x/D)^2}/\pi D \), which corresponds to an infinite-coordinate Bethe lattice. By using Dyson equations, the self-consistency condition is represented by the Green’s function of the conduction bands, as

\[
\hat{G}^{-1}(i\omega_n) = i\omega_n \sigma_0 + \mu \sigma_z - \left( \frac{D}{2} \right)^2 \hat{\Sigma}_c(i\omega_n) \sigma_z, \tag{10}
\]

where \( \hat{G} \) is the non-interacting Green function in the effective impurity model.

There are various numerical methods to solve the effective impurity problem. To discuss quantitatively how the SC and CO states compete with the charge Kondo state, we use here the CTQMC method [22, 23]. In our model, the double expansion technique [30], where the partition function is expanded with respect to both the effective bath and the pair hopping, is efficient to perform Monte Carlo simulations without minus sign problems. In the paper, to discuss how the valence skipping phenomenon is realized, we evaluate the probabilities of empty, singly, and doubly occupied states in each orbital with \( \langle \epsilon_{i\alpha\mathbf{k}} \rangle, \langle s_{i\alpha\sigma\mathbf{k}} \rangle, \) and \( \langle d_{i\alpha\mathbf{k}} \rangle \), where \( \epsilon_{i\alpha\mathbf{k}} = (1-n^\alpha_{i\uparrow})/(1-n^\alpha_{i\downarrow}), s_{i\alpha\sigma\mathbf{k}} = n^\alpha_{i\sigma\mathbf{k}}(1-n^\alpha_{i\uparrow}), \) and \( d_{i\alpha\mathbf{k}} = n^\alpha_{i\uparrow}(1-n^\alpha_{i\downarrow}) \), respectively. In the following, we take \( D \) as unit of energy and set \( \mu = U_{cd} \) and \( E_d = 0 \) to discuss low temperature properties in the system with particle-hole symmetric conditions \( \langle n_c \rangle = \langle n_d \rangle = 1 \).
III. RESULTS

We discuss low temperature properties in the system with itinerant and localized bands. Fixing the interorbital Coulomb interaction as $U_{cd} = 0$, we focus on the effect of the pair hopping in the system to discuss the competition between the charge Kondo and SC states. We first calculate the probabilities of empty, singly, and doubly occupied states to examine the electron configuration in the system. The results are shown in Fig. 1(a). When $J_{ph} = 0$, the system is noninteracting, and the metallic state is realized with $\langle e^c \rangle = \langle d^c \rangle = \langle d^f \rangle = 0.25$. The introduction of the pair hopping increases the probabilities of empty and double occupied states, while it decreases those of single occupied states. In the strong coupling limit, these values $\langle e^c \rangle = \langle d^c \rangle \rightarrow 0.5$ and $\langle s^c \rangle \rightarrow 0$. Similar behavior appears in the localized bands (not shown), which means that the valence skip behavior is well described by the pair hopping. To discuss how the SC state is realized in the system, we also calculate the pair potential in the conduction band $\Delta_c = \langle c^\dagger c \rangle$, as shown in Fig. 1(b). In the intermediate coupling region gradually changed in the SC state, as shown in Fig. 1(a). Around $(J_{ph})_{c1}$, the single occupancy still appears because of weak electron correlations. In the case, the BCS-like SC state is realized, and thereby the critical value $(J_{ph})_{c1}$ approaches zero with decreasing temperatures, as shown in Fig. 1(b). Roughly speaking, we find that the emergence of the phase transition appears to be related with the double occupancy of $\langle d \rangle \sim 0.4$, which helps us to discuss later the effect of the interorbital interaction.

On the other hand, in the stronger coupling region singly occupied states are little realized, as shown in Fig. 1(a). Therefore, paired electrons formed by pair hopping play a crucial role in the region. When paired electrons are itinerant in the lattice $[J_{ph} < (J_{ph})_{c2}]$, the SC state is realized. On the other hand, when $J_{ph} > (J_{ph})_{c2}$, the paired electrons are localized in each site, which is expected not to correspond to the charge Kondo state. To clarify whether or not the charge Kondo state is realized at low temperatures, we show in Fig. 2 the temperature dependence of the pseudo spin correlation $\langle L_s \cdot L_d \rangle$ for the system with $U_{cd} = 0$ and $J_{ph}/D = 0.75$. Its magnitude becomes larger with decreasing temperature at $T \sim |J_{ph}|$. The quantity is almost saturated below $T/D \sim 0.1$, where $\langle e^c \rangle = \langle d^c \rangle \sim 0.5$ and $\langle s^c \rangle \sim 0$. In addition, we could not find the SC state at lower temperatures, suggesting that the charge Kondo state is realized even at zero temperature. This is consistent with the fact that the critical point $(J_{ph})_{c2}$ between the SC and charge Kondo states is little changed with decreasing temperature, as shown in Fig. 1(b).

We next consider how the interorbital interaction $U_{cd}$ stabilizes the CO state $[31, 34]$. When $J_{ph} = 0$, the system is reduced to a conventional Falikov-Kimball model and its low temperature properties have been discussed in detail $[21, 25]$. Figure 3 shows the order parameter at fixed temperatures $T/D = 0.03, 0.05$ and $0.1$. We find that the CO state is realized in the intermediate coupling region $U_{cd}/D \sim 1$ and becomes more stable with...
decreasing temperatures. This is consistent with the fact that the CO state is always a ground state in the system without the pair hopping $J_{ph} = 0$.  

From these results in two limiting cases, we find two distinct ordered states. Now, another question arises how the SC and CO states compete with each other. Here, we fix the condition $U_{cd} + J_{ph} = 0.38D$ to clarify how these two phases are realized. Figure 3 shows order parameters in the system at $T/D = 0.03$. When $J_{ph}/D = 0.23$, the CO state is realized with the order parameter $\rho_c \sim 0.1$. The increase of the pair hopping monotonically decreases this quantity up to $J_{ph}/D \sim 0.26$. The order parameter suddenly vanishes and the finite pair potential appears instead. This implies the existence of the first-order phase transition between CO and SC states. In fact, the SC state solution exists in the case $J_{ph}/D \gtrsim 0.25$ shown as the solid squares in Fig. 4. Note that at the symmetric point ($2U_{cd} = J_{ph} = 0.2533D$), order parameters take the same value within our numerical accuracy. This originates from the fact that the Hamiltonian Eq. (7) is isotropic and these two states are degenerate at zero temperature. Then, we conclude that there exists the first-order phase boundary along the symmetric condition at low temperatures.

By performing similar calculations, we obtain the phase diagram with a fixed temperature $T/D = 0.03$, as shown in Fig. 5. When the system is weakly cor-
in the phase boundary between the SC and charge Kondo states appears in the strong coupling region.

Before closing this paper, we comment on the effect of the single electron hopping (hybridization) between the conduction and localized band, which has been treated in the periodic Anderson model. Since the self-consistency condition Eq. (10) is not changed [36], one can treat this model in the same framework to discuss the possibility of the magnetically ordered state and competition between magnetic and charge Kondo states [37]. However, the single hopping gives rise to minus sign problems in solving the effective impurity model by means of the CTQMC method. Therefore, the quantitative analysis should be restricted at relatively higher temperatures. Furthermore, this single hopping makes singly occupied states active and the nature of the valence skip ions becomes obscure, which is beyond the scope of our paper. Therefore, this interesting question is left for future work.

IV. CONCLUSION

We have investigated the extended Falikov-Kimball model with the Coulomb and pair hopping between the conduction and localized bands to discuss how the valence skipping ions induce spontaneous symmetry breaking state. By combining DMFT with the CTQMC method, we have determined the finite temperature phase diagram, where the SC and CO states compete with the charge Kondo state. It is found that, in the weak coupling region, the Coulomb interaction assists the stability of the SC state, which is a common feature inherent in the multiorbital systems.

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