Molecular Kondo effect in flat-band lattices

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The Kondo effect of a single magnetic impurity embedded in the Lieb lattice is studied by the numerical renormalization group. When the band flatness is present in the local density of states, it quenches the participation of all dispersive electrons in the Kondo singlet formation, and reduces the many-body Kondo problem to a two-electron molecular Kondo problem. The two-electron analogue of the many-body Kondo singlet, a quantum entanglement of two spins, is stable at low temperature, and the impurity contributions to thermodynamical and dynamical quantities are qualitatively different from that obtained in the conventional Kondo effect in systems without flat bands. The existence conditions of the molecular Kondo effect in narrow band systems are also discussed.

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For a half century, the Kondo effect has attracted great scientific interest due to its essential relation to a number of spectacular low temperature phenomena \cite{1}. It is known to be responsible for the essential behaviors of heavy fermions, mixed valent and intermetallic alloys, Kondo insulators, transport and magnetic properties of quantum dots... The Kondo effect is inherently a strongly correlated many-body ground state that contains a quantum entanglement between a localized fermion and itinerant fermions. In this quantum entanglement many itinerant fermions in the Fermi sea are involved in order to quench the magnetic moment of the localized fermion and together form the so-called Kondo singlet state. A molecular analogue of the Kondo singlet state, where only a single fermion is involved in forming the spin singlet state with the localized fermion, was proposed \cite{2,3}. It was suggested to be the underlying physics of the Kondo effect experimentally observed in single molecules \cite{2,3}. The molecular Kondo effect contains key ingredients of the Kondo effect in bulk. At sufficient low temperature, it separates the spin and charge low-lying excitations. The ground state is the spin singlet like the Kondo singlet state in bulk. As temperature increases, the next higher energy state, the spin triplet, populates and forms a full magnetic moment \cite{2}. These properties are exactly the main features of the Kondo effect in bulk. However, the molecular Kondo effect is also distinct from the bulk one by the absence of the Kondo resonance, which results from the coherently cotunneling of electrons between the Fermi sea and the magnetic impurity. Although, the molecular Kondo singlet is the underlying physics of the Kondo effect in bulk, it cannot be isolated from the many-body Kondo singlet state.

In this letter we show the molecular Kondo effect can be observed in flat-band lattices. Unlike the conventional Kondo effect, the molecular Kondo singlet state is only a two electron spin state, which yields essentially an entanglement of two spin qubits. This paves the way for implementing a two electron spin entanglement in solids. In the flat-band lattices, the two-electron Kondo singlet is isolated, leaving all other electrons in the Fermi sea irrelevant. The band flatness quenches the participation of all dispersive electrons in the Kondo singlet formation, and reduces the many-body Kondo problem to a two-electron Kondo problem. The Kondo impurity in the flat band lattices yields the opposite limit of the one in graphene or pseudo-gap systems \cite{5}, since the density of states (DOS) at the flat band is infinite. In the Kondo regime, the impurity contributions to the thermodynamical and dynamical quantities are qualitatively different from that in conventional metals \cite{1}, pseudo-gap systems \cite{5}, Kondo boxes \cite{6}, quantum dots \cite{7}. A simplest model of flat band lattices is the tight-binding model in the Lieb lattice \cite{8,9}. The Lieb lattice is a square lattice with additional sites located in the middle of every edges of the lattice squares. It is the basic structure of layered cuprates, and has attracted research attention since the discovery of high temperature

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{fig1.png}
\caption{(Color online) a, The Lieb lattice structure. b, The local DOS of the tight-binding model in the Lieb lattice at C site (red dotted line) and at A site (blue solid line). c, The local DOS of the tight-binding model with intrinsic SOC in the Lieb lattice at A site (\(\lambda = 0.1\)). d, The DOS of the toy model in Eq. (3). The broadening parameter for these DOS \(\eta = 10^{-5}\).}
\end{figure}
superconductivity [9]. Currently, the Lieb lattice can be realized by an array of optical waveguides [10,12], by loading ultracold atoms in optical lattices [13], and by a molecular design [14]. The Hamiltonian which describes a magnetic impurity embedded in the Lieb lattice reads

\[
H = -t \sum_{\langle i,j \rangle, \sigma} c_{i \sigma}^\dagger c_{j \sigma} + \varepsilon_f \sum_{\sigma} f_{f \sigma}^\dagger f_{f \sigma} + U n_{f \uparrow}^\dagger n_{f \downarrow}^\dagger + V \sum_{\sigma} c_{f \sigma}^\dagger + \text{H.c.}, \tag{1}
\]

where \( c_{i \sigma}^\dagger (c_{i \sigma}) \) is the creation (annihilation) operator of itinerant electron with spin \( \sigma \) at lattice site \( i \). \( t \) is the nearest neighbor hopping parameter. \( f_{f \sigma}^\dagger (f_{f \sigma}) \) represents the creation (annihilation) operator of electron at the magnetic impurity. \( U \) is the local Coulomb interaction of electrons at the magnetic impurity. \( n_{f \sigma}^\dagger = f_{f \sigma}^\dagger f_{f \sigma} \). \( V \) is the hybridization strength between itinerant electrons and the magnetic impurity. We are mainly interested in the case, where the impurity is placed at an edge center site (A site in Fig. 1), since in this case the local DOS exhibits a flat-band feature. We also consider only the half filling case, where the chemical potential equals 0. Without the impurity, the local DOS at a corner site (C site in Fig. 1) linearly vanishes at the Fermi energy like the Dirac electrons, whereas the one at A site exhibits the flat-band feature together with the Dirac electron pseudo-gap (see Fig. 1). With these features, the Lieb lattice allows us to study the Kondo effect in the opposite limits, where the DOS at the Fermi energy are either vanished or infinite. The Kondo problem is completely determined by the hybridization function \( \Gamma(\omega) = \Gamma \rho_c(\omega) \), where \( \Gamma = \pi |V|^2 \) and \( \rho_c(\omega) = \text{Im}[g_c(\omega - i\eta)]/\pi \) is the bare local DOS of itinerant electrons at the impurity site. The impurity contribution to a thermodynamical quantity \( O \) is defined by \( O_{\text{imp}} = O_{\text{tot}} - O_{\text{tot}}^{(0)} \), where \( O_{\text{tot}} \) is the thermodynamical quantity of total system, and \( O_{\text{tot}}^{(0)} \) is the one of the reference system without the impurity [15].

We calculate the thermodynamical and dynamical quantities by the numerical renormalization group (NRG) [15,18]. The NRG was originally constructed for solving the Kondo problem in conventional metals. Within the NRG the hybridization function is discretized by a logarithmic mesh. However, in general the flat-band position falls out of the logarithmic mesh, and without modification the NRG cannot take into account the flat-band feature of the hybridization function. In order to overcome this failure, we broaden the hybridization function \( \Gamma(\omega) = \Gamma \text{Im}[g_c(\omega - i\eta)]/\pi \) by a small parameter \( \eta \). We use the NRG Ljubljana package for our calculations [19]. The energy unit is the half band width \( D = 2\sqrt{2t} = 1 \). The hybridization function is discretized within the adaptive Z-scheme by the logarithmic mesh of the parameter \( \Lambda = 2 \) [19,21]. All calculated quantities are averaged over \( N_z = 8 \) interleaved logarithmic meshes with the twist parameter \( z = 1/N_z \) [15,19,21]. The spectral functions are calculated by using full density matrix algorithm [19,22]. The spin susceptibility is defined by \( T\chi = \langle (S_{\text{tot}}^z)^2 \rangle - \langle S_{\text{tot}}^z \rangle^2 \), where \( S_{\text{tot}}^z \) is the \( z \)-component of the total spin, and \( T \) is temperature [15].

When the impurity is placed at a C site, the hybridization function exhibits a linear pseudo-gap like the one in graphene or in Dirac electrons. This Kondo problem was well studied [5,15]. Our calculations do well reproduce the previous results [5,15]. We notice in this case the obtained results are insensitive to the small broadening parameter \( \eta \) (\( \eta \ll 10^{-3} \)), since the pseudo-gap of the hybridization function is insensitive to small \( \eta \). The situation is quite different when the impurity is placed at a A site, since in this case a flat-band feature exists in the hybridization function. In contrast to the C case, the thermodynamical quantities are sensitive to the broadening parameter \( \eta \), as they are shown in Fig. 2. There are three distinguished regimes. At the very low temperatures, typically smaller than \( \eta \), the impurity entropy and the spin susceptibility approach to zero. This indicates the strong coupling (SC) regime. At low temperatures, but higher than \( \eta \), the impurity entropy and the spin susceptibility are constants, which are insensitive to the small \( \eta \). We call this regime the molecular SC. At high temperature, the impurity entropy and the spin susceptibility approach to their free values. This yields the free orbital (FO) regime as in the conventional Kondo effect. As one can see in Fig. 2 the SC regime strongly depends on the broadening parameter \( \eta \). It seems when \( \eta \to 0 \), the SC regime will disappear. The finite value of \( \eta \) would artificially make the flat band as a narrow band with a narrow Fermi sea. The electrons from this narrow Fermi sea still could quench the magnetic moment and together form the Kondo singlet state. This artificial SC regime always exists as long as \( \eta \) is finite. In the molecular SC regime, the constant values of the

![FIG. 2: (Color online)](image-url)

The temperature dependence of the impurity entropy \( S_{\text{imp}} \) and the spin susceptibility \( T\chi_{\text{imp}} \) for different broadening parameters \( \eta \) when the impurity is placed at A site. The black solid lines are the results obtained by the exact diagonalization of the molecular model in Eq. (2). The model parameters \( \Gamma = 0.01, U = 0.2, \epsilon_f = -0.1, \epsilon_c = 0 \).
impurity entropy and the spin susceptibility are different from those values of the corresponding quantities in the SC, the local moment (LM), and the FO regimes of the Kondo problem in conventional metals, pseudo-gap systems, Kondo boxes, quantum dots. This constitutes a novel regime of the Kondo problem in the presence of band flatness. As we will see, this regime is precisely the SC in a molecule of two orbitals, for instance a ligand orbital and a strongly correlated orbital. Two electrons are distributed over these two orbitals. The Hamiltonian of the molecule reads

$$H_{\text{mol}} = \sum_\sigma (\varepsilon_c c_\sigma^\dagger c_\sigma + \varepsilon_f f_\sigma^\dagger f_\sigma) + U \sum_\sigma n_\sigma^f n_\sigma^f$$

$$+ \sqrt{2 \pi} \sum_\sigma (c_\sigma^\dagger f_\sigma + \text{H.c.}),$$

(2)

where $c_\sigma^\dagger$ and $f_\sigma^\dagger$ represent the creation of an electron at the ligand and the strongly correlated orbitals, respectively. $\varepsilon_c$ and $\varepsilon_f$ are the orbital energy levels. The ligand and the strongly correlated orbitals mimic the conduction band and the magnetic impurity in bulk. The molecular model in Eq. (2) can analytically be analyzed in the strong correlation limit $U \rightarrow \infty$ [2]. When $\Gamma = 0$, the ground state of the molecule is four-fold degenerate and is formed by one electron in the ligand orbital and the other electron in the strongly correlated orbital. One state is the spin singlet, and three others are the spin triplet [2]. The excited states are $c_\sigma^\dagger c_{\sigma'}^\dagger |0\rangle$, and $f_\sigma^\dagger f_{\sigma'}^\dagger |0\rangle$. The latter excited state is excluded from the consideration in the strong correlation limit. When the hybridization is turned on, the spin singlet couples with the ligand excited state $c_\sigma^\dagger c_{\sigma'}^\dagger |0\rangle$, while the spin triplet remains unchanged. This coupling splits the singlet from the triplet, and separates the low-lying spin excitation from the charge one. The energy gain due to the spin singlet formation is of order $\Gamma/\pi |\varepsilon_c - \varepsilon_f|$ [2]. This is the SC regime of the Kondo problem in the molecule. The total entropy and spin susceptibility are zero like the ones of the Kondo effect in bulk. However, the impurity (or strongly correlated orbital) contributions to the entropy and spin susceptibility are not zero. They exactly equal to the opposite values of the entropy and spin susceptibility of the free ligand orbital in order to compensate the free ligand orbital contributions. Without the strongly correlated orbital, two electrons in the ligand orbital form a free orbital. Their entropy is $2 \ln 2$ and their spin susceptibility equals to $1/8$. Therefore, at low temperatures the impurity contribution to entropy is exactly $-2 \ln 2$, and the one to the spin susceptibility equals to $-1/8$, as one can see in Fig. [2]. When temperature increases, the triplet populations, and the singlet-triplet splitting is unimportant. At high temperature, two electrons occupy the charge excited state, and form the FO regime, like in bulk. For finite $U$, we calculate the entropy and the spin susceptibility of the molecule by the exact diagonalization. Figure [2] shows the impurity entropy and spin susceptibility of the molecule are identical to the ones in the Lieb lattice, except for the artificial SC regime due to the artificially broadening of the flat band. In the flat band lattices, only the flat band and the impurity are essential to the Kondo problem, and all dispersive bands are irrelevant. In order to check whether any dispersive band is irrelevant to the Kondo problem or only the pseudo-gap bands in the Lieb lattice are irrelevant, we additionally consider two cases. In the first case, the flat band is isolated from other dispersive bands by energy gaps. This case can be achieved by including the intrinsic spin-orbit coupling (SOC) [23]. This SOC is the spin and direction dependent hopping between next-nearest-neighbor $A$ sites. The SOC Hamiltonian can be written as $H_{\text{SOC}} = i\lambda \sum_{\langle(i,j)\rangle,\sigma} \nu_{ij} \sigma c_i^\dagger c_j \sigma$, where $\lambda$ is the SOC strength, $\nu_{ij} = \pm 1$ depends on the clockwise (anticlockwise) hopping between $A$ sites [23]. The SOC in the Lieb lattice separates the flat band from two dispersive bands by the energy gaps, as one can see in Fig. [1]. In the second case, we study the Kondo problem in a toy model, where the DOS consists of a constant DOS and a flat-band feature. The DOS in this toy model reads

$$\rho_c(\omega) = \left\{ \begin{array}{ll}
\frac{1}{N} \left( \frac{1}{2\eta} + \frac{\eta}{\pi \omega^2 + \eta^2} \right), & \text{for } |\omega| \leq D, \\
0, & \text{otherwise}
\end{array} \right.,$$

(3)

where $N = 1 + 2 \arctan(D/\eta)/\pi$ is the normalized factor of the DOS. The first term in the toy model DOS is the constant DOS, which represents conduction electrons of conventional metals. The second term represents a flat band with the Lorentzian broadening $\eta$. The DOS of this toy model is also plotted in Fig. [1]. In Fig. [3] we plot the impurity entropy and spin susceptibility of these two models. They are precisely identical to the ones of the original Lieb lattice described in Eq. [1]. These results indicate in the presence of a flat band, only the flat band is relevant to the Kondo problem, and all dispersive bands are irrelevant. This

FIG. 3: (Color online) The temperature dependence of the impurity entropy ($S_{\text{imp}}$) and the spin susceptibility ($T_{\text{spin}}$) for the impurity placed at $A$ site of the Lieb lattice with SOC ($\lambda = 0.1$) (the green dashed lines), without SOC (the black solid lines), and of the toy model in Eq. (3) (the red dotted lines). The broadening parameter $\eta = 10^{-6}$. The model parameters $\Gamma = 0.01, U = 0.2, \varepsilon_f = -0.1$. 


dispersive band quenching is independent on the position and properties of the dispersive bands. One may expect in the limit $\eta \to 0$, the artificial SC regime will disappear, and only the molecular SC is stable at low temperature. In the flat band lattices, the net hopping vanishes, and one may suggest that the flat band state yields essentially an analogue of the ligand orbital. However, the Bloch state of the flat band in the Lieb lattice is a combination of $A$-site electrons in both the $x$ and $y$ directions $\psi(k) = \cos(k_y/2)c_{A_x}(k) - \cos(k_x/2)c_{A_y}(k)$, where $c_{A_x}(k)$ represents the Bloch electron of a $A$ site in the $\alpha$ direction. Therefore, if the impurity hybridizes with the flat band state then it would also result the hybridizations with the electrons at $A$ sites in both the $x$ and $y$ directions. In the considered model in Eq. (1), the impurity hybridizes with electrons at a single $A$ site either in the $x$ or $y$ direction. In this case, the impurity effectively hybridizes with electrons at both the flat and dispersive bands. This yields the Kondo problem in many band systems, but the band flatness quenches the participation of all dispersive electrons in the Kondo singlet formation, and reduces the many-body Kondo effect to the two-electron molecular one.

The scattering in the Lieb lattice due to the impurity is determined by the $T$-matrix, which essentially relates to the impurity spectral function. The quasiparticle interference also relates to the impurity spectral function. In Fig. 4 we plot the spectral function of impurity in the molecular SC regime. In contrast to the Kondo effect in conventional metals, the spectral function of impurity does not exhibit the Kondo resonance at the Fermi energy. Instead of the Kondo resonance, two narrow peaks and two broader peaks appear on the incoherent background of the dispersive bands of the Lieb lattice. The narrow peaks are the spin excitation and the broader peaks are the charge excitation as the ones in the molecule [2]. The separation of the spin and charge excitations is essentially an electron correlation effect.

In summary, we have showed how the band flatness prevents the participation of dispersive electrons in the Kondo singlet formation and reduces the many-body Kondo problem to the two-electron one. The impurity contributions to the thermodynamical and dynamical quantities in the molecular Kondo effect are qualitatively different in comparison with the ones in the conventional Kondo effect. From the obtained results of the toy model, we conclude that the molecular Kondo effect can exist not only in the flat band systems, but also in any systems with a narrow band. The necessary condition of the narrow band is $\eta < T_K$, where $\eta$ is the half width of the narrow band, and $T_K$ is the Kondo temperature of the two-electron molecule. The molecular Kondo temperature depends only on the impurity properties and the hybridization. In strong correlation regime, $T_K \approx |V|^2/|\varepsilon_f - \varepsilon_c|$ [2], and it would higher than the one in the conventional Kondo effect. The molecular Kondo effect would be observed in the temperature range $\eta < T < T_K$. This hints a possibility for experimental observation of the molecular Kondo effect or an entanglement of two spin qubits in materials.

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