UNIVERSALITY CLASS OF NON-FERMI LIQUID BEHAVIOR IN MIXED VALENCE SYSTEMS[1]

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ABSTRACT

A generalized Anderson single-impurity model with off-site Coulomb interactions is derived from the extended three-band Hubbard model, originally proposed to describe the physics of the copper-oxides. Using the abelian bosonization technique and canonical transformations, an effective Hamiltonian is derived in the strong coupling limit, which is essentially analogous to the Toulouse limit of the ordinary Kondo problem. In this limit, the effective Hamiltonian can be exactly solved, with a mixed valence quantum critical point separating two different Fermi liquid phases, *i.e.* the Kondo phase and the empty orbital phase. In the mixed valence quantum critical regime, the local moment is only partially quenched and X-ray edge singularities are generated. Around the quantum critical point, a new type of non-Fermi liquid behavior is predicted with an extra specific heat $C_{imp} \sim T^{1/4}$ and a singular spin-susceptibility $\chi_{imp} \sim T^{-3/4}$. At the same time, the effective Hamiltonian under single occupancy is transformed into a resonant-level model, from which the correct Kondo physical properties (specific heat, spin susceptibility, and an enhanced Wilson ratio) are easily rederived. Finally, a brief discussion is given to relate these theoretical results to observations in UPd_xCu_{5-x} ($x = 1, 1.5$) alloys, which show single-impurity critical behavior consistent with our predictions.

I. INTRODUCTION

Correlated electron systems ranging from heavy-fermions to high-temperature supercon-
ductors exhibit a fascinating variety of anomalous behavior. An issue of considerable current
debate is to what extent these systems in the normal state can be described as Fermi liquids
(FL) where the low-energy excitations have a one-to-one correspondence to those of a nonin-
teracting Fermi gas with the well-known behavior of a specific heat $C = \gamma T$, a temperature
independent Pauli susceptibility χ, and a low temperature electrical resistivity $\rho \approx AT^2$.
Most previous investigations on heavy-fermion systems, in particular, on the mixed valence
problem are carried out within the framework of the FL theory. In the meantime a phe-
nomenological marginal Fermi liquid (MFL) theory [1], proposed for high-temperature su-
perconductors to explain certain features of the observed diversified anomalies, has brought
about a lot of new developments in this active field of research.

Recently, a lot of strong evidence of non-FL behavior has been reported for several
heavy fermion systems [2], including $U_xY_{1-x}Pd_3$ [3] and UPd_xCu_{5-x} alloys [4–6]. In some
of these systems, the non-FL behavior may be due to a $T = 0$ quantum phase transition
of cooperative origin [2], while in the others the singular behavior of thermodynamical
and transport properties is consistent with a single-impurity critical scaling [6]. Since no
reliable methods have been devised so far to study the microscopic mechanism for the non-
FL behavior in any lattice models, it is thus expected that the investigations of the related
impurity models would shed some light on the basic physics of the lattice models, in the same
sense as the original Anderson single-impurity model vs the single band Hubbard model (or
Anderson lattice model). Various impurity models have been studied to explore the possible
non-FL behavior [7–18]. In particular, the two-channel Kondo system, intensively studied
using different methods [7–10] displays a kind of MFL behavior. However, it is not clear at
all how to directly relate such a two-channel Kondo model to the real correlated f-electron
heavy-fermion systems and high-temperature superconductors. In fact, a long standing
puzzle of the mixed valence problem, namely to understand the complexity of phenomena

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in realistic systems in terms of fundamental physical concepts [19], is still not fully resolved. However, it seems to us that the key issue is whether the FL picture is correct for the mixed valence state.

The mixed valence phenomena [20] usually occur in rare-earth compounds in which the proximity of the 4f-level to the Fermi surface leads to substantial charge (valence) fluctuations and instabilities of the magnetic moment. Basically, the mixed valence state can be thought of as a mixture of two bonding states $4f^n(5d6s)^m$ and $4f^{n-1}(5d6s)^{m+1}$, which are nearly degenerate from the quantum mechanical point of view. This situation must be understood in terms of the hybridization of the above two configurations so that the hybridized level is only partially occupied in the low-energy excitations. Although such a situation bears a strong resemblance to the crossover of the single-impurity problem from free moment behavior at high temperature to a strong-coupling FL regime in the Kondo ground state. However, that crossover does not coincide with significant valence change in most mixed valence systems [20]. It was argued that the Friedel sum rule (in the sense of local charge neutrality) is important for the mixed valence problem and it should be satisfied for both valence states. In this sense the usual Anderson model is not complete (because the Friedel sum rule cannot be satisfied for two different valence states by varying only one parameter (the $f-$ level)), so one should extend it to include the screening mechanism from the $5d6s$ electrons to describe the $4f$ charge fluctuations [21,19].

Recently, the interest to this problem has been revived in connection with high T_c superconductors. Varma and others [13–16] have considered a generalized Anderson model with finite-range Coulomb interactions, equivalent to a single-site version of the extended three-band Hubbard model proposed originally to describe the physics of copper-oxide superconductors. The numerical evidence for a mixed-valence quantum critical point came from a Wilson renormalization group study [13], while a strong coupling limit was argued and considered for this critical point later [15]. Inspired by these studies, two of us [14] have shown that using the renormalization-group analysis a phase diagram with a mixed valence quantum critical regime separating the Kondo phase and the empty orbital phase,

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can be deduced. It has also been shown [14] that the strong coupling limit can be derived straightforwardly from the original Hamiltonian using the canonical transformations and an exact solution to this model can be found in this limit. However, the physics behind the mixed valence state has not been fully revealed. The two basic important questions are: How to derive a complete effective model Hamiltonian in the strong coupling limit and what are the generic physical properties of the mixed valence state?

In the present paper, we address these unsolved problems in the infinite-U generalized Anderson single-impurity model with finite-range Coulomb interactions. Through two successive canonical transformations in the bosonic representation, we can derive an effective Hamiltonian in a particular strong coupling limit, which is analogous to the Toulouse limit of the ordinary Kondo problem [22]. In this limit, the effective Hamiltonian can be exactly solved, with a mixed valence quantum critical point separating two different Fermi liquid phases, $i.e.$ the Kondo phase and the empty orbital phase. In this mixed valence quantum critical regime, the local moment is only partially quenched and X-ray edge singularities are generated. Around this critical point, a new type of non-Fermi liquid behavior is predicted with an extra specific heat $C_{imp} \sim T^{1/4}$ and a singular spin-susceptibility $\chi_{imp} \sim T^{-3/4}$. In the meantime, the effective Hamiltonian under single occupancy is transformed into a resonant-level model [23], from which the correct Kondo physical properties (specific heat, spin susceptibility, and enhanced Wilson ratio) can be easily rederived. Finally, a brief discussion is given to relate our results with the experimental observations in UPd_xCu_{5-x} ($x = 1, 1.5$) alloys.

The arrangement of the paper is as follows: We first derive the model Hamiltonian from the extended three-band Hubbard model in Section II. Then, in Section III a nonperturbative approach for this single impurity model is formulated and a complete effective Hamiltonian is presented. In Section IV, the exact calculations of the physical properties in the strong-coupling limit are presented. Finally, discussions on experiments are given in Section V, while concluding remarks are made in Section VI.

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II. DERIVATION OF THE LOCAL IMPURITY MODEL FROM THE
EXTENDED THREE-BAND HUBBARD MODEL

The extended three-band Hubbard model is based on the observation that the chemistry of the copper-oxides is unique in that charge fluctuations between the cations and the anions controlled by their mutual interactions occur at low-energies [24]. Such dynamical effects were expected to qualitatively change the low-energy response, compared with the single band Hubbard model and its large Hubbard U limit, the $t-J$ model. The model is composed of d hole states on the copper sites (one hole per copper in the undoped material) in $d_{x^2-y^2}$ orbitals which are strongly hybridized with p σ-orbitals on the neighboring oxygen sites. As the undoped material is a magnetic insulator, the holes on the copper sites must be localized by a reasonably strong on-site Coulomb interaction. Also included are the finite-range Coulomb repulsions between oxygen electrons on nearest-neighbor sites of the localized copper electrons. The corresponding Hamiltonian is given by:

$$
H = \sum_{i,\sigma} \epsilon_d d_{i,\sigma}^\dagger d_{i,\sigma} + \sum_{\vec{k},\sigma}(\epsilon_{\vec{k}} - \mu) p_{\vec{k},\sigma}^\dagger p_{\vec{k},\sigma} + U \sum_i d_{i,\uparrow}^\dagger d_{i,\uparrow} d_{i,\downarrow}^\dagger d_{i,\downarrow}
$$
$$
+ \frac{1}{\sqrt{N}} \sum_{i,\vec{k},\sigma}(t_{i,\vec{k}} p_{\vec{k},\sigma}^\dagger d_{i,\sigma} + h.c.) + \frac{1}{2N} \sum_{i,\vec{k},\vec{k}',\sigma} V_{i,\vec{k},\vec{k}'}(p_{\vec{k},\sigma}^\dagger p_{\vec{k}',\sigma} - p_{\vec{k}',\sigma} p_{\vec{k},\sigma}^\dagger)(\sum_{\sigma'} d_{i,\sigma'}^\dagger d_{i,\sigma'} - \frac{1}{2}), \quad (1)
$$

where $p_{\vec{k},\sigma}$ is the Bloch representation of the oxygen orbitals, while $V_{i,\vec{k},\vec{k}'}$ is the Fourier transform of the Coulomb interactions of the $i-$ site copper with neighboring oxygens, and N is the total number of copper-oxygen cells. The rest of notation has obvious meaning. As pointed out in the Introduction, the above lattice model has so far proven intractable to give us reliable information on the low-energy physics of the system. However, one can regard strong coupling in the lattice models as a low-dimensional critical phenomenon involving long-time fluctuations at each localized site, but no critical fluctuations in space. The long-time fluctuations at each site are independent because of the local conservation laws when coherent effects and inter-impurity interactions are weak. Therefore, one can use a single-impurity model to describe the copper-oxides or heavy-fermion metals under the physical hypothesis that the essential new physics is local in real space, on the scale

of a lattice constant, so all the interesting effects are in the time or frequency domain. If the singularities found in the impurity problem do not depend on any special symmetries lost when going from the single impurity to the lattice, they are likely to be relevant to the behavior of the full lattice problem as well. Consider now the single-site (copper site) version of Eq. (1) in the following form:

$$
H = \sum_{\sigma} \epsilon_d d_\sigma^\dagger d_\sigma + \sum_{\vec{k},\sigma} (\epsilon_{\vec{k}} - \mu) p_{\vec{k},\sigma}^\dagger p_{\vec{k},\sigma} + U d_\uparrow^\dagger d_\uparrow d_\downarrow^\dagger d_\downarrow
$$
$$
+ \frac{1}{\sqrt{N}} \sum_{\vec{k},\sigma} (t_{\vec{k}} p_{\vec{k},\sigma}^\dagger d_\sigma + h.c.) + \frac{1}{2N} \sum_{\vec{k},\vec{k}',\sigma} V_{\vec{k},\vec{k}'} (p_{\vec{k},\sigma}^\dagger p_{\vec{k}',\sigma} - p_{\vec{k}',\sigma} p_{\vec{k},\sigma}^\dagger)(\sum_{\sigma'} d_{\sigma'}^\dagger d_{\sigma'} - \frac{1}{2}), \qquad (2)
$$

where we set the single impurity at the origin of the coordinates and, as usual, assume the $d_{x^2-y^2}$ orbitals are non-degenerate so that the quantum numbers (l_d, m_d) describing the orbital angular momentum, are fixed. It should be pointed out that this single-impurity model is still a three-dimensional system with two different angular momentum orbitals of the d-electrons and p-electrons. In the following, we have to reduce this three dimensional model to a one-dimensional model by projecting the p σ-orbitals onto the $d_{x^2-y^2}$ orbitals.

First of all, we transform the plane wave representation of the p-electrons to the spherical representation in view of the assumed spherical symmetry about the impurity site.

$$
p_{\vec{k},\sigma} = \sum_{l,m} < \hat{k} \mid l, m > C_{k,\sigma,l,m}, \qquad (3)
$$

where we have used the definition $\vec{k} = (k, \hat{k})$ and the quantum number m can take values $-l, -l+1, ..., +l$. If we project the p σ-orbitals onto the d orbitals, the angular quantum number l is required to take only one value, that is the angular quantum number of the d orbital $l = l_d$. In what follows, this quantum number is dropped, and the quantum number m is regarded as a "channel" index of the p orbital electrons. Since the dispersion relation of the p-electrons also has spherical symmetry, the kinetic energy term in Eq. (2) $\sum_{\vec{k},\sigma}(\epsilon_{\vec{k}}-\mu)p_{\vec{k},\sigma}^\dagger p_{\vec{k},\sigma}$ is transformed into $\sum_{k,\sigma,m}(\epsilon_k - \mu)C_{k,\sigma,m}^\dagger C_{k,\sigma,m}$, which implies there are several conduction electron channels in the reduced model. At the same time, the hybridization term between the d- and p-electrons $\frac{1}{\sqrt{N}}\sum_{\vec{k},\sigma}(t_{\vec{k}}p_{\vec{k},\sigma}^\dagger d_\sigma + h.c.)$ is changed into $\frac{1}{\sqrt{N}}\sum_{k,\sigma}(t_k C_{k,\sigma,m_d}^\dagger d_\sigma + h.c.)$.

As required by symmetry, the localized d orbitals can hybridize only with p orbitals with the same angular quantum numbers. Due to the non-degeneracy of the d orbitals, there is only one channel with $m = m_d$ of p-electrons hybridizing with the local d orbitals, which in the following is called hybridizing channel and the others are called screening channels.

Second, the finite range Coulomb interaction between the localized orbitals and the delocalized orbitals, or the X-ray edge (XRE) like potential scattering, is considered. Due to the spherical symmetry about the impurity site, the scattering potential $V_{\vec{k},\vec{k}'}$ depends only on the angle between $\hat{k}$ and $\hat{k}'$, so it can be expanded as

$$\sum_{l,m} V_{k,k',l,m} < \hat{k} \mid l,m >< l,m \mid \hat{k}' >,$$

where the only remaining term in the summation over the angular momentum is $l = l_d$. Finally, putting everything together, the complete form of the reduced one-dimensional single-impurity Hamiltonian is obtained as:

$$H = \sum_{k,\sigma,m} (\epsilon_k - \mu) C_{k,\sigma,m}^\dagger C_{k,\sigma,m} + \sum_\sigma \epsilon_d d_\sigma^\dagger d_\sigma + U d_\uparrow^\dagger d_\uparrow d_\downarrow^\dagger d_\downarrow + \frac{t}{\sqrt{N}} \sum_{k,\sigma} (C_{k,\sigma,m_d}^\dagger d_\sigma + h.c.)$$
$$+ \frac{1}{2N} \sum_{k,k',\sigma} \sum_{\{m = -l_d, .. + l_d\}} V_m (C_{k,\sigma,m}^\dagger C_{k',\sigma,m} - C_{k',\sigma,m} C_{k,\sigma,m}^\dagger)(\sum_{\sigma'} d_{\sigma'}^\dagger d_{\sigma'} - \frac{1}{2}), \qquad (4)$$

where, without loss of any generality, the hybridization strength t_k and the Coulomb interaction parameters $V_{k,k',m}$ have been further assumed to be momentum independent, as in the usual treatments of the Anderson single-impurity model. This is the so-called local copper-oxide model or generalized Anderson single-impurity model with finite-range Coulomb interactions used to describe the local version of non-FL properties of the copper-oxide compounds [13–15]. Here we have presented an explicit derivation. Although the derivation itself is given in terms of copper-oxygen orbitals, valid only for cuprates, the charge fluctuation physics, incorporated here via including the $d-$orbitals and finite range Coulomb interactions between d and p electrons, is also materialized in other mixed valence compounds, especially in heavy fermion systems. Therefore, this model can be applied to these systems as well. It is worth mentioning that the infinite dimensional technique has also been used to study the above extended three-band Hubbard model [17], and a single-channel

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generalized Anderson single-impurity model with self-consistent condition has been derived. Since the infinite-dimensional approximation overemphasizes the dimensional symmetries, it, probably, will miss some other important symmetry properties in the considered correlated electron systems, and the most important mixed valence physics we are concerned with (the screening effects) is not included in that generalized Anderson single-impurity model.

III. BOSONIZATION FOR THE GENERALIZED ANDERSON
SINGLE-IMPURITY MODEL

Usually, the interesting low-energy physics contained in the above single-impurity model involves only two configurations: $n_d = 0$ and $n_d = 1$, and we can remove the $n_d = 2$ configuration by letting $U \rightarrow \infty$. According to the numerical RG analysis for the usual Anderson impurity model, apart from the particle-hole symmetric case, reducing to the Kondo model, particular attention should be paid to the asymmetric case [25]. In the infinite-U limit, the model Hamiltonian is defined by $H = H_h + H_s$, where

$$H_h = \sum_{k,\sigma} \epsilon_k C_{k,\sigma,0}^\dagger C_{k,\sigma,0} + \epsilon_d n_d + \frac{h}{2} \sum_\sigma \sigma n_{d,\sigma} + t \sum_\sigma (C_{\sigma,0}^\dagger d_\sigma + h.c.) + \frac{h}{2} \sum_{k,\sigma} \sigma C_{k,\sigma,0}^\dagger C_{k,\sigma,0}$$

$$+ V \sum_\sigma (C_{\sigma,0}^\dagger C_{\sigma,0} - \frac{1}{2})(n_d - 1) + \frac{J}{4} \sum_{\sigma,\sigma'} C_{\sigma,0}^\dagger \vec{\sigma} C_{\sigma',0} \sum_{\mu,\nu} d_\mu^\dagger \vec{\sigma} d_\nu$$

$$H_s = \sum_{k,\sigma,m>0} \epsilon_k C_{k,\sigma,m}^\dagger C_{k,\sigma,m} + \sum_{\sigma,m>0} V_m (C_{\sigma,m}^\dagger C_{\sigma,m} - \frac{1}{2})(n_d - \frac{1}{2}) + \frac{h}{2} \sum_{k,\sigma,m>0} \sigma C_{k,\sigma,m}^\dagger C_{k,\sigma,m}, \quad (5)$$

where $C_{\sigma,m} = \frac{1}{\sqrt{N}} \sum_k C_{k,\sigma,m}$ is the conduction electron operator at the origin of the coordinates, $n_d = \sum_\sigma n_{d,\sigma}$, N is the number of the lattice sites, and we have separated the Hamiltonian into the hybridizing ($m = 0$) and screening parts ($m \neq 0$). The chemical potential of the conduction electrons has been chosen to be zero and the energy level of the local impurity ϵ_d is also assumed to be very close to it because of the character of the mixed valence state. We include a uniform external magnetic field h to calculate the total spin susceptibility enhancement. The infinite U limit keeps the low-energy physics of the model, but we should work under a local constraint $n_d \leq 1$, which is really crucial for determining

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the physical behavior of the low-energy excitations. Equally, we can rewrite H_h in another form, which is useful for the following analysis.

$$H_h = \sum_{k,\sigma} \epsilon_k C_{k,\sigma,0}^\dagger C_{k,\sigma,0} + \epsilon_d n_d + \frac{h}{2} \sum_\sigma \sigma n_{d,\sigma} + t \sum_\sigma (C_{\sigma,0}^\dagger d_\sigma + h.c.) + \frac{h}{2} \sum_{k,\sigma} \sigma C_{k,\sigma,0}^\dagger C_{k,\sigma,0}$$

$$+ V_0 \sum_\sigma (C_{\sigma,0}^\dagger C_{\sigma,0} - \frac{1}{2})(n_{d,\sigma} - \frac{1}{2}) + V_0' \sum_\sigma (C_{\sigma,0}^\dagger C_{\sigma,0} - \frac{1}{2})(n_{d,\bar{\sigma}} - \frac{1}{2}) + V_\perp \sum_\sigma C_{\sigma,0}^\dagger C_{\bar{\sigma},0} d_{\bar{\sigma}}^\dagger d_\sigma, \quad (6)$$

where $V_0 = (V + \frac{J_\perp}{4})$ is the parallel spin scattering potential, $V_0' = (V - \frac{J_\perp}{4})$ is the opposite spin scattering potential, and $V_\perp = \frac{J_\perp}{2}$ is the spin-flip scattering potential.

We first bosonize the screening part. Note that it has only one Fermi point for each channel and the dispersion is linearized $\epsilon_k = (k - k_F)/\rho$ with a cutoff k_D and $\rho = (h v_F)^{-1}$, so we can define the bosonic operators as [26],

$$b_{k,\sigma,m} = \frac{1}{\sqrt{kN}} \sum_{q=0}^{k_D-k} C_{q,\sigma,m}^\dagger C_{q+k,\sigma,m}, \quad b_{k,\sigma,m}^\dagger = \frac{1}{\sqrt{kN}} \sum_{q=k}^{k_D} C_{q,\sigma,m}^\dagger C_{q-k,\sigma,m}, \quad k > 0,$$

which obey the standard commutation relations. Since the spin degrees of freedom of the screening channel electrons are trivially involved, they can be separated from H_s, which then becomes

$$H_s^b = \sum_{k,m>0} \frac{k}{\rho}(a_{k,m}^\dagger a_{k,m} + e_{k,m}^\dagger e_{k,m}) + \sum_{k,m>0} V_m \sqrt{\frac{2k}{N}}(a_{k,m}^\dagger + a_{k,m})(n_d - \frac{1}{2})$$

$$+ \frac{\sqrt{2}h}{4\pi} \sum_{k>0,m} \sqrt{\frac{k}{N}} \int dx[(e_{k,m}e^{ikx} + e_{k,m}^\dagger e^{-ikx})], \quad (7)$$

where $a_{k,m} = \frac{1}{\sqrt{2}}(b_{k,\uparrow,m} + b_{k,\downarrow,m})$ and $e_{k,m} = \frac{1}{\sqrt{2}}(b_{k,\uparrow,m} - b_{k,\downarrow,m})$ are the charge- and spin-density operators, respectively. Moreover, we can assume $V_m = V_s$ for all $m > 0$ without loss of generality, so the channel index can be dropped. Thus, the screening part is simplified as a single spinless channel:

$$H_s^b = \sum_{k>0} \frac{k}{\rho} a_k^\dagger a_k + \sum_{k>0} \tilde{V}_s \sqrt{\frac{k}{N}}(a_k^\dagger + a_k)(n_d - \frac{1}{2}), \quad (8)$$

where we have dropped the spin-density operators because they are not involved in the interactions with the local impurity, while the charge-density part is kept: $a_k = \frac{1}{\sqrt{N_s}} \sum_{m>0} a_{k,m}$, $\tilde{V}_s \equiv \sqrt{2N_s}V_s$ and N_s is the number of the screening channels. Using the inverse bosonization, we can transform bosons back to fermions:

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$$H_s^f = \sum_k \epsilon_k s_k^\dagger s_k + \frac{\tilde{V}_s}{2N} \sum_{k,k'} (s_k^\dagger s_{k'} - s_{k'} s_k^\dagger)(n_d - \frac{1}{2}). \tag{9}$$

Interestingly enough, the strong electron-phonon interaction accompanying a valence change on a localized impurity bears the same form as H_s^b. So in the abelian representation, H_s can be thought of including the effects due to the large cell volume change (15 percent) accompanying the charge fluctuations, which is also expected to significantly alter the dynamics in the mixed valence problem. Therefore, the physics we will discuss in the strong-coupling limit to some extent reflects some essential aspects of the real mixed valence systems.

The same bosonization procedures can be used for the hybridizing electrons as well, and the boson operators are defined as before. Restricted to the low-lying excitations, the hybridizing Hamiltonian is expressed as:

$$\begin{aligned}
H_h^b &= \sum_{k>0,\sigma} \frac{k}{\rho} b_{k,\sigma}^\dagger b_{k,\sigma} + \epsilon_d n_d + \frac{h}{2}(n_{d,\uparrow} - n_{d,\downarrow}) + t\sum_\sigma (C_\sigma^\dagger d_\sigma + h.c.) + V_\perp \sum_\sigma C_\sigma^\dagger C_{\bar{\sigma}} d_{\bar{\sigma}}^\dagger d_\sigma \\
&+ V_0 \sum_{k>0,\sigma} \sqrt{\frac{k}{N}} (b_{k,\sigma}^\dagger + b_{k,\sigma})(n_{d,\sigma} - \frac{1}{2}) + V'_0 \sum_{k>0,\sigma} \sqrt{\frac{k}{N}} (b_{k,\sigma}^\dagger + b_{k,\sigma})(n_{d,\bar{\sigma}} - \frac{1}{2}) + \\
&+ \frac{h}{4\pi} \sum_{k>0} \sqrt{\frac{k}{N}} \int dx [(b_{k,\uparrow}^\dagger e^{ikx} + b_{k,\uparrow} e^{-ikx}) - (b_{k,\downarrow}^\dagger e^{ikx} + b_{k,\downarrow} e^{-ikx})]. \tag{10}
\end{aligned}$$

Here $C_\sigma(x) = \sqrt{k_D} exp\{\sum_{k>0} \frac{1}{\sqrt{kN}}(b_{k,\sigma} e^{ikx} - b_{k,\sigma}^\dagger e^{-ikx})\}$ is the fermion expression in terms of the bosons.

In order to derive an effective Hamiltonian in the Toulouse limit, we perform the following two canonical transformations

$$U = exp\{\sum_{k>0} \frac{1}{\sqrt{kN}}(a_k - a_k^\dagger)(n_d - \frac{1}{2})\}, \quad S = exp\{\sum_{\{k>0,\sigma\}} \frac{1}{\sqrt{kN}}(b_{k,\sigma} - b_{k,\sigma}^\dagger)(n_{d,\sigma} - \frac{1}{2})\}.$$

As a matter of fact, the first canonical transformation transfers the singularities of the screening channel into the hybridizing channel via the local impurity. The second canonical transformation not only makes the phase shifts due to hybridization and part of the parallel-spin XRE scattering compensate each other, but also simplifies the spin-flip scattering in the hybridizing channel. This way the hybridizing electrons become free for a special strong coupling limit, which shares the same physical meaning as the ordinary Toulouse limit of

the usual single-impurity single-channel Kondo model. The transformed model Hamiltonian is given by:

$$\tilde{H} = \sum_{k>0,\sigma} \frac{k}{\rho} b_{k,\sigma}^\dagger b_{k,\sigma} + (\epsilon_d - V_0' k_D) n_d + t \sum_\sigma (d_\sigma s_0 + h.c.) + V_\perp k_D \sum_\sigma d_\sigma^\dagger d_\sigma + \sum_{k>0} \frac{k}{\rho} a_k^\dagger a_k$$

$$+ (V_0 - \frac{1}{\rho}) \sum_{k>0,\sigma} \sqrt{\frac{k}{N}} (b_{k,\sigma}^\dagger + b_{k,\sigma})(n_{d,\sigma} - \frac{1}{2}) + V'_0 \sum_{k>0,\sigma} \sqrt{\frac{k}{N}} (b_{k,\sigma}^\dagger + b_{k,\sigma})(n_{d,\bar{\sigma}} - \frac{1}{2}) +$$

$$+ \frac{h}{4\pi} \sum_{k>0} \sqrt{\frac{k}{N}} \int dx [(b_{k,\uparrow} - b_{k,\downarrow}) e^{ikx} + (b_{k,\uparrow}^\dagger e^{ikx} - b_{k,\downarrow}^\dagger) e^{-ikx}]$$

$$+ (\bar{V}_s - \frac{1}{\rho}) \sum_{k>0} \sqrt{\frac{k}{N}} (a_k^\dagger + a_k)(n_d - \frac{1}{2}), \tag{11}$$

Note that the $\frac{h}{2}(n_{d,\uparrow} - n_{d,\downarrow})$ term in H_h has been exactly canceled by the canonical transformation S, which is similar to the Emery-Kivelson approach for the two-channel Kondo system [10]. A fermionic form is obtained by the inverse bosonization $\tilde{H}_{eff} = H_T + \delta H$, where

$$H_T = \sum_{k,\sigma} (\epsilon_k + \frac{h}{2}\sigma) C_{k,\sigma}^\dagger C_{k,\sigma} + (\epsilon_d - V_0' k_D) n_d + V_\perp k_D \sum_\sigma d_\sigma^\dagger d_\sigma$$

$$+ t \sum_\sigma (d_\sigma s_0 + h.c.) + \sum_k \epsilon_k s_k^\dagger s_k,$$

$$\delta H = (V_0 - \frac{1}{\rho}) \sum_\sigma (C_\sigma^\dagger C_\sigma - \frac{1}{2})(n_{d,\sigma} - \frac{1}{2}) + V_0' \sum_\sigma (C_\sigma^\dagger C_\sigma - \frac{1}{2})(n_{d,\sigma} - \frac{1}{2})$$

$$+ (\tilde{V}_s - \frac{1}{\rho})(s_0^\dagger s_0 - \frac{1}{2})(n_d - \frac{1}{2}). \tag{12}$$

This effective Hamiltonian, when $V_0 = \tilde{V}_s = \frac{1}{\rho}$ and $V_0' = 0$, reduces to H_T, which is the same as the strong coupling Hamiltonian argued by the renormalization-group analysis [14]. It is obvious that H_T is analogous to the Toulouse limit of the ordinary Kondo problem. It should be emphasized that the full effective model Hamiltonian in the strong coupling limit is derived here exactly, from which the corresponding physical properties in different phases can be calculated explicitly.

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IV. PHYSICAL PROPERTIES OF THE MODEL HAMILTONIAN IN THE TOULOUSE STRONG COUPLING LIMIT

A. Exact solution of the Toulouse limit Hamiltonian

Now, let us first study the strong-coupling limit Hamiltonian H_T with $V_0 = \tilde{V}_s = \frac{1}{\rho}$ and $V_0' = 0$, where only part of degrees of freedom of the local impurity $\alpha \equiv \frac{1}{\sqrt{2}}(d_\uparrow + d_\downarrow)$ is coupled to the conduction electrons, while the remaining part $\beta \equiv \frac{1}{\sqrt{2}}(d_\uparrow - d_\downarrow)$ is decoupled except for the constraint [14], [15]. Thus, the effective Hamiltonian is:

$$H_T = \sum_{k,\sigma}(\epsilon_k + \frac{h}{2}\sigma)C_{k,\sigma}^\dagger C_{k,\sigma} + \sum_k \epsilon_k s_k^\dagger s_k + (\epsilon_d - V_\perp k_D)n_\beta$$
$$+(\epsilon_d + V_\perp k_D)n_\alpha + \sqrt{2}t(s_0^\dagger \alpha^\dagger + h.c.), \tag{13}$$

where the local constraint $n_\alpha + n_\beta \leq 1$ will play a crucial role in determining the behavior of the system, and thus we must handle it exactly. In impurity zero-occupancy, the hybridizing and screening electrons are completely free with a zero phase shift due to the Friedel sum rule. In impurity single-occupancy, the localized impurity disappears, but the total energy of the system has a shift $(\epsilon_d - V_\perp k_D)$, and according to the Friedel sum rule the hybridizing electrons and the screening electrons have a unitarity phase shift $\frac{\pi}{2}$ per spin. This corresponds to the behavior of the Kondo model exactly at its FL fixed point. If we want to calculate the physical properties, the leading irrelevant interactions should be involved, equivalent to driving the system away from its fixed point [28].

When the impurity occupancy fluctuates between zero and one, it requires that $\epsilon_d \approx -V_\perp k_D$, corresponding to the mixed valence quantum critical point found in Ref. [13]. The crucial point is that H_T conserves n_β [14,15], which makes the following calculations available. The strong coupling limit Hamiltonian in the subspaces of $n_\beta = 0, 1$ are the following, without any constraints

$$H_{n_\beta=0} = \sum_{k,\sigma}(\epsilon_k + \frac{h}{2}\sigma)C_{k,\sigma}^\dagger C_{k,\sigma} + \sum_k \epsilon_k s_k^\dagger s_k + (\epsilon_d + V_\perp k_D)n_\alpha + \sqrt{2}t(s_0^\dagger \alpha^\dagger + h.c.), \tag{14}$$

$$H_{n_\beta=1} = \sum_{k,\sigma}(\epsilon_k + \frac{h}{2}\sigma)C_{k,\sigma}^\dagger C_{k,\sigma} + \sum_k \epsilon_k s_k^\dagger s_k + (\epsilon_d - V_\perp k_D). \tag{15}$$

Thus, we can carry out our calculations in the subspaces of n_β. Any eigenstates of H_T should be decomposed of the known eigenstates in the subspaces $n_\beta = 0, 1$:

$$| \Psi > = | \phi >_{n_\beta=0} + | \phi >_{n_\beta=1} . \tag{16}$$

In the $n_\beta = 0$ subspace, the constraint is satisfied for any α, so the quadratic Hamiltonian can be exactly solved, and a useful expectation associated with α is derived as:

$$< T_\tau \alpha(\tau)\alpha^\dagger(0) >_{n_\beta=0} = -T\sum_n \frac{e^{i\omega_n\tau}}{i\omega_n - \epsilon_\alpha + i\Gamma sign(\omega_n)} \approx \frac{1}{\pi\Gamma}\frac{\pi T}{sin(\pi T\tau)}, \tag{17}$$

where $\epsilon_\alpha = (\epsilon_d + V_\perp k_D)$, $\Gamma = \rho t^2$ is the resonance width of the α particle with the conduction electrons, and the phase shift of s-electrons at the Fermi point due to the presence of the local impurity α is found to be $\frac{\pi}{2} - tan^{-1}(\frac{\epsilon_\alpha}{\Gamma})$. Generally, it is known that the impurity energy level is not exactly pinned at the chemical potential, being very close to it. However, for simplicity, we assume the extreme condition letting $\epsilon_\alpha = 0$, so the above phase shift is chosen $\pi/2$ approximately. In the subspace $n_\beta = 1$, the condition $n_\alpha = 0$ is required by the local constraint, so the conduction electrons become free. More importantly, the essential physics of this mixed valence quantum critical regime is contained in the Green function of β in the restricted Hilbert space, which can be expressed as

$$G_\beta(\tau) = - < T_\tau \beta(\tau)\beta^\dagger(0) >$$
$$= -\theta(\tau) < \phi \mid \beta(\tau)\beta^\dagger(0) \mid \phi >_{n_\beta=0} + \theta(-\tau) < \phi \mid \beta^\dagger(0)\beta(\tau) \mid \phi >_{n_\beta=1} . \tag{18}$$

Due to the conservation of n_β, the first term can be regarded as an XRE absorption process, while the second term as an XRE emission process. ¿From the well-known work on XRE problem [27], the retarded Green's function β is proved to be

$$G_\beta^R(\tau) \approx -\theta(\tau)[\frac{\pi T}{\Gamma sin(\pi T\tau)}]^{1/4}. \tag{19}$$

This result shows that the single-particle Green function of β impurity displays XRE singularities or Anderson orthogonality catastrophe at this mixed valence quantum critical point. Based on these results, we find that

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$$< n_\beta > \sim T^{1/4}, \qquad < n_\alpha > = \frac{1}{2}, \qquad T \to 0. \tag{20}$$

Thus, we have $< n_d > = 1/2$, and from the Friedel sum rule, the local impurity *approximately* has a phase shift $\pi/4$ per spin at the Fermi point at zero temperature. Moreover, the correlation function of the charge density $\rho_d = n_\alpha + n_\beta - \frac{1}{2}$ can be evaluated as

$$< \rho_d(\tau)\rho_d(0) > \approx (\frac{1}{\pi\Gamma})^2 [\frac{\pi/\beta}{sin(\pi\tau/\beta)}]^2, \qquad \tau > 0. \tag{21}$$

However, the correlation function of the spin density $\sigma_d^z \equiv \alpha^\dagger\beta + \beta^\dagger\alpha$ is more subtle because of the local constraint. For $\tau > 0$, it is written as

$$< \sigma_d^z(\tau)\sigma_d^z(0) > = < \alpha^\dagger(\tau)\beta(\tau)\beta^\dagger(0)\alpha(0) >_{n_\beta=0} + < \beta^\dagger(\tau)\alpha(\tau)\alpha^\dagger(0)\beta(0) >_{n_\beta=1} .$$

When the local constraint is carefully considered, the nonzero contribution to the first expectation value is

$$< e^{H_0\tau}\alpha^\dagger\beta e^{-H_1\tau}\beta^\dagger\alpha >_{n_\beta=0} = < e^{H_0\tau}\alpha^\dagger e^{-H_1\tau}\alpha >_{n_\beta=0},$$

while the nonzero contribution to the second term is

$$< e^{H_1\tau}\beta^\dagger\alpha e^{-H_0\tau}\alpha^\dagger\beta >_{n_\beta=1} = < e^{H_1\tau}\alpha e^{-H_0\tau}\alpha^\dagger >_{n_\beta=0},$$

where H_0 is the effective Hamiltonian in the $n_\beta = 0$ subspace, and H_1 is the effective Hamiltonian in the $n_\beta = 1$ subspace. These expectation values can be evaluated in the same way as the retarded Green function of β [27]. We thus derive the final result

$$< \sigma_d^z(\tau)\sigma_d^z(0) > \approx 2[\frac{1}{\Gamma}\frac{\pi T}{sin(\pi T\tau)}]^{1/4}, \qquad \tau > 0. \tag{22}$$

The longitudinal spin-spin correlation function is dramatically different from the usual single-impurity model ($1/\tau^2$ in the low temperature limit). Here we have assumed $\epsilon_d \approx 0$. Since the local impurity decouples from the magnetic field and hybridizing electrons at this limit, the singular part of χ_{imp} and C_{imp} vanishes exactly. A perturbative calculation around the solvable strong coupling limit is needed to explore the generic behavior of the mixed valence phenomena.

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B. Toulouse limit in the single-occupancy

We now turn to the discussions away from the strong coupling limit. As a test, we have to recover the well-known results of the single-impurity model in the Kondo limit. Since $n_{d,\uparrow} + n_{d,\downarrow} = 1$ in the Kondo lmit, we have the following effective Hamiltonian:

$$\tilde{H} = \sum_{k>0,\sigma} \frac{k}{\rho} b_{k,\sigma}^{\dagger} b_{k,\sigma} + V_{\perp} k_D \sum_{\sigma} d_{\sigma}^{\dagger} d_{\sigma} + (V_0 - \frac{1}{\rho}) \sum_{k>0,\sigma} \sqrt{\frac{k}{N}} (b_{k,\sigma}^{\dagger} + b_{k,\sigma})(n_{d,\sigma} - \frac{1}{2})$$

$$+ V'_0 \sum_{k>0,\sigma} \sqrt{\frac{k}{N}} (b_{k,\sigma}^{\dagger} + b_{k,\sigma})(n_{d,\sigma} - \frac{1}{2})$$

$$+ \frac{h}{4\pi} \sum_{k>0} \sqrt{\frac{k}{N}} \int dx [(b_{k,\uparrow} - b_{k,\downarrow}) e^{ikx} + (b_{k,\uparrow}^{\dagger} - b_{k,\downarrow}^{\dagger}) e^{-ikx}], \tag{23}$$

where the hybridization term disappears due to the single occupancy constraint and we have dropped the screening channel because it decouples from the the impurity. Moreover, the charge degrees of freedom for the hybridizing electrons can also be separated out if we introduce the charge and spin-density operators as $e_k = \frac{1}{\sqrt{2}}(b_{k,\uparrow} + b_{k,\downarrow})$ and $b_k = \frac{1}{\sqrt{2}}(b_{k,\uparrow} - b_{k,\downarrow})$, respectively. After that, the effective Hamiltonian for the Kondo phase is obtained as:

$$H_{eff}^{K} = \sum_{k>0} \frac{k}{\rho} b_k^{\dagger} b_k + V_{\perp} k_D \sum_{\sigma} d_{\sigma}^{\dagger} d_{\sigma} + \frac{1}{\sqrt{2}}(V_0 - V'_0 - \frac{1}{\rho}) \sum_{k>0} \sqrt{\frac{k}{N}} (b_k^{\dagger} + b_k)(n_{d,\uparrow} - n_{d,\downarrow})$$

$$+ \frac{\sqrt{2}h}{4\pi} \sum_{k>0} \sqrt{\frac{k}{N}} \int dx [(b_{k,m} e^{ikx} + b_{k,m}^{\dagger} e^{-ikx})]. \tag{24}$$

It is very useful to perform the following canonical transformation

$$P = exp\{-\frac{1}{2} \sum_{k>0} \frac{1}{\sqrt{kN}} (b_k - b_k^{\dagger})(d_{\uparrow}^{\dagger} d_{\uparrow} - d_{\downarrow}^{\dagger} d_{\downarrow})\}. \tag{25}$$

When we transform the bosons back to fermions, H_{eff}^{K} becomes

$$\tilde{H}_{eff}^{K} = \sum_{k} (\epsilon_k + \frac{h}{\sqrt{2}}) C_k^{\dagger} C_k + V_{\perp} \sqrt{k_D} \sum_{k} (C_k^{\dagger} d_{\downarrow}^{\dagger} d_{\uparrow} + d_{\uparrow}^{\dagger} d_{\downarrow} C_k) + \frac{\sqrt{2}h}{4}(n_{d,\uparrow} - n_{d,\downarrow})$$

$$+ [\frac{1}{\sqrt{2}}(V_0 - V'_0 - \frac{1}{\rho}) + \frac{1}{2\rho}] \frac{1}{2N} \sum_{k,k'} (C_k^{\dagger} C_{k'} - C_{k'} C_k^{\dagger})(n_{d,\uparrow} - n_{d,\downarrow}) + \frac{\sqrt{2}h}{4}(n_{d,\uparrow} - n_{d,\downarrow}). \tag{26}$$

Note that due to the single-occupancy constraint $n_{d,\uparrow} + n_{d,\downarrow} = 1$, the local impurity is reduced to $SU(2)$ spin-1/2 operators:

$$d_{\uparrow}^{\dagger} d_{\downarrow} = S^{+}, \quad d_{\downarrow}^{\dagger} d_{\uparrow} = S^{-}, \quad \frac{1}{2}(d_{\uparrow}^{\dagger} d_{\uparrow} - d_{\downarrow}^{\dagger} d_{\downarrow}) = S^z.$$

In fact, the local impurity orbital can also be expressed as a $U(1)$ spin-1/2 representations in terms of spinless fermions without any constraints:

$$S^+ = f^\dagger, \quad S^- = f, \quad S^z = f^\dagger f - \frac{1}{2},$$

which is in fact the one-site Jordan-Wigner transformation for a spin-1/2 Pauli operator.

Thus, the final version of the Kondo effective Hamiltonian is

$$\tilde{H}_{eff}^K = \sum_k (\epsilon_k + \frac{h}{\sqrt{2}}) C_k^\dagger C_k + V_\perp \sqrt{k_D} \sum_k (C_k^\dagger f + f^\dagger C_k) + \frac{h}{\sqrt{2}} (f^\dagger f - \frac{1}{2})$$
$$+ [\sqrt{2}(V_0 - V_0' - \frac{1}{\rho}) + \frac{1}{\rho}] \frac{1}{2N} \sum_{k,k'} (C_k^\dagger C_{k'} - C_{k'} C_k^\dagger)(f^\dagger f - \frac{1}{2}). \tag{27}$$

This is a single-channel resonant-level model [23], from which the well-known Toulouse limit Hamiltonian [22] can be deduced when $V_0 - V_0' = \frac{1}{\rho}(1 - \frac{\sqrt{2}}{2})$:

$$\tilde{H}_{eff}^K = \sum_k (\epsilon_k + \frac{h}{\sqrt{2}}) C_k^\dagger C_k + V_\perp \sqrt{k_D} \sum_k (C_k^\dagger f + f^\dagger C_k) + \frac{h}{\sqrt{2}} (f^\dagger f - \frac{1}{2}). \tag{28}$$

Here it is exactly derived from the Anderson single-impurity model with the single-occupation constraint. Using the Toulouse limit conditions, the Fourier transformation of the f-electron propagator $G_f(\omega)$ is evaluated as

$$G_f(\omega) = [\omega - \frac{h}{\sqrt{2}} + i\Gamma_K sign(\omega)]^{-1}, \tag{29}$$

where $\Gamma_K = \rho V_\perp^2 k_D / 2$. The corresponding density of states is

$$\rho_f(\omega) = \frac{1}{\pi} \frac{\Gamma_K}{(\omega - \frac{h}{\sqrt{2}})^2 + (\Gamma_K)^2}.$$

This expression brings out the essential feature of the Kondo problem. In the strong coupling regime, the spin degrees of freedom of the local impurity have been quenched out by a conduction electron (forming a spin singlet), and other conduction electrons just hybridize with the impurity charge degrees of freedom with Lorentzian width Γ_K, or they only feel a resonant scattering potential provided by the spin singlet at the origin. Thus, the change of the free energy due to this hybridization may be calculated by using the density of states:

$$\delta F_{imp} = \frac{1}{\pi} \int_{-\infty}^{\infty} d\omega f(\omega) tan^{-1}(\frac{\Gamma_K}{\omega - \frac{h}{\sqrt{2}}}), \tag{30}$$

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where $f(\omega) = (e^{\beta\omega} + 1)^{-1}$. Then, it is straightforward to evaluate the impurity contribution to the entropy $lim_{T\to 0}lim_{h\to 0}S_{imp} = 0$, the specific heat $C_{imp} = \frac{\pi}{3\Gamma_K}T$, and the spin susceptibility $\chi_{imp} = \frac{1}{2\pi\Gamma_K}$. Thus, the known universal Wilson ratio $R_W = (\frac{T\chi_{imp}}{C_{imp}})/(\frac{T\chi_{bulk}}{C_{bulk}}) = 2$ is recovered [28,29].

C. Generic properties in the mixed valence quantum critical regime

Let us now concentrate on the physical properties of the mixed valence regime around the mixed valence quantum critical point. The effective Hamiltonian is given by $H_{eff}^{MV} = H_0 + \delta H$, where

$$
\begin{aligned}
H_0 &= \sum_{k,\sigma}(\epsilon_k + \frac{h}{2}\sigma)C_{k,\sigma}^\dagger C_{k,\sigma} + \sum_k \epsilon_k s_k^\dagger s_k + (\epsilon_d - V_\perp k_D)n_\beta \\
&\quad + (\epsilon_d + V_\perp k_D)n_\alpha + \sqrt{2}t(s_0^\dagger\alpha^\dagger + h.c.) \\
\delta H &= \frac{1}{2}(V_0 + V_0' - \frac{1}{\rho})\sum_\sigma(C_\sigma^\dagger C_\sigma - \frac{1}{2})(\rho_d - \frac{1}{2}) + \frac{1}{2}(V_0 - V_0' - \frac{1}{\rho})\sum_\sigma \sigma C_\sigma^\dagger C_\sigma \sigma_d^z \\
&\quad + (\tilde{V}_s - \frac{1}{\rho})(s_0^\dagger s_0 - \frac{1}{2})\rho_d,
\end{aligned}
\tag{31}
$$

where $\epsilon_d \approx -V_\perp k_D$ and δH is the perturbation away from the mixed valence quantum critical point. Obviously, there is a decoupling of charge and spin densities for the hybridizing electrons which makes our following calculations transparent. After that separation, we get

$$
\begin{aligned}
H_0 &= \sum_k(\epsilon_k + \frac{h}{\sqrt{2}})g_k^\dagger g_k + \sum_k \epsilon_k p_k^\dagger p_k + \sum_k \epsilon_k s_k^\dagger s_k + (\epsilon_d - V_0'k_D + V_\perp k_D)n_\alpha \\
&\quad + (\epsilon_d - V_0'k_D - V_\perp k_D)n_\beta + \sqrt{2}t(s_0^\dagger\alpha^\dagger + h.c.) \\
\delta H &= \frac{1}{\sqrt{2}}(V_0 + V_0' - \frac{1}{\rho})(p_0^\dagger p_0 - \frac{1}{2})(\rho_d - \frac{1}{2}) + \frac{1}{\sqrt{2}}(V_0 - V_0' - \frac{1}{\rho})(g_0^\dagger g_0 - \frac{1}{2})\sigma_d^z \\
&\quad + (\tilde{V}_s - \frac{1}{\rho})(s_0^\dagger s_0 - \frac{1}{2})\rho_d.
\end{aligned}
\tag{32}
$$

Here the spinless $p-$ and $g-$electrons describe the charge and spin degrees of freedom of the hybridizing electrons, respectively. H_0 corresponds to our mixed valence quantum critical point in the strong coupling limit. As follows from our calculated charge density and spin density correlation functions of the local impurity of H_0, only interactions associated with

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the spin density correlation function in the perturbations are singular. We also know the local propagator of the spin part of the hybridizing electrons

$$G_g(\tau) = - < T_\tau g_0^\dagger(\tau)g_0(0) >= k_D T \sum_n \int dk \frac{e^{i\omega_n \tau}}{i\omega_n - \frac{k}{\rho} - \frac{h}{\sqrt{2}}} \approx \rho \frac{\pi T}{sin(\pi T \tau)},$$

but $G_g(0) \approx \frac{\rho h}{\sqrt{2}}$ for $h \to 0$.

To the second order in perturbation, the singular contribution of δH to the impurity free energy reads as:

$$\Delta F_{imp} = -\frac{1}{2}\int_0^{1/T} d\tau < \delta H(\tau)\delta H(0) >$$
$$= -\frac{\lambda^2}{2}\{G_g^2(0)\int_0^{1/T} d\tau < \sigma_d^z(\tau)\sigma_d^z(0) > + \int_0^{1/T} d\tau G_g^2(\tau) < \sigma_d^z(\tau)\sigma_d^z(0) >\}, \qquad (33)$$

where $\lambda = \frac{1}{\sqrt{2}}(V_0 - V_0' - \frac{1}{\rho})$. It turns out that the first term yields the dominant contribution to χ_{imp}, while the second term yields the dominant contribution to C_{imp}. At low temperatures $(T \ll \Gamma)$, the asymptotic forms of the propagators can be used in the expression of ΔF_{imp} to yield

$$\Delta F_{imp} = -\frac{2\lambda^2 \rho^2 h^2}{\Gamma}(\frac{\Gamma}{\pi T})^{3/4}\int_0^{1/2T} \frac{\pi T}{sin^{1/4}(\pi T \tau)}d\tau - 2\lambda^2 \rho^2 \Gamma(\frac{\pi T}{\Gamma})^{5/4}\int_0^{1/2T} \frac{\pi T}{sin^{9/4}(\pi T \tau)}d\tau.$$
$$(34)$$

All integrals must be regularized by introducing an ultraviolet cut-off Γ^{-1}. Finally, the low-temperature singular behavior of the spin susceptibility and specific heat is found to be

$$\chi_{imp} = \frac{2\lambda^2 \rho^2}{\Gamma}A(\frac{\Gamma}{\pi T})^{3/4}, \qquad C_{imp} = \frac{\pi\lambda^2 \rho^2}{16}A(\frac{\pi T}{\Gamma})^{1/4},$$

where $A \equiv \frac{\Gamma(3/8)\Gamma(1/2)}{\Gamma(7/8)}$ and $\Gamma(x)$ is the Euler Gamma function. Higher order perturbation terms in λ yield subdominant contributions at low temperatures, and will not modify these results. Therefore, the behavior of susceptibility and specific heat obtained here is generic in the mixed valence regime. The spin susceptibility of the local impurity explicitly reveals the mixed valence physics around the strong coupling limit: *not fully quenched magnetic moment and exhibition of the XRE singularities.* Put it another way, *the local moment*

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fluctuations are essential for the mixed valence state. When we consider the leading power-law singularity of the spin susceptibility and specific heat, we find the effective Wilson ratio $T\chi_{imp}/C_{imp} = 32/\pi^2$, which should be observable in experiment. The present method allows us to see explicitly how the dominant singular behavior of the thermodynamic quantities is governed by the leading irrelevant interactions in the strong coupling Hamiltonian, and thereby correctly captures the generic properties of the generalized Anderson single-impurity model in the mixed valence phase.

V. EXPERIMENTS ON UPd_xCu_{5-x} ALLOYS

Now we try to relate the above obtained results to real strongly correlated f-electron heavy fermion systems, *e.g.* UPd_xCu_{5-x} alloys in which U ions have partially-filled f-electron shells and give rise to magnetic moments interacting with the spin and charge of the conduction electrons. What is striking about these materials is the non-FL behavior of their physical properties which exhibit weak power law or logarithmic divergences in temperature and suggest the existence of a critical regime at $T = 0$ [2,4–6].

The parent compound UCu_5 is a prototype Kondo impurity system at high temperatures. As temperature is lowered, the intersite interactions drive a transition to a long-range antiferromagnetic (AFM) order of incompletely compensated uranum moments at $15K$. But as Pd is substituted on the Cu sites, the AFM order is suppressed, with the ordering temperature being driven to zero. In particular, the recent neutron scattering experiments [5] showed that the magnetic response function for x=1 and x=1.5 has no appreciable momentum (except for the ionic form factor) and temperature dependence and has a scale invariant form $S(\omega) \sim \omega^{-1/3}$ at very low energy scale (less than 10 mev). Moreover, the specific heat and spin susceptibility measurements [4] also showed that between 1K and 10K the temperature variations for x=1 and x=1.5 $C_{imp}/T \sim \chi_{imp}$ apparently deviate from the logarithmic temperature dependence (expected for a two-channel Kondo model at low temperatures), and can be much better represented by a power law $C_{imp}/T \sim \chi_{imp} \sim T^{-\Delta}$ with $\Delta = 0.32$.

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Furthermore, the neutron data at various energies and temperatures [5] have been fitted by a single scaling function, and it has been argued that the existence of such a scaling behavior provides a strong evidence in favor of single-impurity critical phenomena [6]. The conformal dimension of the spin correlation extracted from this fitting $\Delta = 1/3$ is consistent with the specific heat, magnetic susceptibility and resistivity data [6]. On the other hand, it is very clear that neither the single channel Kondo (predicting the FL behavior) nor the two-channel Kondo (leading to logarithmic singularities) can provide any acceptable explanation for such a striking behavior. It is thus natural to expect that the additional charge fluctuations inherent in the mixed valence phenomena, may shed some light on this puzzle.

Here we propose a possible explanation for these experimental observations in terms of the generalized Anderson model considered in this paper. First, UPd_xCu_{5-x} with x=1 and x=1.5 may be described as mixed valence states because the f-electrons of U-ion is only partially filled and the impurity energy level is split in the crystalline field into a large number of sublevels with possibly one of them being close to the chemical potential of the conduction electrons. Second, there are probably strong screening interactions from the off-site conduction electrons and strong impurity-phonon interaction due to the large lattice distortion accompanying the impurity occupancy changes. Finally, due to the presence of strong screening and phonon interactions, the motion of the U-ion must drag a heavy screening cloud with it. Hence its motion is very "slow", so the correlations from the inter-impurity interaction are rather weak. Thus, we can use our generalized Anderson single-impurity model to describe these materials.

According to our calculations, we have found that the extra specific heat and spin susceptibility in the mixed valence quantum critical regime can be expressed as $C_{imp}/T \sim \chi_{imp} \sim T^{-3/4}$ in the strong-coupling limit. As for the magnetic response function $S(\omega)$ from the neutral scattering measurements, we can obtain it after performing Fourier transformation for the spin-spin density correlation derived in the strong coupling limit of the mixed valence regime. We found that in the extremely low-energy scale $S(\omega) \sim \omega^{-3/4}$. Apparently, the singularity exponent derived from our theoretical calculations (-3/4) is stronger than the

experimental results $\sim -1/3$. A possible way to recoincide these results is to note that in our treatment we have pushed the impurity scattering to the unitarity limit (phase shift $\pi/2$), while in realistic systems the unitarity limit may not be reached, so the exponents might be different. [30]. In view of the experimental relevance, it is very important to find other ways to treat this intriguing problem for cross-checking.

VI. CONCLUDING REMARKS

To summarize, in this paper we have considered a generalized Anderson model with screening channels, which can be considered as a single-site version of the three-band Hubbard model originally proposed to describe the cuprates. Using the bosonization technique and canonical transformations we have found the strong coupling Toulouse limit of the effective Hamiltonian which can be solved exactly. The physical properties around the mixed valence quantum critical point separating the two FL phases (the Kondo and the empty orbital phases) have been calculated explicitly to predict a new universality class of non-FL behavior.

Our strong coupling treatment of the mixed valence problem provides the following physical picture for the mixed valence state. In the hybridizing channel, the phase shift due to hybridization is compensated by the parallel-spin XRE scattering via transformation S, while the XRE scattering in the screening channel is converted into an effective hybridization with the local impurity via transformation U. However, only "half" of the local impurity (α particle) hybridizes with the screening electrons (in fact "holes") and gives rise to a standard FL behavior. The other "half" of the local impurity (β particle) does not mix with the screening electrons and its expectation value $< n_\beta > \sim T^{1/4}$ at low temperatures. Nevertheless, its dynamic fluctuations lead to XRE singularities and a divergent power-law susceptibility which are consistent with observations in UPd_xCu_{5-x} alloys with x=1 and x=1.5.

The non-trivial physics shown in this paper is grasped due to a careful treatment of the

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single occupancy constraint in the Toulouse limit. The essence of this constraint is to satisfy the unitarity condition, i.e., to use a complete set in the Hilbert space. Any mean-field type treatment of the constraint will certainly miss this basic point.

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