Valence transition in the periodic Anderson model

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Abstract. A very rich phase diagram has recently been found in CeCu$_2$Si$_2$ from high pressure experiments where, in particular, a transition between an intermediate valence configuration and an integral valent heavy fermion state has been observed. We show that such a valence transition can be understood in the framework of the periodic Anderson model. In particular, our results show a breakdown of a mixed-valence state which is accompanied by a drastic change in the f occupation in agreement with experiment. This valence transition can possibly be interpreted as a collapse of the large Fermi surface of the heavy fermion state which incorporates not only the conduction electrons but also the localized f electrons. The theoretical approach used in this paper is based on the novel projector-based renormalization method (PRM). With respect to the periodic Anderson model, the method was before only employed in combination with the basic approximations of the well-known slave-boson mean-field theory. In this paper, the PRM treatment is performed in a more sophisticated manner where both mixed as well as integral valent solutions have been obtained. Furthermore, we argue that the presented PRM approach might be a promising starting point to study the competing interactions in CeCu$_2$Si$_2$ and related compounds.

PACS. 71.10.Fd Lattice fermion models (Hubbard model, etc.) – 71.27.+a Strongly correlated electron systems; heavy fermions – 75.30.Mb Valence fluctuation, Kondo lattice, and heavy-fermion phenomena

1 Introduction

Since the discovery of a superconducting state formed by heavy quasi-particles in CeCu$_2$Si$_2$ this and related compounds have attracted a lot of scientific interest. Despite its long history only recently a whole variety of new physical phases has been observed which was possible by the intriguing development of experimental techniques. By substituting Si by Ge in the parent compound CeCu$_2$Si$_2$ a continuous change from a heavy fermion (HF) superconducting phase to an antiferromagnetic state was observed. An even more complex phase diagram has been found in pure CeCu$_2$Si$_2$ by applying high pressure. There two superconducting phases with different pairing mechanisms have been found besides an antiferromagnetic and a HF phase. Furthermore, a transition between intermediate and integral valence states has been observed. (For a recent review on superconductivity in Ce based HF materials see Ref. [5].)

From the theoretical point of view the periodic Anderson model (PAM) is considered to be the basic microscopic model for the investigation of HF systems. The PAM describes the interaction between localized, strongly correlated f and itinerant conduction electrons. In the limit of infinitely large Coulomb repulsion on f sites the PAM can be written as

\[ \mathcal{H} = \mathcal{H}_0 + \mathcal{H}_1, \]

\[ \mathcal{H}_0 = \varepsilon_f \sum_{i,m} \hat{f}_{im}^\dagger \hat{f}_{im} + \sum_{k,m} \varepsilon_k c_{km}^\dagger c_{km}, \]

\[ \mathcal{H}_1 = \frac{1}{\sqrt{N}} \sum_{k,i,m} V_k \left( \hat{f}_{im}^\dagger c_{km} c_{km}^\dagger - h.c. \right). \]

Here, \( \varepsilon_f \) and \( \varepsilon_k \), both measured from the chemical potential, are the excitation energies of localized f and itinerant conduction electrons. As a simplification, often both types of electrons are assumed to have the same angular momentum index m with \( \nu_f \) values, \( m = 1...\nu_f \). The infinitely large local Coulomb repulsion is taken into account by Hubbard operators

\[ \hat{f}_{im}^\dagger = f_{im}^\dagger \prod_{\tilde{m}(\neq m)} (1 - f_{\tilde{m}}^\dagger f_{\tilde{m}}) \]

which enable either empty or singly occupied f sites.

Due to the complexity of the PAM, most theoretical studies only focus on certain aspects of the rich phase diagrams of rare earth materials. Slave-boson mean-field (SB) methods, large-N expansions, and the dynamical mean-field theory have been applied to discuss the interplay...
between RKKY and Kondo interactions. Thereby, a transition between an antiferromagnetic phase and a paramagnetic state was discussed. On the other hand, to describe the valence transition and HF superconductivity in CeCu$_2$Si$_2$ an extended PAM was studied. This model includes an additional Coulomb interaction between $f$ and conduction electrons and was discussed within a slave-boson fluctuation approximation. 

In this paper we apply a novel projector-based renormalization method (PRM) to the PAM with the aim to address the question whether a valence transition, as experimentally observed in CeCu$_2$Si$_2$ [3,4], can occur in the plain model. For that purpose we extend in this paper our previous work on the PAM [10], which was restricted to the HF phase. The PRM provides a natural way to discuss the interplay of competing interactions which naturally emerge from the renormalization treatment of the PAM. Therefore, we believe that the PRM represents a suited approach for a deeper understanding of the rich phase diagram of CeCu$_2$Si$_2$ or of related compounds. However, in this paper we concentrate on the valence transition, nevertheless, we are able to sketch how superconducting phases and RKKY interactions could also be included in our approach.

This paper is organized as follows. In the next section we briefly describe the novel PRM approach [2] that is applied to the PAM in Sec. 3. Here, the Hubbard operators, introduced to take into account the infinitely large Coulomb repulsion on $f$ sites, cause the main problems of any theoretical approach. It will turn out that the well-known SB theory [11,12] as well as our recent analytical approach based on the PRM [10] do not sufficiently prevent from unphysical states with doubly occupied $f$ sites. In contrast, the modified PRM treatment of Sec. 3 strictly suppresses doubly occupied $f$ sites by taking into account electronic correlations by means of the Hubbard operators. Results are presented in Sec. 4 where mixed valent as well as integral valent states are found, and a valence transition is observed. Furthermore, we compare our results with the solutions of the SB theory and our PRM approach of Ref. [10]. Finally, we summarize in Sec. 5.

2 Methodology

The PRM approach [2] starts from a decomposition of a given many-particle Hamiltonian, $\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_1$, where the perturbation $\mathcal{H}_1$ should not contain any terms that commute with the unperturbed part $\mathcal{H}_0$. Thus, $\mathcal{H}_1$ represents transitions between eigenstates of $\mathcal{H}_0$ with different eigenenergies. In the following, we assume that the eigenvalue problem of $\mathcal{H}_0$ is solved,

$$\mathcal{H}_0 | n^{(0)} \rangle = E_n^{(0)} | n^{(0)} \rangle.$$ 

A crucial idea of the PRM is the definition of projection operators by

$$\mathbf{P}_\lambda \mathcal{A} = \sum_{m,n} | n^{(0)} \rangle \langle m^{(0)} | (\mathcal{A} | m^{(0)} \rangle - | n^{(0)} \rangle) \times \Theta(\lambda - | E_n^{(0)} - E_m^{(0)} |).$$

Note that $\mathbf{P}_\lambda$ and $\mathbf{Q}_\lambda = 1 - \mathbf{P}_\lambda$ are super-operators acting on ordinary operators $\mathcal{A}$ of the unitary space. $\mathbf{P}_\lambda$ projects on those parts of $\mathcal{A}$ which are formed by transition operators $| n^{(0)} \rangle \langle m^{(0)} |$ with energy differences $| E_n^{(0)} - E_m^{(0)} |$ less than a given cutoff $\lambda$. (The condition $\lambda < | E_n^{(0)} - E_m^{(0)} |$ less than a given cutoff $\lambda$.) On the other hand, $\mathbf{Q}_\lambda$ projects on the high-energy transitions of an operator. Note, in particular, that in Eq. (2) neither $| n^{(0)} \rangle$ nor $| m^{(0)} \rangle$ have to be low-energy eigenstates of $\mathcal{H}_0$.

Next, an effective Hamiltonian $\mathcal{H}_\lambda$ is derived from the original Hamiltonian $\mathcal{H}$ by an unitary transformation

$$\mathcal{H}_\lambda = e^{X_\lambda} \mathcal{H} e^{-X_\lambda},$$

where the anti-Hermitian generator of the transformation, $X_\lambda = -X_\lambda^\dagger$, shall be chosen in such a way that only transition operators (between eigenstates of $\mathcal{H}_0$) with transition energies less than the given cutoff $\lambda$ contribute to $\mathcal{H}_\lambda$. Thus, the condition

$$\mathbf{Q}_\lambda \mathcal{H}_\lambda = 0$$

must be fulfilled and will be used below to determine $X_\lambda$. Note that it is straightforward to evaluate Eqs. (3) and (4) in perturbation theory [9]. However, using an appropriate ansatz for the generator $X_\lambda$, the effective Hamiltonian $\mathcal{H}_\lambda$ can also be calculated in non-perturbative manner.

A renormalization scheme can be derived if the elimination procedure for the interaction $\mathcal{H}_1$ is not performed in one step but rather a sequence of unitary transformations of the form

$$\mathcal{H}_{(\lambda - \Delta \lambda)} = e^{X_{\lambda, \Delta \lambda}} \mathcal{H}_\lambda e^{-X_{\lambda, \Delta \lambda}},$$

is applied to the original Hamiltonian $\mathcal{H}$. Thus, transitions between eigenstates of $\mathcal{H}_0$ caused by the interaction $\mathcal{H}_1$ are eliminated in steps where the respective transition energies are used as renormalization parameter $\lambda$. Furthermore,

$$\mathbf{Q}_{(\lambda - \Delta \lambda)} \mathcal{H}_{(\lambda - \Delta \lambda)} = 0$$

is used to specify the generator $X_{\lambda, \Delta \lambda}$ of the unitary transformation. Note that Eqs. (5) and (6) describe a renormalization step that decreases the cutoff of the Hamiltonian from $\lambda$ to $(\lambda - \Delta \lambda)$, as one can see from a comparison with Eqs. (3) and (4). Therefore, difference equations for the $\lambda$ dependence of the Hamiltonian can be derived from (5) and (6), and we call the resulting equations for the parameters of the Hamiltonian renormalization equations. Note, that the solutions of these renormalization equations strongly depend on the parameters of the original Hamiltonian $\mathcal{H}_0$, and that the limit $\lambda \to 0$ provides the desired effective Hamiltonian without any interactions.
3 Renormalization of the PAM

In the following, we want to apply the framework of the PRM as discussed above to the PAM. It is well known that much of the physics of the PAM \[1\] can be understood in terms of an uncorrelated model, that is for vanishing Coulomb repulsion on \( f \) sites where the Hubbard operators \( f_{k,m}^{\dagger} \) are replaced by usual fermionic operators \( f_{k,m}^{\dagger} \). This model can be solved exactly. However, the parameters have to be renormalized appropriately. Various theoretical methods have been developed to generate renormalized Hamiltonians. Most popular is the one derived from slave-boson mean-field (SB) theory \[11,12\]. Note however that only HF type solutions can be obtained in this way. In particular, the SB solution breaks down if the original \( f \) level is located too far below the Fermi level \[13\] or, equivalently, if the hybridization strength between \( f \) and conduction electrons becomes too weak.

In the Hamiltonian \[1\] the Hubbard operators \( f_{k,m}^{\dagger} \) take care of the infinitely large local Coulomb repulsion on \( f \) sites where the Hubbard operators \( f_{k,m}^{\dagger} \) are replaced by usual fermionic operators \( f_{k,m}^{\dagger} \). The factor \( \frac{1}{N} \) has been generated. Here, we have introduced Fourier transformed \( f \) operators,

\[
\tilde{f}_{k,m}^{\dagger} = \frac{1}{\sqrt{N}} \sum_{i} f_{k,m}^{\dagger} e^{i\mathbf{k}\mathbf{R}_i}.
\]

The initial parameter values of the original model (at cut-off \( \lambda = A \)) are

\[
\mu_{f,\lambda} = \varepsilon_f, \quad \Delta_{k,\lambda} = 0, \quad \varepsilon_{k,\lambda} = \varepsilon_k, \quad E_A = 0.
\]

To perform the PRM scheme we also need the commutator of the unperturbed Hamiltonian with the hybridization. For convenience, we introduce the unperturbed Liouville operator \( L_{0,\lambda} \) which is defined by \( L_{0,\lambda} \mathcal{A} = [H_{0,\lambda}, \mathcal{A}] \) for any operator variable \( \mathcal{A} \), and to simplify the calculations, the one-particle operators \( f_{k,m}^{\dagger} \) and \( c_{k,m} \) are considered as approximate eigenoperators of \( L_{0,\lambda} \),

\[
L_{0,\lambda} \tilde{f}_{k,m}^{\dagger} c_{k,m} \approx (\varepsilon_{f,\lambda} + D\Delta_{k,\lambda} - \varepsilon_{k,\lambda}) \tilde{f}_{k,m}^{\dagger} c_{k,m}.
\]

Here, we introduced the local \( f \) energy,

\[
\varepsilon_{f,\lambda} = \mu_{f,\lambda} - D\Delta_{\lambda},
\]

and defined \( D = 1 - \langle \hat{n}_f \rangle + \langle \hat{n}_f^{\dagger} \rangle / v_f \) and \( \Delta_{\lambda} = \frac{1}{N} \sum_k \Delta_k \lambda \). The factors \( D \) in Eqs. \([10]\) and \([11]\) are caused by the Hubbard operators in the renormalization ansatz \([5]\). Similar expressions without factors \( D \) have also been found in Ref. \([10]\) where a renormalization ansatz consisting of fermionic quasi-particles has been used.

As one can see from Eq. \([11]\), the operator product \( \tilde{f}_{k,m}^{\dagger} c_{k,m} \) can also be interpreted as an approximate eigenoperator of the Liouville operator \( L_{0,\lambda} \). The corresponding eigenvalues are excitation energies and can be used to rewrite \( H_{1,\lambda} \),

\[
H_{1,\lambda} = \sum_{k,m} \Theta_{k,\lambda} V_k \left( \tilde{f}_{k,m}^{\dagger} c_{k,m} + \text{h.c.} \right),
\]

where the \( \Theta \) functions

\[
\Theta_{k,\lambda} = \Theta (\lambda - |\varepsilon_{f,\lambda} + D\Delta_{k,\lambda} - \varepsilon_{k,\lambda}|)
\]

restrict the particle-hole excitations to transition energies smaller than \( \lambda \).
3.2 Renormalization equations

Next we want to follow the discussion of Ref. [10] to derive renormalization equations for the parameters of the renormalized Hamiltonian \( H_\lambda \). It turns out that the actual calculations are only slightly modified by the new renormalization ansatz [8] which now includes correlated Hubbard operators.

To evaluate the new Hamiltonian \( \tilde{H}_{\lambda - \Delta \lambda} \) according to Eq. (10), an unitary transformation has to be performed to eliminate excitations within the energy shell between \( \lambda - (\Delta \lambda) \) and \( \lambda \). As in Ref. [10], we use the following operator ansatz for the generator \( X_{\lambda, \Delta \lambda} \) of the unitary transformation,

\[
X_{\lambda, \Delta \lambda} = \sum_{k,m} \Theta_k(\lambda, \Delta \lambda) A_k(\lambda, \Delta \lambda) \left( \hat{f}_{km}^\dagger \hat{c}_{km} - \hat{c}_{km}^\dagger \hat{f}_{km} \right)
\]

where the \( \Theta_k(\lambda, \Delta \lambda) \) are products of two \( \Theta \) functions,

\[
\Theta_k(\lambda, \Delta \lambda) = \Theta_{k,\lambda} \left[ 1 - \Theta_{k,(\lambda - \Delta \lambda)} \right].
\]

Note that the \( \Theta_k(\lambda, \Delta \lambda) \) confine the excitations which have to be eliminated by the renormalization step from \( \lambda \) to \( \lambda - (\Delta \lambda) \). The unknown parameters \( A_k(\lambda, \Delta \lambda) \) have to be fixed in such a way so that only transition with energies smaller than the new cut-off \( \lambda - (\Delta \lambda) \) contribute to \( \tilde{H}_{\lambda - \Delta \lambda} \).

As described in Ref. [10], equations for the parameters \( A_k(\lambda, \Delta \lambda) \) of the generator of the unitary transformation as well as for the parameters of the renormalized Hamiltonian \( H_\lambda \) can be found by comparing the coefficients of the operators in the renormalization ansatz [8] at cutoff \( \lambda - (\Delta \lambda) \) and in the explicitly evaluated unitary transformation [8].

Thus, we obtain the following equations:

\[
A_k(\lambda, \Delta \lambda) = \Theta_k(\lambda, \Delta \lambda) \frac{2 \sqrt{D V_{k}}} {2 \sqrt{D}} \arctan \left[ \frac{2 \sqrt{D V_{k}}}{\mu_{f,\lambda} + D (\Delta_{k,\lambda} - \Delta_{\lambda}) - \varepsilon_{k,\lambda}} \right]
\]

\[
\varepsilon_{k,(\lambda - \Delta \lambda)} - \varepsilon_{k,\lambda} = \frac{1}{2} \left[ \mu_{f,\lambda} + D (\Delta_{k,\lambda} - \Delta_{\lambda}) - \varepsilon_{k,\lambda} \right]
\times \left\{ \cos \left[ 2 \sqrt{D} A_{k}(\lambda, \Delta \lambda) \right] - 1 \right\}

- \sqrt{D V_{k}} \sin \left[ 2 \sqrt{D} A_{k}(\lambda, \Delta \lambda) \right],
\]

\[
\Delta_{k,(\lambda - \Delta \lambda)} - \Delta_{k,\lambda} = - \frac{1}{D} \left[ \varepsilon_{k,(\lambda - \Delta \lambda)} - \varepsilon_{k,\lambda} \right]
\]

\[
\mu_{f,(\lambda - \Delta \lambda)} - \mu_{f,\lambda} = - \frac{1}{D} \sum_{k,m} \left[ \varepsilon_{k,(\lambda - \Delta \lambda)} - \varepsilon_{k,\lambda} \right] \times \left[ 1 + (\nu_f - 1) \left\{ \hat{c}_{km}^\dagger \hat{c}_{km} \right\} \right]
\]

\[
+ \frac{\nu_f - 1}{4 D^{3/2}} \sum_{k} \left\{ \left[ \mu_{f,\lambda} + D (\Delta_{k,\lambda} - \Delta_{\lambda}) - \varepsilon_{k,\lambda} \right] \times \sin \left[ 2 \sqrt{D} A_{k}(\lambda, \Delta \lambda) \right] - 2 \sqrt{D} V_{k} \left\{ \cos \left[ 2 \sqrt{D} A_{k}(\lambda, \Delta \lambda) \right] - 1 \right\} \times \left( \hat{f}_{km}^\dagger \hat{c}_{km} + \text{h.c.} \right) \right\}
\]

\[
- \frac{\nu_f - 1}{2D} \sum_{k} \left[ \mu_{f,\lambda} - D (\Delta_{k,\lambda} - \Delta_{\lambda}) - \varepsilon_{k,\lambda} \right] \times A_{k}(\lambda, \Delta \lambda) \left( \hat{f}_{km}^\dagger \hat{c}_{km} + \text{h.c.} \right) = E(\lambda - \Delta \lambda) - E_{\lambda}
\]

Note that besides the factor \( 1/D \) in Eq. (14) these renormalization equations exactly agree with those derived in Ref. [10]. However, the underlying Hamiltonians differ significantly because now the renormalization ansatz [8] contains correlation effects by means of the Hubbard operators. It will turn out that the Hubbard operators not only complicate the further evaluation of the renormalization equations but also successfully prevent the system from unphysical multiple occupation of the \( f \) sites.

In deriving the renormalization equations [10]-[16] a factorization approximation has been employed so that the obtained equations still depend on expectation values which have to be determined simultaneously (see Ref. [10] for details). Furthermore, an expansion in \( 1/\nu_f \) has been avoided (and spin fluctuations have been neglected) so that the derived renormalization equations are valid for large as well as small degeneracies \( \nu_f \). The limit \( \lambda \rightarrow 0 \) provides the parameters \( \tilde{\varepsilon}_k, \tilde{\mu}_f, \Delta_k, \) and \( \tilde{E} \) of the effective Hamiltonian \( \tilde{H} = H_{\lambda \rightarrow 0} - H_{0, \lambda \rightarrow 0} \),

\[
\tilde{H} = \sum_{k,m} \tilde{\varepsilon}_k \hat{c}_{km}^\dagger \hat{c}_{km} + \tilde{\mu}_f \sum_{k,m} \hat{f}_{km}^\dagger \hat{f}_{km} + \sum_{k,m} \Delta_k \left( \hat{f}_{km}^\dagger \hat{f}_{km} \right)_{NL} + \tilde{E},
\]

we are interested in. Here, it is important to notice that the renormalized Hamiltonian \( \tilde{H} \) no longer contains the hybridization between conduction and localized electrons. However, \( \tilde{H} \) is not a non-interacting fermionic system because \( \tilde{H} \) still takes into account electronic correlations by means of the Hubbard operators \( \hat{f}_{km}^\dagger \). Note that these correlations turn out to be crucial for a description of integral
valent states. On the other hand, the Hubbard operators \( \hat{f}_{km}^\dagger \) also cause challenging difficulties in the further theoretical treatment because they do not obey the usual fermionic anticommutator relations.

### 3.3 Approximate solutions

In the following we want to develop a strategy to solve the renormalization equations (12)-(16) approximately. Here, similar approximations as in Ref. [10] shall be used to decouple the renormalization of the different \( k \) values. In this way, all relevant quantities can be expressed as functions of a renormalized \( f \) energy \( \tilde{\varepsilon}_f \) which is determined by numerical minimization of the free energy.

As in Ref. [10], we use the following approximations for further evaluation of the renormalization equations (12)-(16).

(i) All expectation values (which occur due to the exploited factorization approximation) are assumed to be independent from the renormalization parameter \( \lambda \) and are calculated using the full Hamiltonian \( \mathcal{H} \).

(ii) To decouple the renormalization of the different \( k \) values, the \( \lambda \) dependence of the renormalized \( f \) level is neglected, \( \mu_f, \lambda - D \Delta \lambda \approx \tilde{\varepsilon}_f \). The spirit of this approximation is similar to that assumed in the SB theory where a renormalized \( f \) energy is also used from the very beginning. Note that \( \tilde{\varepsilon}_f \) has to be interpreted as local \( f \) energy of the renormalized model (17).

At this point it is important to notice, that our old analytical solution of Ref. [10] can be easily obtained if the Hubbard operators in the final Hamiltonian (17) are replaced by usual fermionic operators. Formally, one employs

(iii) \( \sum_{k,m} \hat{f}_{km}^\dagger \hat{f}_{km} \approx \sum_{k,m} f_{km}^\dagger f_{km} \) and

\[ (\hat{f}_{km}^\dagger \hat{f}_{km})_{\text{NL}} \approx D (f_{km}^\dagger f_{km})_{\text{NL}}. \]

to ensure that, on a mean-field level, the renormalized Hamiltonian does not generate unphysical states. However, as already discussed above, the obtained effective model does not prevent anymore from multiple occupation of \( f \) sites if (iii) has been employed. We have already argued that such an approximation can only lead to useful results as long as only very few \( f \) type states below the Fermi level are occupied. Thus, only HF-like solutions can be observed in this way. To obtain the analytical solution of Ref. [10], one also has to employ

(iv) \( \frac{1}{N} \sum_k \Delta_{k,\lambda} \approx \tilde{\Delta} \approx 0 \)

for further simplification.

In the following we only want to employ approximations (i) and (ii). In particular, we keep the Hubbard operators in the final Hamiltonian (17) so that both mixed valent and integral valent states can be described.

Eqs. (13) and (10) can be easily integrated between the lower cutoff \( \lambda \to 0 \) and the cutoff of the original model \( A \),

\[ \tilde{\Delta}_k = - \frac{1}{D} [\tilde{\varepsilon}_k - \varepsilon_k], \]

\[ \tilde{E} = -N \langle \hat{n}_f \rangle [\tilde{\varepsilon}_f - \varepsilon_f] + \frac{D - 1}{D} \langle \hat{n}_f \rangle \sum_k [\tilde{\varepsilon}_k - \varepsilon_k]. \]

As already mentioned above, the approximations (i), (ii) decouple the different \( k \) values from each other so that Eq. (12) and (16) are completely similar to those obtained for the Fano-Anderson model (compare Ref. [10]). Thus, two quasi-particle branches are obtained,

\[ \tilde{\varepsilon}_k = \frac{\tilde{\varepsilon}_f + \varepsilon_k}{2} - \frac{\text{sgn}(\tilde{\varepsilon}_f - \varepsilon_k)}{2} W_k, \]

\[ \tilde{\omega}_k := \tilde{\varepsilon}_f + D \tilde{\Delta}_k = \frac{\tilde{\varepsilon}_f + \varepsilon_k}{2} + \frac{\text{sgn}(\tilde{\varepsilon}_f - \varepsilon_k)}{2} W_k, \]

where

\[ W_k = \sqrt{(\tilde{\varepsilon}_k - \tilde{\varepsilon}_f)^2 + 4D|V_k|^2}. \]

Note that the one-particle energies (20) and (21) still depend on two unknown quantities: the renormalized \( f \) level \( \tilde{\varepsilon}_f \) and the \( f \) occupation number \( \langle \hat{n}_f \rangle \) (that determines \( D \) as defined above).

In Ref. [10] all expectation values as well as the renormalized \( f \) level \( \tilde{\varepsilon}_f \) have been determined by functional derivative of the free energy. However, here, this approach can not easily be applied because the Hubbard operators contained in the renormalized Hamiltonian (17) do not fulfill the usual fermionic anti-commutator relations. Furthermore, the derivation of the free energy would also lead to problematic \( \delta \) functions that are caused by the abrupt change of the statistic of the quasi-particle excitations at \( \tilde{\varepsilon}_f \). (In Ref. [10] these contributions do not appear because both \( c \)-like and \( f \)-like excitations are caused by fermionic quasi-particles.) Therefore, a different approach has to be developed to determine the renormalized \( f \) level \( \tilde{\varepsilon}_f \) and the expectation values.

In the following, the expectation values of the original Hamiltonian \( \mathcal{H} \) will be calculated using the renormalized one-particle operators as derived in Ref. [10],

\[ e_{km}^\dagger(\lambda \to 0) = \tilde{u}_{km}^\dagger + \tilde{c}_{km}, \]

\[ \tilde{f}_{km}^\dagger(\lambda \to 0) = -D \tilde{v}_{km}^\dagger + \tilde{u}_{km}^\dagger, \]

where we defined

\[ |\tilde{u}_{km}|^2 = \frac{1}{2} \left( 1 - \frac{\varepsilon_k - \tilde{\varepsilon}_f}{W_k} \text{sgn}(\tilde{\varepsilon}_f - \varepsilon_k) \right), \]

\[ |\tilde{v}_{km}|^2 = \frac{1}{2D} \left( 1 + \frac{\varepsilon_k - \tilde{\varepsilon}_f}{W_k} \text{sgn}(\tilde{\varepsilon}_f - \varepsilon_k) \right). \]

Thus, the required expectation values of the full Hamiltonian \( \mathcal{H} \) can be traced back to those calculated with respect to the renormalized Hamiltonian \( \tilde{\mathcal{H}} \) because \( \langle A \rangle = \langle \tilde{A} \rangle \).
lim_{\lambda \to 0} \langle A(\lambda) \rangle_{\mathcal{H}_\lambda} holds,
\begin{equation}
\left\langle c_{km}^\dagger c_{km} \right\rangle = \frac{1}{2} \left[ 1 - \frac{\varepsilon_k - \tilde{\varepsilon}_f \text{sgn}(\tilde{\varepsilon}_f - \varepsilon_k)}{W_k} \right] f(\tilde{\varepsilon}_k) \tag{26}
\end{equation}

\begin{equation}
+ \frac{1}{2} \left[ 1 + \frac{\varepsilon_k - \tilde{\varepsilon}_f \text{sgn}(\tilde{\varepsilon}_f - \varepsilon_k)}{W_k} \right] \tilde{f}(\tilde{\varepsilon}_k),
\end{equation}

\begin{equation}
\langle \hat{\tilde{f}}_{km}^\dagger \hat{f}_{km} + \text{h.c.} \rangle = \begin{cases}
-2 \text{sgn}(\tilde{\varepsilon}_f - \varepsilon_k) \frac{D[V_k]}{W_k} [f(\tilde{\varepsilon}_k) - \tilde{f}(\tilde{\varepsilon}_k)].
\end{cases}
\end{equation}

Here, we introduced the Fermi function
\begin{equation}
f(\tilde{\varepsilon}_k) := \langle c_{km}^\dagger c_{km} \rangle_{\mathcal{H}} = \frac{1}{1 + e^{\beta(\tilde{\varepsilon}_k - \varepsilon_k)}},
\end{equation}
and defined
\begin{equation}
\tilde{f}(\tilde{\varepsilon}_k) := \frac{1}{D} \langle \hat{\tilde{f}}_{km}^\dagger \hat{f}_{km} \rangle_{\mathcal{H}}.
\end{equation}

Note that the factor \(D\) in Eq. (28) has been introduced to underline the similarities of Eq. (26) and (27) with the corresponding results of the analytical treatment of Ref. [10].

In principle, the \(f\) occupation number \(\langle \tilde{n}_{f} \rangle\) could also be calculated using the renormalized one-particle operators. However, here we alternatively employ the particle conservation under unitary transformations. Thus, we obtain
\begin{equation}
\langle \tilde{n}_{f} \rangle = \frac{1}{2} \sum_{k} \left[ 1 + \frac{\varepsilon_k - \tilde{\varepsilon}_f \text{sgn}(\tilde{\varepsilon}_f - \varepsilon_k)}{W_k} \right] f(\tilde{\varepsilon}_k)
\end{equation}

\begin{equation}
+ \frac{1}{2} \sum_{k} \left[ 2D - 1 - \frac{\varepsilon_k - \tilde{\varepsilon}_f \text{sgn}(\tilde{\varepsilon}_f - \varepsilon_k)}{W_k} \right] \tilde{f}(\tilde{\varepsilon}_k).
\end{equation}

For actual calculations one needs to evaluate Eq. (28) in order to determine the expectation values of the full Hamiltonian as given in Eqs. (26) and (27) with the corresponding results of the analytical solution of Ref. [10].

Because of the unusual properties of the Hubbard operators, there is no straightforward way to evaluate Eq. (28) and further approximations are necessary. As long as the renormalized \(f\) level is situated \textit{above} the chemical potential a mean-field treatment of the electronic correlations contained in \(\mathcal{H}\) might be sufficient, and we would find \(\tilde{f}(\tilde{\varepsilon}_k) \approx f(\tilde{\varepsilon}_k)\) as directly obtained by employing approximation \textbf{(iii)} mentioned above. On the other hand, here we are also interested in solutions of the PAM with a renormalized \(f\) level \textit{below} the Fermi level which require a theoretical treatment of the electronic correlations in \(\mathcal{H}\) \textit{beyond} a mean-field approximation. Therefore, Eq. (28) is evaluated as follows
\begin{equation}
\langle \hat{f}_{km}^\dagger \hat{f}_{km} \rangle_{\mathcal{H}} = \frac{1}{\text{Tr} e^{-\beta H}} \text{Tr} \left( e^{\beta \tilde{H}} e^{-\beta \tilde{H}} \hat{f}_{km}^\dagger \hat{f}_{km} e^{-\beta \tilde{H}} \right)
\end{equation}

\begin{equation}
\approx f(\tilde{\varepsilon}_k) \left\langle \langle \hat{f}_{km}^\dagger \hat{f}_{km} \rangle_{\mathcal{H}} \right\rangle_{\mathcal{H}}
\end{equation}

where the approximated \(f\) excitation energy as derived in Eq. (10) has been used. Thus, (28) can be rewritten as
\begin{equation}
\tilde{f}(\tilde{\varepsilon}_k) := \frac{1}{1 + \nu f} \frac{1}{N} \sum_{k} f(\tilde{\varepsilon}_k).
\end{equation}

Unfortunately, approximation (30) does not offer a direct link to the mean-field result, \(\tilde{f}(\tilde{\varepsilon}_k) \approx f(\tilde{\varepsilon}_k)\), for renormalized \(f\) energies above the Fermi level. Thus, differences between the presented treatment and the analytical solution of Ref. [10] will appear.

At this point all physical quantities can be calculated as function of the renormalized \(f\) energy \(\tilde{\varepsilon}_f\). Because we have employed approximation \textbf{(ii)} it is not possible anymore to use the renormalization equation (15) for \(\mu_{F,\lambda}\) to determine \(\tilde{\varepsilon}_f\). Therefore, the local \(f\) energy \(\tilde{\varepsilon}_f\) is considered as a free parameter and is determined by minimization of the free energy. Because of the unusual anticommutator relations of the Hubbard operators \(\hat{f}_{km}^\dagger\), the free energy can not be directly determined. Instead,
\begin{equation}
\frac{dF}{d\tilde{\varepsilon}_f} = \sum_{k,m} \frac{d\tilde{\varepsilon}_f}{d\tilde{\varepsilon}_f} \langle c_{km}^\dagger c_{km} \rangle_{\mathcal{H}} + \frac{d\tilde{\varepsilon}_f}{d\tilde{\varepsilon}_f} \sum_{k,m} \langle \hat{f}_{km}^\dagger \hat{f}_{km} \rangle_{\mathcal{H}}
\end{equation}

\begin{equation}
+ \frac{d\tilde{\varepsilon}_f}{d\tilde{\varepsilon}_f} \left( \langle \hat{f}_{km}^\dagger \hat{f}_{km} \rangle_{\mathcal{H}} \right)_{\mathcal{H}} + \frac{dE}{d\tilde{\varepsilon}_f}
\end{equation}

is numerically integrated in order to calculate the free energy \(F\) as function of the renormalized \(f\) energy \(\tilde{\varepsilon}_f\). Note that Eq. (31) has been obtained from the renormalized Hamiltonian [17]. Actual results are discussed in the next section.

4 Results

It is believed that the one-particle energy \(\varepsilon_f\) of the localized \(f\) electrons is smoothly changed in CeCu$_2$Si$_2$ due to pressure [4]. Therefore, we want to discuss the physical properties of the PAM as a function of \(\varepsilon_f\).

At first let us consider an one-dimensional PAM with a linear dispersion relation \(\varepsilon_k\) for the conduction electrons in the energy range between \(-1\) and \(1\), and a \(k\) independent hybridization \(V_k = V\). The other parameters are chosen as follows \(\nu f V^2 = 0.36\), chemical potential \(\mu = 0\), and \(T = 0.00001\) where all energies are given in units of the half bandwidth.

As one can see from Figs. 1 and 2, we obtain two different types of solutions depending on the value of the unrenormalized \(f\) level \(\varepsilon_f\). First of all, we obtain the usual SB type solutions with intermediate valence states \(n_f < 1\) where the renormalized energy \(\tilde{\varepsilon}_f\) is energetically located above the Fermi energy. If the unrenormalized energy \(\varepsilon_f\) is lowered the renormalization contributions are no longer sufficient to push \(\tilde{\varepsilon}_f\) above the Fermi level, and the renormalized \(f\) energy \(\tilde{\varepsilon}_f\) is located far below the Fermi energy.
In this case, the averaged $f$ occupation $n_f$ is almost exactly 1 and an integral valence state is obtained.

Figs. 1 and 2 also reveal the very good agreement between the HF type solutions of the presented PRM approach and the analytical results of Ref. [10]. In this way it is proven that the Hubbard operators can be replaced by usual fermionic operators (compare approximation (iii) in Sec. 3.3) because in this case only very few $f$ sites can only be either empty or singly occupied as already discussed above.

For comparison, the results of the analytical solution of Ref. [10] and of the SB mean-field theory are shown as well in Figs. 1 and 2. As one can see from Eqs. (20) and (21), the well-defined transition between the two different solution types is of particular interest. As expected, for the HF-like solution the $f$-charge is always smaller than 1 due to hybridization processes between $f$ and $c$-electrons. Simultaneously heavy quasiparticle bands are formed at the Fermi surface. To describe the HF behavior the full Anderson model has to be considered. As the bare $f$-level moves to smaller energies a transition to an integral valence charge of $n_f = 1$ is observed (similar to the Anderson impurity model [14]). In this case only the $c$ electrons should form the Fermi surface. The well-defined transition can also be interpreted as a collapse of the large Fermi surface of the HF state which is formed by conduction as well as by localized $f$ electrons. Note, however, that the question whether localized electrons contribute to the Fermi sea volume or not is still controversially discussed in the literature [15].

As one can see from Figs. 1 and 2, the obtained valence transition is much more pronounced for small degeneracies $\nu_f$, and a smooth transition can be expected in the limit $\nu_f \rightarrow \infty$ of the SB theory. Therefore, a sharp valence change in generalized SB theories can only be obtained if a rather large additional Coulomb repulsion between $f$ and conduction electrons is present in the system [18]. However, the case where the averaged $f$ occupation $n_f$ is almost exactly 1 and an integral valence state is obtained.

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The electronic band covers an energy range between -1.5 and 
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Fig. 3. Panel (a) and (b) [(c) and (d)] show the results
for the renormalized f level $\tilde{\varepsilon}_f$ and the f occupation number $n_f = \langle \tilde{n}_f \rangle$ for a two-dimensional [three-dimensional] system
with $100 \times 100 [26 \times 26 \times 26]$ lattice sites. As in Figs. 1 and 2,
a linear dispersion relation $\varepsilon_k = \varepsilon(|k|)$ has been chosen, and
the electronic band covers an energy range between -1.5 and
0.5 [-1.8 and 0.2] where $\mu = 0$, $\nu_f = 4$, $\nu_f/V^2 = 0.36$, and
$T = 0.00001$. (Energies are given in units of the half band-
width.) Note that the conduction band has been energetically
shifted in in order to ensure a filling comparable to the one-
dimensional case of Fig. 1 because a smaller filling of the con-
duction band reduces the change in the f occupation $n_f$ at the
transition point.

However, here we have shown that such a valence transition
can also be obtained in the plain PAM if corrections for
small degeneracies $\nu_f$ are properly taken into account.

One of the advantages of the analytical PRM is the
opportunity to consider much larger systems than accessible
by numerical methods. Therefore, we are also able to study two- and three-dimensional systems of reasonable
sizes. In this way we can easily show that the observed valence transition is not an unique phenomenon of the
one-dimensional PAM. The valence transition also occurs
in two- and three-dimensional systems as can be seen
in Fig. 3. Therefore, the observed behavior has to be considered as a general feature of the PAM, and our results
should also be of relevance for actual physical HF systems
like CeCu$_2$Si$_2$ or related compounds.

5 Discussion and Summary

The occurrence of a valence transition in the plain PAM is
the main finding of this paper. In contrast, a rather large
additional Coulomb repulsion has been claimed to be neces-
sary for the valence transition in an extended PAM [4]

The studies of Refs. [4,8] were based on a slave-boson
fluctuation approximation that extends the well-known
slave-boson mean-field theory [11,12] but still employs the
limit of large degeneracy $\nu_f \to \infty$. Our results show (com-
pare Figs. 1 and 2) that the observed valence transition
becomes smooth in this limit. Therefore, it is reasonable
that an additional interaction was found to be necessary
in order to obtain a valence transition in an approach em-
ploying $\nu_f \to \infty$.

Our work also shows the importance of taking care of a
physical f occupation in theoretical approaches. In par-
cular, it turns out that a completely uncorrelated model
is not able to prevent from unphysical multiple occupation
of f sites, and no integral valence states can be found
in this way. In contrast, the presented PRM approach to
the PAM explicitly suppresses unphysical multiple f occu-
pation which is, in particular, crucial for integral valence
states.

We obtain two solution types: a mixed valence state
with a renormalized f level $\tilde{\varepsilon}_f$ above the Fermi energy
and an integral valence state with $\tilde{\varepsilon}_f$ below the Fermi level.
Furthermore, parameter regimes exist where the transition
between the two solution types is accompanied by a
drastic change in the f occupation. Such a sharp valence
transition occurs in one-dimensional as well as in two- and
three-dimensional systems so that this behavior has to be
considered as a general feature of the PAM. Note that a
similar valence transition has been experimentally found
in CeCu$_2$Si$_2$ from high pressure experiments [3,4].

In the case of an integral valence state one would ex-
pect that the system can be described by a Kondo Hamil-
tonian which is gained from the PAM by the Schrieffer-
Wolff transformation [16] for $V/|\varepsilon_f| \ll 1$. Note, however,
that in the present approach spin fluctuations have been
neglected altogether but Kondo-like and RKKY-like inter-
actions as well as higher charge fluctuation terms are
automatically generated during the renormalization pro-
cedure. These contributions will have to be considered
in the future. One might expect that additional spin and
charge fluctuations might possibly give rise to magnetic
and superconducting phases both for the intermediate va-
lence and for the integer valence regime. Also, one may
speculate that the magnitude of the magnetic moment
will be different for these cases due to additional screen-
ing processes.

The PRM approach presented in this paper only ad-
resses the question for the valence transition in the plain
PAM. However, as mentioned above, the PRM scheme of-
fers great opportunities to include additional interactions
which are automatically generated during the renormali-
zation procedure. Therefore, extensions of the PRM treat-
ment might be promising starting points to study the com-
peting interactions in CeCu$_2$Si$_2$ and related compounds
in more detail.

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