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Spin fluctuations and heavy fermion behavior

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Abstract

A heuristic approach to the relation of spin fluctuations (SF) and the heavy fermion (HF) state will be presented. The appearance of SF in the eigenstates of the periodic Anderson model is discussed in terms of relevant length scales, something already known for the Kondo problem but this time presented in a slightly more general framework. It will be shown that a specific form of SF can produce a HF-like state. The magnetic ordering, its small magnetic moment (using a Stoner-like criterion), charge transfer, and the magnetic field effect will be discussed.

1. Introduction

A heuristic approach to the relation of spin fluctuations (SF) and the heavy fermion (HF) state will be presented. The relevance of SFs to the HF state will be discussed in general terms, after which, more specifically, the appearance of SF in the eigenstates in the periodic Anderson model (PAM) is focused on [1]. The answer is already known for theories based on the Kondo problem [2–11] with its singlet ground state. However, we would like to analyze this in a more general framework, in terms of the relevant interaction length scales. It will be shown that a specific form of SF can produce a HF-like state with a magnetic ordering. Only the case of a ferromagnetic and an antiferromagnetic ordering will be discussed in this article. But other types of ordering can easily be treated on the same basis. The model used has close similarities with the well-known Stoner model [12–15]. In the case of the Stoner model rigid bands are used while here a more flexible band model is used. The small magnetic moment [16,17] will be explained using a Stoner-like criterion. Since the ligand hybridization is so small charge transfer considerations can be done separately from any model considerations used to evaluate the Hamiltonian. We will show that charge transfer considerations lead to extra restrictions any used model consideration must satisfy. Also the effect of magnetic fields on such a state will be discussed. It has to be stressed that the treatment as presented in this article is not meant as some kind of ultimate and definitive truth. However, we believe that the argumentations presented in this article may lead to a better understanding of HF properties and can lead to suggestions for new experiments.

2. Heavy fermions

Heavy fermion (HF) behavior occurs in the group of intermetallics containing always an actinide (in most cases U) or a rare earth (in most cases Ce) element. Examples of such compounds are CeRu2Si2, CeNiSn, URu2Si2, UPt3, UBe13, UPd2Al3. They exhibit a strange combination of striking low-temperature properties (for a general review see Refs. [18–25]) e.g. the very heavy “electron” mass as deduced from thermodynamic
experiments, an extremely high Grüneisen parameter [20] (expressing a strong volume dependence of the energy levels of the system) and an uncommon magnetic ordering. In very delicate neutron experiments the presence of a small magnetic moment [16,17] on the magnetic ion sites can be observed. Most theories either predict no magnetic moment at all or an ordered state with too big a moment. It cannot be excluded that this small moment emerges from lattice imperfections. But even if so, it is very hard to explain how lattice imperfections can produce such a small moment. We believe that these small magnetic moments, even if induced by lattice imperfections, reveal something essential about the HF state. The observation of an apparent heavy electron mass indicates a high density of states (DOS) at the Fermi level. Concurrently, the Fermi liquid temperature can be considered to be strongly renormalized $T_{FL} \approx 100\; K$ [18–21]. The observed apparent heavy mass, the extremely high Grüneisen parameter and the small magnetic moment are only three of the many amazing properties observed in HFs. In HF systems there usually exists one typical energy scale of the order of $1.5k_B T^* \approx \mu_B B^*$. $B^*$ and $T^*$ are, respectively, the characteristic field and temperature needed to destroy the HF state. The latter is always in the range of 10–100 K, indicating that the width of the peak in the DOS at the Fermi level is very small. For the “physics of HFs” this width will be the relevant energy scale. Being much smaller than usual, doors are opened for the observation of phenomena usually unobservable. At high temperatures these systems can be described in terms of localized moments [27–31]. If in the HF state any low-temperature magnetic ordering is observed, it usually is antiferromagnetic. At present, it is not clear if this extra magnetic ordering comes from the HF state as such or if it is an extra phenomenon which interacts with the HF state. Usually, HF systems have a complicated chemical structure. They exhibit a high degree of anisotropy in most of their properties. Some of these systems, like, for example, UPt$_3$, UPd$_2$Al$_3$, and CeCuSi$_2$ will even exhibit unusual superconductivity at low temperatures [32–36,21] with a complicated phase diagram. In addition, HF systems exist which exhibit a gap very much like in semiconductors, e.g. CeNiSn [31], and this list of interesting properties is by no means complete. Each property in itself is already fascinating. However, it is rather difficult to explain in one coherent model the combination of all these properties. It is usually easy to select a subset of experimental facts to support any given theory. On the other hand, a person is probably quickly driven schizophrenic in an attempt to explain all of these properties at once. In our theoretical analysis we therefore would like to focus on the understanding of the heavy electron mass, the high Grüneisen parameter, and the small magnetic moment, in the hope that all the other interesting properties can be explained on the same basis.

3. Relevance of spin fluctuations

Our treatment falls into the class of models trying to explain the HF behavior in terms of bandstructures. Two bands arise from the small (ligand) hybridization of $10\; meV$ [37,38] of a broad conduction band and a dispersionless $f$-band. An enormous peak in the density of states (DOS), heavy mass, with a gap-like structure in the middle of it is formed. Its width is of the order of this ligand hybridization. The strong volume dependence of the hybridization is causing the high Grüneisen parameter. The bare $f$-level is found to be $2\; eV$ below the chemical potential, while the narrowness of an $f$-shell causes double occupancy of such a shell to correspond to an energy gain of $5\; eV$, the on-site repulsion. The average energy is in both cases too far separated from the chemical potential for the so-formed hybridization peaks to be close enough to the Fermi level to be observable in a thermodynamical experiment. Some new kind of renormalization argument for the position of the effective $f$-level must be found.

Already from theoretical studies of small solvable systems containing only a finite number of magnetic ion sites [7] but also e.g. for Kondo systems with their singlet ground state [2–4] the importance of spin degrees of freedom for the ground state properties emerges. As from the experimental side, in the low-temperature entropy as determined from thermodynamical experiments the spin degrees of freedom turn up predominantly. Also the observed small magnetic moment [16,17] seems to point in the direction of spin fluctuations. Intuitively, one can visualize electrons wandering around as delocalized states. These states want to sit down on an $f$-site because the energy related to this is lower than the Fermi energy. Double occupancy of a certain site will be avoided. Since, due to the on-site repulsion, the average energy per electron related to this will be higher than the Fermi level. If a certain site is occupied by an electron with a certain spin this original electron can be pushed out by an electron of opposite spin, causing the occurrence of on-site SFs. Of course processes involving identical spins will also appear. Such processes will only be noticed by the loss of coherence. This picture also applies for the single-site Kondo problem. But as Nozieres pointed out in HF systems there are not enough conduction electrons present to compensate a full moment per magnetic ion if the interaction between these ions is neglected [42]. Therefore, we will be mainly interested in the (coherent) intersite SFs.
4. The model Hamiltonian

Our description of the HF systems is based on the well-studied periodic Anderson model (PAM) [1]. Restricting ourselves to only one f-state per unit cell and site, the Hamiltonian reads

\[ H_U = \sum_{k, \sigma} \left( T(k) \delta \frac{\epsilon(k) + \epsilon_{f0}}{2} c_{ka} + T(k) \delta \frac{\epsilon(k) + \epsilon_{f0}}{2} f_{ka} \right) + \sum_{k} \left( \epsilon(k) c_{ka}^\dagger c_{ka} + \sum_{\sigma} \epsilon_{f} f_{ka\sigma}^\dagger f_{ka\sigma} \right) + \sum_{i\sigma} U n_{i\uparrow} n_{i\downarrow}, \]

where \( c_{ka}^\dagger \) and \( c_{ka} \) are the creation and annihilation operators of the delocalized conduction electrons characterized by wave number \( k \) and spin quantum number \( \sigma \). The energy related to such a bare state is the known dispersion relation for conduction electrons \( \epsilon(k) = \frac{\hbar^2 k^2}{2m^*} \) (\( m^* \) being the effective mass of the bare conduction electrons). The operator \( f_{ka\sigma} \) is defined as

\[ f_{ka\sigma} = \frac{1}{N_i} \sum_{\xi} e^{-i\mathbf{k} \cdot \mathbf{r}_{\xi}} f_{\xi\sigma}, \]

where \( f_{\xi\sigma}^\dagger \) is the creation operator of an f-state at site \( \xi \) with spin \( \sigma \). The energy belonging to such a state is \( \epsilon_{f} \). The ligand hybridization between two neighboring f-like states in the case of HF systems is estimated to be negligible [37, 38]. We only have to consider the hybridization between localized and conduction electron states, denoted as \( T(k, i) \). It can be straightforwardly shown that \( T(k, i) = T(k) \delta \frac{\epsilon(k) + \epsilon_{f0}}{2} \), therefore, \( \sum_{k} T(k, i) c_{ka}^\dagger c_{ka} = \sum_{k} T(k) f_{ka}^\dagger f_{ka} \). We assume the energy of the bare f-state \( \epsilon_{f} \) to be lower than the Fermi level (FL) \( \epsilon_F \). A doubly occupied f-level \( \epsilon_{f} \) has a total energy exceeding \( \epsilon_F \) by more than the Fermi energy, \( E_{\text{double}} - E_{\text{single}} = U, \epsilon_{f} > \epsilon_F \), where \( U \) denotes the energy of on-site repulsion. This is the simplest case represented in real space, \( \sum_{\xi} U n_{\xi\sigma} n_{\xi\sigma} \), with \( n_{\xi\sigma} \) defined as \( f_{\xi\sigma}^\dagger f_{\xi\sigma} \). The remaining terms are readily diagonalized in reciprocal space.

5. Spin fluctuations in the periodic Anderson model

We would like to investigate the appearance of SF in the eigenstates of the PAM. The answer is already known for theories based on the Kondo problem with its singlet ground state [2-6] and similar theories [7-11]. Here we would like to analyze such fluctuations in a more general framework (without actually solving the eigenvalue/eigenvector problem of \( H_U \)) in terms of the relevant length scales. In our analysis we will argue that eigenstates must contain \( n_{i\sigma} \) which depend on time, i.e. they fluctuate. Some exclusions have to be made. The argument here presented will only hold for pure eigenstates. We also exclude \( n_{i\sigma} = 0 \), but since we are usually interested in the ground state properties this is of no concern here.

To study SF involves a study of \( n_{i\sigma} - n_{i\sigma+\sigma} \) and not just \( n_{i\sigma} \). Since \( \epsilon_{f} \) is 2 eV below the chemical potential and the on-site repulsion is 5 eV, fluctuations containing charge degrees of freedom will be strongly suppressed. This makes it reasonable to refer to fluctuations in \( n_{i\sigma} \) as SF. We will start by studying the time evolution of the relevant operators:

\[ \frac{1}{i\hbar} \frac{d}{dt} f_{i\sigma}^\dagger = \frac{1}{N_i} \sum_{k} T_{\text{cond}}(i, j) c_{i\sigma}^\dagger, \]

where \( c_{i\sigma}^\dagger \) and \( c_{i\sigma} \) are related in the same way as \( f_{i\sigma}^\dagger \) and \( f_{i\sigma} \). Obviously, this could also be formulated in terms of Green’s functions.

In the tight-binding scheme [43], \( T_{\text{cond}}(i, j) \) is related to the hybridization between atomic orbitals which make up the conduction electron states. The only way an occupied f-state on a given site \( i \) can get to another f-state at site \( j \) is via the conduction electron states. The precise nature of \( T_{\text{cond}}(i, j) \) (or \( \epsilon(k) \)) determines the linking between different sites. We can distinguish two extreme limiting cases, i.e. \( T_{\text{cond}}(i, j) = 0 \) (or \( \epsilon(k) = \epsilon_F \)), and \( T_{\text{cond}}(i, j) \equiv T_{\text{cond}}(\epsilon(k) = \epsilon_F) \). In the first case, the conduction electrons are localized. The wave functions will no longer have any overlap. The sites are decoupled, and we are back to a oversimplified version of a free “atom” at each site. Such an “atom” is composed out of an f-state at a certain site and the Wannier state of the conduction electrons at the same site (see Ref. [7]). In the other case the overlap between wave functions stemming from any two sites \( i \) and \( j \) and with it the exchange between them is independent of the particular choice of \( i \) and \( j \). By varying the dispersion relation \( \epsilon(k) \), the behavior of the system will continuously transform from a collection of uncoupled free “atoms” at each site into a PAM in which more and more different magnetic ions are strongly coupled. For \( \epsilon(k) = \frac{\hbar^2 k^2}{2m^*} \), \( T_{\text{cond}}(i, j) \) can be calculated in a straightforward manner. Different band indices relate to different sets of sites coupling in real space. For a cubic lattice, disregarding electron–electron interaction among conduction electrons, the lowest band index will lead to \( T_{\text{cond}}(i, j) \propto (R/\Delta R_{ij})^2 \cos(\pi \Delta R_{ij}/R) \) (an oscillating term times a damping term). \( \Delta R_{ij} = R_j - R_i \) is along the three main crystallographic directions and \( R \) is the lattice constant in the corresponding direction. Analogous results can be reduced for the other band...
indices. A length scale $\Delta l$ can be defined as the distance at which $\sum_{j \neq i} |T_{\text{cond}}(i,j)|$ is smaller than say 10% of $|T_{\text{cond}}(i,i)|$. We define $A_{ij}^\ast$ as

$$A_{ij}^\ast = \sum_{j,j \neq i} T_{\text{cond}}(i,j) c_{ij}^\ast.$$  \hspace{1cm} (4)

The change in the density of conduction electrons at site $i$ ($c_{i\sigma}$) in an infinitely small time element $\delta t$ is due to the exchange of electrons to the f-state at the same site ($f_{i\sigma}$) and the exchange to the conduction electron states of the other sites ($c_{i\sigma}^\dagger$, $j \neq i$), which is governed by both $T_{\text{cond}}(i,j)$ and the respective occupation densities. Primarily, only sites within the volume defined by $\Delta l$ have to be considered. Note that thanks to the intermediating role of the other sites, coherence is maintained throughout the lattice, even for $T_{\text{cond}}(i,j)$ having a limited range ($\Delta l$). We found $\Delta l$ to be something like 8 times the lattice spacing. It is interesting to compare this analysis with the well-known Ruderman–Kittel–Kasuya–Yoshida (RKKY) theory [44, 47].

As the spin direction is still arbitrary, it implies that if $n_{i\sigma}$ is a constant, $n_{i-\sigma}$ must also be a constant. So for pure eigenstates, $n_{i-\sigma}$ must be a good quantum number and can be treated as a regular constant on the right-hand side of Eq. (3). In this case, Eqs. (3) and (4) cannot have a solution for which $n_{i\sigma}$ is a constant in time. Therefore, no eigenstates of $H_U$ can be found for which $n_{i\sigma}$ is a constant. We are not able to do this without making any extra assumptions. From the following argumentation the approximation $A_{ij}^\ast \approx c \times I_{\text{operator}}$, with $c$ being small compared to $T_{\text{cond}}(i,i)$, seems to be reasonable. This is even exact for the case $\sigma(k) = c$. The influence of the other sites on the central site is constant in time. Any state $|\phi\rangle$ of the system can be seen as $|\phi\rangle = \sum_\alpha |\alpha i\rangle$ where each state $|\alpha i\rangle$ is connected to a specific combination of occupied and non-occupied conduction electron states ($c_{i\sigma}$) within the volume defined by $\Delta l$. If the volume is small enough, the occupation densities of $c_{i\sigma}$ for $i$ within this volume will be, on the average, mainly influenced by sites outside the volume. The expectation value for the total number of conduction electrons within the volume will also be fixed by this outside world. The $|\alpha i\rangle$’s belonging to states having the same number of conduction electrons within the volume will be of almost equal size. This restricts the sub-Hilbert space of $|\phi\rangle$. On the other hand, the volume must be big enough for $T_{\text{cond}}(i,j)$ to contain enough oscillations, sign reversals. If so the restriction $A_{ij}^\ast |\phi\rangle \approx c \times I_{\text{operator}} |\phi\rangle$, $|c| \ll |T_{\text{cond}}(i,i)|$ is almost always satisfied for $|\phi\rangle$ from this already restricted sub-Hilbert space. For a typical conductor such as aluminum these approximations are found to be reasonable. From both theoretical and experimental studies of all kinds of small molecules it is known that $8^3 = 512$ atoms” is already enough for the “molecule” to have bulk-like properties. Eqs. (3) and (4) reduce to a simple set of coupled inhomogeneous differential equations for $f_{i\sigma}$ and $c_{i\sigma}^\dagger$, which can be solved straightforwardly. No solutions for which $n_{i\sigma}$ is a constant in time is found. This proves that under the used assumptions systems like this cannot have eigenstates which do not have fluctuations in $n_{i\sigma}$.

6. Treating a specific form of spin fluctuations

Two types of fluctuations containing spin degrees of freedom are imaginable; fluctuations between f-states on different sites, and fluctuations between an f-state on a certain site and delocalized states. Of course, combinations of these two are also possible. We concentrated on the type in which an f-state with a certain spin on a certain site is annihilated and an f-state on a different site but with an opposite spin is created (intersite SF). The “sea” of delocalized states is just treated as an intermediary between the sites. To treat these SF we rewrite $H_U$ in the form

$$H_S = \sum_{k\sigma} \left( T(k)_0 f_{i\sigma}^\dagger c_{k\sigma} + T(k)_0^* c_{i\sigma}^\dagger f_{k\sigma}^\dagger \right)$$

$$+ \sum_{k\sigma} \left( \tilde{\varepsilon}(k) c_{i\sigma}^\dagger c_{k\sigma} + \sum_{k\sigma} \left[ \tilde{\varepsilon}_f + \frac{1}{2} U \right] f_{k\sigma}^\dagger f_{k\sigma} \right)$$

$$+ \sum_{kk'} \left[ S(-k,k') f_{k\downarrow}^\dagger f_{k'\uparrow}^\dagger + S(-k,k')^* f_{k'\dagger}^\dagger f_{k\dagger}^\dagger \right],$$  \hspace{1cm} (5)

with

$$S(-k,k') = \frac{U}{2N_k} \sum_{k, k'} f_{k + k_0 f_{k'} + k_0} \text{ being an operator,}$$  \hspace{1cm} (6)

where $N_k$ stands for the number of k-vectors in one Brillouin zone. Note that as long as $S(-k,k')$ is a operator $H_S \equiv H_U$. The Fourier \text{cq Wannier representation of the last term in } H_S \text{ can be rewritten as}$

$$\sum_{kk'} \left[ S(-k,k') f_{k_\downarrow}^\dagger f_{k_\uparrow}^\dagger + S(-k,k')^* f_{k_\dagger}^\dagger f_{k_\dagger}^\dagger \right]$$

$$= \sum_{i,j} \left[ S(R_i, R_j) f_{i\dagger}^\dagger f_{j\dagger} + S(R_i, R_j)^* f_{i\dagger}^\dagger f_{i\dagger} \right].$$  \hspace{1cm} (7)

Disregarding the fact that $S$ is an operator, the SF we set out to study can be recognized on the right-hand side of Eq. (7). Eventually, we will treat $S(-k,k')$ in Eqs. (6) and (7) in a (special) self-consistent mean field approximation (SCMFA), so that the type of intersite SF in which an f-state on a certain site with a certain spin is annihilated and an f-state on a different site but with an opposite spin...
is created are explicitly accounted for. The \( U \)-term in the original \( H_U \) could as well have been represented as \( (\gamma f_i f_j + \text{Hermitian conjugate}) \). But thanks to adding and subtracting of extra terms (like \( \gamma f_i f_j \)), a relatively simple representation in reciprocal space for \( H_U \) is found (Eqs. (6) and (7)). In this expression the intersite coupling we set out to study can be easily recognized (Eq. (7)). Using \( K = (k + k')/2 \) and \( \Delta k = (k - k')/2 \), \( S \) can be rewritten as

\[
S(-k', k) = \frac{U}{2N_k} \sum f_{Ak+k_{k1}} f_{-Ak+k_{k1}} = S(\Delta k)
\]

as long as the symmetry of the lattice is conserved. The solution \( S(\Delta k) = S_0 \delta(\Delta k) \) for the SCMFA-scheme satisfies both this lattice translation symmetry and momentum conservation. Magnetic structures can break the lattice symmetry. The eventual magnetic structure of the HF state is expected to be very much dependent on e.g. the (indirect) exchange effects, the anisotropy energy, the relative positions and orientations of the magnetic ions and their f-shells, and the presence of a magnetic structure of another origin. In what follows, we shall only consider ferromagnetic and antiferromagnetic ordering. This is introduced in our model Hamiltonian by assuming

\[
S(-k, k') = S_0 \delta_{k,k'+Q} = |S_0| e^{i\phi} \delta_{k,k'+Q}.
\]

where \( S_0 \) is allowed to be a complex number. The chosen \( Q \)-vector will determine the eventually found magnetic structure. The absolute value of \( S_0 \) will still be determined in the SCMFA-sceme as described before, while its complex phase \( \phi \) will determine the direction of the local moment (which is also taken as a given thing). In this article we will only discuss the ferromagnetic \( Q = 0 \) and the antiferromagnetic case \( Q = \frac{1}{2}K_{BZ} \). Where \( K_{BZ} \) is the Brillouin zone lattice vector defined by the crystal lattice structure. Other magnetic structures could be easily discussed on the same footing.

7. The ferromagnetic case

In the case of ferromagnetic ordering \( Q = 0 \). The important term concerning magnetism in \( H_S \) as defined in Eq. (7) is \( H_S^F = \sum_k |S_0|^2 e^{i\phi k_{Ak}} f_{Ak}^\dagger f_{Ak} + |S_0| e^{-i\phi k_{Ak}} f_{Ak+1}^\dagger f_{Ak} \) in which \( S_0 \) is no longer an operator but an expectation value. Introducing the spin vector operator on the \( f_i \)-state \( S, H_S^F \) can be rewritten as \( \sum_k S_0(k) S(k). S_0(k) \) is a spin vector having a \( x \)-component equal to \( S_0 \cos \phi \) a \( y \)-component equal to \( S_0 \sin \phi \) and a \( z \)-component equal to 0. An interaction like this will lead to a ferromagnetic ground state with each \( k \)-state having a \( f_i \)-component with its spin aligned along the direction \( -S_0(k) \) (energy loss of \( -|S_0| \)) and an excited state with its \( f_i \) spin component aligned parallel to \( S_0(k) \) (energy gain of \( |S_0| \)). Both states have their ordered moment perpendicular to the \( z \)-direction in which the SF occur. Treating \( |S_0| \) as an expectation value, the eigenvalues and eigenvectors of \( H_S \) can be calculated in terms of \( |S_0| \):

\[
A_1^F(k) = \frac{1}{2} [e_\gamma + \frac{1}{2} U + \epsilon(k) - |S_0|] \pm \sqrt{\left( e_\gamma + \frac{1}{2} U - \epsilon(k) - |S_0| \right)^2 + 4\left( T(k_o) \right)^2},
\]

(9)

\[
A_2^F(k) = \frac{1}{2} [e_\gamma + \frac{1}{2} U + \epsilon(k) + |S_0|] \pm \sqrt{\left( e_\gamma + \frac{1}{2} U - \epsilon(k) + |S_0| \right)^2 + 4\left( T(k_o) \right)^2}.
\]

To simplify the expressions we made use of the fact that \( T(k_o) \approx e_\gamma + \frac{1}{2} U - |S_0| \). This is a broad condution band \( \epsilon(k) \) hybridized (via \( T(k_o) \)) with a dispersionless band \( e_\gamma + \frac{1}{2} U - |S_0| \), respectively, \( e_\gamma + \frac{1}{2} U + |S_0| \). This relates to \( f_i \)-states with their moment in the \( +S_0 \)- and the \( -S_0 \)-direction, respectively (see Fig. 1). Using the found eigenvectors and the definition of \( S(\Delta k) \) we can calculate \( S_0 \):

\[
S_0 = \langle |S(\Delta k)| \rangle_{\text{thermal average}} = \frac{U}{2N_k} \left( \sum_k \right) \left( n^{1-}_1(k) - n^{2-}_1(k) \right).
\]

(11)

\[
\Delta N(T) = N^{1-}_1(T) - N^{2-}_1(T).
\]

(12)

In these equations \( n^{1-}_1(k) \) and \( n^{2-}_1(k) \) are the occupation densities of, respectively, \( A_1^{1-}(k) \) and \( A_2^{1-}(k) \), and \( N^{1-}_1(T) \) and \( N^{2-}_1(T) \) the total density of occupied states, in respectively \( A_1^{1-} \) and \( A_2^{1-} \). Note that, since \( \Delta N(T) \) is temperature dependent so will \( S_0(T) \).

\( \mu \) and \( |S_0| \) are connected by the fact that the total number of particles \( n = N^{1+}_1 + N^{2+}_1 \) is fixed combined with \( |S_0| \approx \frac{1}{2} U/N_k \times \Delta N \). Using the typical numbers \( \mu \approx 5.6 \text{ eV} \); \( U \approx 5 \text{ eV} \); \( \epsilon_\gamma \approx 2 \text{ eV} \); \( T_0 \approx 2-10 \text{ meV} \); \( n \approx 10^{26} \text{ m}^{-3} \), it is possible to show that \( |S_0| \approx 0.5 \text{ eV} \). Defining \( \Delta \equiv \epsilon_\gamma + \frac{1}{2} U - |S_0| - \mu \), we can show that \( \Delta \approx 3.13 \times 10^{-6} \text{ eV} \). Since \( \epsilon_\gamma + \frac{1}{2} U - |S_0| - \mu \approx -2 \text{ meV} \), \( \mu \) will be in the flat part of the \( A_1^{1-} \)-band (and not in the gap between the \( A_1^{1-} \) and \( A_2^{1+} \) band). \( S_0 \) is approximately 0.5 eV. The precise values of the chosen typical numbers is not essential for finding a solution in which \( \mu \) is positioned in the flat part of the \( A_1^{1-} \) band. There is a whole area in parameter space (caused by the big contrast in \( k \)-dependence of the \( \epsilon(k) \) and the \( \epsilon_\gamma \) band in combination with the smallness of hybridization between them). Using an argumentation
conduction band I \( \text{local moment} \)

The \( \pm \) denotes to either being parallel (\( + \)) or opposite (\( - \)) to this direction. We find

\[
J_k^{\pm} = \frac{1}{2} \sqrt{2 - \frac{1}{N_{\text{even}}}} \sum \left[ e^{-\frac{i}{2} \left( \frac{1}{2} R_j + R_{(j+1)} \right)} \right. \\
\times \left( e^{i k R_0} f^{\dagger}_{j+1} + e^{-i k R_0} f^{\dagger}_{j} \right] 
\]

where an antiferromagnetic ordering is easy recognized. Note that the \( J_k^{+} \)-state and the \( J_k^{-} \)-state have their moments pointing precisely in the opposite directions. \( \phi \) not only determines the axis along which the moments are pointing but also a preferential direction. \( J_k \) has a lower energy than \( J_{k+} \). We introduce the term “unreduced Brillouin zone” (UBZ) for the Brillouin zone as dictated by the crystal lattice, and the term “reduced Brillouin zone” (RBZ) for the Brillouin zone which is dictated by the antiferromagnetic structure.

The system consists of a conduction electron part formed by \( \epsilon(k) \) and \( \epsilon(k + Q) \), a localized electron part formed by \( \epsilon_f \) and \( \epsilon_f + \frac{1}{2} U \), and a hybridization-like interaction between them formed by terms like \( T(k) \).

Dealing with sets of four-order equations, eigenvalues and eigenvectors can be calculated straightforwardly. Using the fact that \( T_0 \approx U \) and \( T_0 \approx S_0 \) it can be shown that

\[
A_1^+ (k) = \frac{1}{2} \left[ \epsilon_f + \frac{1}{2} U + \epsilon(k) - |S_0| \right] \\
\pm \sqrt{\left( \epsilon_f + \frac{1}{2} U - \epsilon(k) - |S_0| \right)^2 + 4T(k)k_0^2} \\
\text{for } 0 < |k_{\text{along } Q\text{ direction}}| < |Q|, \tag{14a} \\
A_1^-(k) = \frac{1}{2} \left[ \epsilon_f + \frac{1}{2} U + \epsilon(k + Q) - |S_0| \right] \\
\pm \sqrt{\left( \epsilon_f + \frac{1}{2} U - \epsilon(k + Q) - |S_0| \right)^2 + 4T(k)k_0^2} \\
\text{for } |Q| < |k_{\text{along } Q\text{ direction}}| < |K_{\text{UBZ}}|, \tag{14b} \\
A_2^+ (k) = \frac{1}{2} \left[ \epsilon_f + \frac{1}{2} U + \epsilon(k) - |S_0| \right] \\
\pm \sqrt{\left( \epsilon_f + \frac{1}{2} U - \epsilon(k) + |S_0| \right)^2 + 4T(k)k_0^2} \\
\text{for } |Q| < |k_{\text{along } Q\text{ direction}}| < |K_{\text{UBZ}}|, \tag{15a} \\
A_2^- (k) = \frac{1}{2} \left[ \epsilon_f + \frac{1}{2} U + \epsilon(k + Q) - |S_0| \right] \\
\pm \sqrt{\left( \epsilon_f + \frac{1}{2} U - \epsilon(k + Q) + |S_0| \right)^2 + 4T(k)k_0^2} \\
\text{for } |Q| < |k_{\text{along } Q\text{ direction}}| < |K_{\text{UBZ}}|. \tag{15b} 
\]

These so-found bands have strong similarities with the bands as found in the ferromagnetic case. The shape (see upper part in Fig. 2) of the bands can therefore be understood in an analogous fashion. It was checked that for the set of typical numbers mentioned earlier the cross point for which \( \epsilon(k) = \epsilon(k + Q) \) corresponds to an energy...
being well above $e_f + \frac{1}{2}U - |S_0|$ and need not be considered in our calculations.

The observed magnetic moment of an eigenstate will have two origins: one stemming from its conduction electron parts $c_{kT}$ and $c_{k+Q}$ and the other stemming from its antiferromagnetic $f_{kT}$-like part. Note, the spin-up/down direction of the conduction electrons is perpendicular to the direction of antiferromagnetic ordering stemming from the $f_{kT}$ part. At $|k|=0$, $\Lambda_1$ (k) is almost purely $c_{kT}$ like and therefore a magnetic moment in the spin-up direction is observed for these states. Going towards $k = \pm \frac{1}{2}Q$ the contribution of the $c_{kT}$ component will slowly diminish and with it the contribution of the $f_{kT}$ part will slowly increase. Concurrently, the magnetic moment of the conduction electrons slowly decreases while the size of the moment involved in the antiferromagnetic ordering slowly increases (see lower part in Fig. 2). For the $k_1$-vector for which $\varepsilon(k_1) = e_f + \frac{1}{2}U - |S_0|$, the contribution from both parts ($c_{kT}$ and $f_{kT}$) are equal. After this the $f_{kT}$-contribution will rapidly grow, and the eigenstates will only contain a small component of $c_{kT}$. The antiferromagnetic structure will get rapidly dominant. Up to now the $c_{k+Q}$ contribution to the eigenstates was negligible with respect to the $c_{kT}$-contribution. At $k = \pm Q$ the contributions from $c_{kT}$ and $c_{k+Q}$ to the eigenstates are equal and therefore the magnetic moment of the conduction electrons is precisely zero. Going even further towards $k = \pm \frac{1}{2}K_{UBZ}$ the $c_{k+Q}$-contribution starts to increase while the $f_{kT}$-contribution starts to diminish. Now the $c_{kT}$-contribution is negligible causing the moment of the conduction electrons to grow, in the opposite direction, and the moment related to the local moment antiferromagnetism to diminish accordingly. At $k_2$ defined by $\varepsilon(k_2 + Q) = e_f + \frac{1}{2}U - |S_0|$ the moments are equal, while at $k = \frac{1}{2}K_{UBZ}$ the eigenstates will be almost conduction electron like having a moment pointing downwards. In the RBS scheme only the (a) solutions of the eigenvalues (Eqs. (14a) and (15a)) are left but with a double degeneracy. Since the bandstructures are so similar to the ferromagnetic case it is not surprising that in determining $|S_0|$ in the SCMFA scheme the same expressions as Eqs. (13)-(16) are found. Using the same set of typical numbers we find similar results, $[e_f + (1/2)U - |S_0|] - A_1(K_{UBZ}) < \Delta < T_0$ ($S_0 \approx 0.5$ eV), and $\mu$ is in the flat part of the $\Lambda_1$-band. The average occupation density per site was determined to be 0.90, while a mass enhancement between 80 and 400 is found depending on the precise value taken for $T_0$. The critical temperature is approximately 15 K.

9. The small magnetic moment

Time reversal symmetry requires that a sign reversal of the quasi-momentum vector $k$ accompanied with a sign reversal of the magnetic moments must leave systems which satisfy this symmetry unchanged. In the theory as presented in this article this corresponds to $\phi$ and $\phi + \pi$, both equally legitimate solutions of the problem. A way to break time reversal symmetry is e.g. by the presence of a magnetic ordering of another origin or a magnetic field. Suppose for some reason we end up with a twofold degenerate hybridization like sharp peak in the DOS at the Fermi level, distinguishable by having identical types of magnetic ordering but the sign of the local moments reversed. As e.g. for the model presented here for the case in which time reversal symmetry must be conserved (no magnetic field and no magnetic ordering of another origin). An argumentation much like the Stoner theory [12-15] could be used. As in our theory the Fermi energy is very close to the sharp edge so typical for hybridization like peaks. The introduction of an exchange interaction $I$ between these two sets causes the two peaks to shift with respect to one another as long as $I \times \Delta N > 1$, where $\Delta N$ is the difference in occupation densities at the Fermi
level between the two peaks. Due to the closeness of the Fermi level to the sharp edge only a very small shift is already sufficient to cause $\Delta N = 0$, regardless of $I$. The shape of the bands is such that the number of uncompensated local moments per site is extremely small. Note that this argument not only holds for antiferromagnetic ordering but also for ferromagnetic ordering.

10. Charge transfer effects

The problem of charge transfer between a bare f-level (in this section addressed as A) and the conduction electron states (in this section addressed as B) will be discussed in a fashion similar to the “Miedema approach” [46]. Since the ligand hybridization $T_0$ is so small we can discuss the effects of charge transfer separately from the model used to evaluate the Hamiltonian. The outcome of the charge transfer considerations must be treated as an extra restriction for the used model. To satisfy photon emission experiments [30,40], we do not start with an empty f-level but with a single occupied f-level having a contact potential (without charge transfer and without hybridization) $\phi_0 = \mu_A - \mu_B$ of 2 eV. Charge transfer causes the effective contact potential to change into (still without hybridization) $\phi = \phi_0 - P \Delta n_B$. $P$ has to be determined experimentally, being of the order of 25 eV and $\Delta n_B$ is the electron transfer from A to B. $P$ contains an electronic charge squared divided by something like a capacitance. We introduce $D(E)_i$ as the respective density of states ($i = \{A, B\}$) and start with two electrons per unit cell:

$$\int^\mu \delta E (D(E)_A + D(E - \phi)_B) = 2, \quad (16)$$

and the charge transfer is given by

$$\Delta n_B = \int^\mu \delta E D(E - \phi)_B - 1. \quad (17)$$

From this set of two equations the chemical potential and the charge transfer can be calculated. This is independent of the used model to evaluate the Hamiltonian. Since $D(E)_A$ is much narrower than $D(E)_B$ in a HF compound it is a good approximation to set $\phi = 0$, dictating the charge transfer to be

$$\Delta n = \frac{\phi_0}{P} \approx 0.08, \quad (18)$$

setting the occupation density per f-shell to be approximately 0.92 independent of the used model treatment.

Of course, charge transfer will also affect the hybridization but since there are many causes affecting it, like the presence of a kind of polaron effect in HFs, it is not fair to single one out.

11. Spin fluctuations in magnetic fields

A magnetic field along the z-axis has in principle two major ways of affecting the system described by the Hamiltonian $H_S$, a Zeeman contribution to $e\mathbf{r} \cdot B = e\mathbf{r} \pm \mu_B B$, and conduction electron states getting more and more Landau level like. The slope of the Landau levels as a function of field is inversely proportional to the effective mass. In HFs an enormous mass enhancement is present only in a small region around the Fermi level. Thanks to the complicated spatial distribution of Landau levels, also a field effect is expected for the hybridization strength.

For our considerations we only take into account the effect of the Zeeman energy. The whole calculation has to be done anew, but the results can also be understood on a more informal basis. All the formulas presented in this section, however, stem from the exact calculations.

If two pure f-like levels with an energy $e_\mathbf{r} \pm \frac{1}{2} U + \mu_B B$ and $e_\mathbf{r} + \frac{1}{2} U - \mu_B(B)$ would experience a hybridization like interaction via $S(Ak, B)_o$, two new energy levels will be formed: for $x = \frac{1}{4}S(B)(1 + \frac{1}{x})$, the effect of the magnetic field on $A_1\pm^\pm(k)$ bands can be introduced by replacing $S_0$ into $S_0(B)(1 + x)$, leading to the results as found in the exact calculation:

$$A_1^\pm_1(k, S_0(B), B)$$

$$= A_1^\pm_1(k, S_0(B), B = 0) - \left|S_0(B)\right| 1/2 \left(\frac{\mu_0 B}{S_0(B)}\right)^2 \left[1 \pm \frac{e_\mathbf{r} + \frac{1}{2} U - S(B) - e(k)}{\sqrt{(e_\mathbf{r} + \frac{1}{2} U - S(B) - e(k))^2 + 4 T(k)^2}}\right], \quad (19)$$

$$A_2^\pm_1(k, S(B), B)$$

$$= A_2^\pm_1(k, S(B), B = 0) - \left|S_0(B)\right| 1/2 \left(\frac{\mu_0 B}{S_0(B)}\right)^2 \left[1 \pm \frac{e_\mathbf{r} + \frac{1}{2} U + S(B) - e(k)}{\sqrt{(e_\mathbf{r} + \frac{1}{2} U + S(B) - e(k))^2 + 4 T(k)^2}}\right]. \quad (20)$$

Note the presence of both terms like $S(B)$ and $S(B = 0)$. The chemical potential $\mu(B)$ as well as $S_0(B)$ will be field dependent. From the exact calculations it turns out that the field effect on $\mu(B)$ will be such $\Delta N^-$ and with it $S_0(B)$ are as constant as possible. The $A_1^\pm_1(k, B)$-band will have a decreasing field dependence.
Without doing the actual calculations these trends can also be understood. Take for a moment the field effect on $\mu(B)$ less negative than on the $A_1^{-1}$-band. For $B$ not too close to $B^\ast$ the distorting effect on the shape of the band can be disregarded. A small increase in field would cause the $A_1^{-1}$-band to shift downwards more rapidly than $\mu(B)$. With respect to $A_1^{-1}$, $\mu(B)$ shifts upwards. Due to the shape of the bands this would cause $\Delta N^-$ and with it $S_0(B)$ to even further increase pushing the $A_1^{-1}$-band below the chemical potential, etc. A runaway situation is created which will not stop until the complete $A_1^{-1}$-band is below $\mu(B)$. Analogously, if the field effect of $\mu(B)$ is more negative than the $A_1^{-1}(k, B)$-band, a runaway situation is created, but now in the opposite direction. At least as long as distorting effects on the $A_1^{-1}$-band can be disregarded, $\mu(B)$ will adjust itself in such a manner as to keep $\Delta N^-$ (and with it $S_0(B)$) as constant as possible. The relation between $\mu(B)$ and $S_0(B)$ as found in the actual SCMFA scheme, incorporating also the distortion effect, is

$$\mu(B) = \mu(B = 0) - S_0(B) + \frac{1}{2} \left( \frac{\mu_0 B^\ast}{S(B)} \right)^2$$

$$- \frac{1}{2} \left( \frac{\mu_0 B^\ast}{S(B)} \right)^2 S_0(B)$$

$$\times \left[ 1 + \frac{\epsilon_k + \frac{1}{2} U - S_0(B) - \epsilon(k)}{\sqrt{\epsilon_k + \frac{1}{2} U - S_0(B) - \epsilon(k))^2 + 4 T_0(k)^2}} \right]^{-1/2}.$$  

(21)

The chemical potential must also keep the number of particles fixed at all times, determining $\mu(B)$. A field region exist for which $\mu(B)$ is within the flat part of the $A_1^{-1}(B)$-band (peak-like structure). For low fields $\mu(B)$ is fixed with respect to its original position relative to the $A_1^{-1}$-band. $S_0(B)$ is found to be a constant ($S_0(B = 0)$) and a constant mass is observed. For fields close to $B^\ast$ the shift of the $A_1^{-1}(k, B)$-band with respect to $A_1^{-1}(k, B = 0)$ is big enough for the dispersion relation of $\epsilon(k)$ to cause a distorting effect on the shape of the band. $\mu(B)$ starts to shift upwards with respect to $A_1^{-1}$. This will cause the mass to be even further enhanced close to $B^\ast$. To calculate the precise enhancement is a very delicate matter and still needs closer examination.

$$\mu_0 B^\ast = k_B T^\ast \left[ \frac{1}{S(B = 0)} \left( \frac{3}{2} S(B = 0) \right)^{1/2} \right]^{-1/2} \left[ 1 - \epsilon(k) - \epsilon_k + \frac{1}{2} U - S_0(B = 0) \right]$$

$$- \frac{1}{2} \sqrt{\left( \epsilon_k + \frac{1}{2} U - S_0(B = 0) - \epsilon(k))^2 + 4 T_0(k)^2}}.$$  

(22)

For the typical numbers mentioned earlier, this will lead to $\mu_0 B^\ast \approx 142 k_B T^\ast$. The width of the peak-like structure in the $A_1^{-1}$-band at the Fermi level is almost not affected by the magnetic field except for a field close to $B^\ast$. The field effect on the critical temperature is mostly negligible except for a region close to $B^\ast$. For $B \geq B^\ast$ the peak in the DOS is just below $\mu(B^\ast)$ but it still exists. No HF behavior is observed at zero temperature. A small increase in temperature causes a temperature window to open around $\mu$, which, if big enough (high enough temperature) can partly incorporate the still present peak in the DOS. This could cause the HF state to be seen again in experiments. Of course, further increase in temperature will kill the HF state ($B^\ast \approx 35-40 T$).

12. Summary

After discussing what we wanted to explain, the relevance of SF to the HF problem was discussed. The model system used in this article is based on the PAM with only one $f$-state per unit cell and site. In our point of view, the most simple system we could think of which still contains all the basic ingredients. The occurrence of SF in the eigenstates of this version of the PAM was discussed in terms of relevant length scales, something already known for the specific case of the Kondo problem but this time presented in a more general framework. After this a specific from of SF was focused on. Using a SCMFA scheme we were able to show that these SF can produce a HF like state. To not get side tracked from the HF problem the preference for a certain type of magnetic ordering of the HF-state is taken as a given thing. A method was developed to introduce this in the framework of our model. Two specific cases of ordering, ferromagnetic and antiferromagnetic, were treated. But other types of ordering could easily be treated on the same footing. The occurrence of a small magnetic moment was explained in general terms using a Stoner-like criterion. Also charge transfer effects were discussed, being an extra restriction the model must satisfy. It has to be stressed that this article is meant as a heuristic approach and not as some ultimate and definite truth. Hopefully, it will lead to a deeper insight and new suggestions for experiments.
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