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## Impurity-spin screening in low-density Fermi liquids

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We consider the problem of a magnetic impurity, described by the Anderson impurity model, in a low carrier density system. Such a system might be realized experimentally in strongly doped semiconductors containing magnetic impurities. We focus on the simple cases of a one-hole impurity (e.g.,  $\text{Cu}^{2+}$ ) or a one-electron impurity (like  $\text{Ce}^{3+}$ ) hybridizing with a nearly filled or nearly empty band. We show that the physics of these systems is in various respects distinct from the Kondo effect of systems with partly filled valence bands. Although the local susceptibility is strongly enhanced by the interactions, we find at low doping ( $\delta$ ) a mass reduction of the quasiparticles at the Fermi energy ( $E_F$ ), if a (singlet) bound state is stable at zero doping. We show analytically that this is caused by band-edge effects. We show further that vastly different behavior can be expected, depending on the filling of the impurity. For a one-electron impurity (Ce) interacting with an almost-filled valence band in the  $U = \infty$  limit, there is a one-particle-like bound state close to  $E_F$ . As the doping is increased this state turns into a traditional Kondo resonance. In the case of a nearly filled impurity, however, the gap state is a two-particle singlet bound state, causing a singularity in the vertex function of the diagrammatic approach to the Kondo problem. In this limit the so-called noncrossing approximation breaks down. At intermediate doping levels it is no longer possible to identify a small parameter and for small and intermediate dopings we argue that the system is not characterized by a single energy scale.

### I. INTRODUCTION

The Anderson impurity model has been successful for the description of spectroscopic and thermodynamic properties of Ce compounds.<sup>1</sup> For metallic Ce compounds it is natural to study the Anderson model for a parameter range where the Fermi energy is far from the band edges of the conduction band. In this case one finds that the low-energy physics is determined by the Kondo singlet (KS), being a bound state of the impurity spin and a conduction-electron spin-compensation cloud. It is usually assumed that the conduction band is very broad and structureless. This leads to certain simplifications. For instance, the conduction-electron spectral function ( $\text{Im} \sum_k G_{kk}/\pi$ ) is unchanged by the interaction with the impurity.<sup>2</sup> One can also show that the local susceptibility, defined by the magnetization of the impurity divided by the field acting on the impurity, is equal to the change in the total susceptibility of the system when the impurity is introduced. Moreover, this assumption about a broad and structureless band is vital for the scaling properties (universality) of the Kondo problem.

Another limit of the model which has been thoroughly investigated is the case where a partly filled impurity interacts with a completely filled valence band.<sup>3,4</sup> This situation is thought to be representative for at least the local electronic properties of the 3d Mott-Hubbard insulators, and a good description of spectroscopic<sup>5,6</sup> and magnetic<sup>7,8</sup> properties is obtained in a number of cases. These studies have been mainly focused on the Cu  $d^9$  (spin-degenerate) case, which is believed to be relevant for high- $T_c$  superconductivity.<sup>9,10</sup> If one adds a single lig-

and hole, this might get bound to a Cu-spin into the so-called local singlet (LS).<sup>3,11,12</sup> Superficially this state has some similarities with the KS; it is singlet and, for  $U \rightarrow \infty$ , it is stabilized by spin-flip processes. However, it binds because of the presence of a band cutoff, instead of the Fermi cutoff in the case of the KS. Therefore, the LS exist *by virtue of strong irregularities in the density of states*.

We imagine a strongly doped semiconductor to which a low concentration of magnetic impurities has been added. Although we believe that our conclusions apply to a broader class of magnetic impurities, we specialize on the simple cases of a Cu or Ce impurity coupling to either a nearly filled valence band, or a nearly empty conduction band. Further, we focus on a parameter regime where a gap state exists in the undoped system. In this paper we address the question how the local- and Kondo singlet regimes connect as a function of doping. Because we consider nearly filled (or empty) impurities there is no electron-hole symmetry for the itinerant electrons, and the answer to the question above depends crucially on the sign of the carriers. The only controlled expansion for the Kondo problem exploits  $1/N_d$  ( $N_d$  is the degeneracy of the localized level) as a small parameter. We find that this expansion gets better for low-carrier concentration in the case of a nearly filled (empty) impurity and electron (hole) like carriers. On the other hand, in the opposite situation (Cu in  $p$ -type or Ce in  $n$ -type semiconductors)  $1/N_d$  perturbation theory breaks down, and the physics might be different in the crossover regime between LS and KS.

The basic problem is the existence of two small pa-

rameters,  $1/N_d$  and the carrier concentration ( $\delta$ ). In the nearly filled impurity  $n$ -type case these cooperate and the expansion converges with, roughly speaking,  $\delta/N_d$ . However, they compete in the nearly filled impurity  $p$ -type case and there is an intermediate region as a function of doping where no small parameter exists. This can be seen easily, using the variational method which has proven to be quite convenient for the Ce compounds. One introduces a many-electron basis set and expresses the ground state as a linear combination of these basis states. In Fig. 1 we introduce an equivalent basis set for the Cu compounds, mapping electrons on holes and holes on electrons. This basis set is designed for describing singlet states. The state  $a$  in Fig. 1 has a  $d^{10}$  configuration with all the valence-band states up to the Fermi energy filled. In state  $b$  a  $3d$  electron has hopped into the unoccupied part of the valence band. Since any of the ten  $3d$  electrons can hop, the coupling between these states is of the order  $\sqrt{N_d}V$ , where  $N_d = 10$  is the degeneracy of the  $3d$  level and  $V$  is a one-particle hopping matrix element. As in the the Ce case, we use a model where

$$N_d|V|^2 = \tilde{V}^2 \quad (1)$$

is independent of  $N_d$ .<sup>13</sup> This leads to a  $1/N_d$  expansion, where the coupling between the states in each row is of the order  $(1/N_d)^0$ , while the coupling between states in neighboring rows is down by one order in  $1/N_d$ .<sup>13</sup> In the limit  $N_d \rightarrow \infty$ ,  $U$  (Coulomb interaction)  $\rightarrow \infty$  one has only to account for the states  $a$  and  $b$ , and one finds straightforwardly for the Kondo temperature<sup>14</sup>

$$T_K = T_F \exp(\pi \varepsilon_d / N_d \Gamma), \quad (2)$$

where  $T_F$  is the width of the *unoccupied* part of the valence band, and  $\varepsilon_d$  and  $\Gamma$  are the  $d$ -level position and width, respectively. Keeping  $U$  large ( $c$ ,  $f$ , and  $i$  do not contribute), the  $1/N_d$  corrections can be obtained by also including the states  $d$  and  $e$ , which leads to a modification of the prefactor. For the case when the Fermi energy is far from the band edges (large doping) such a descrip-

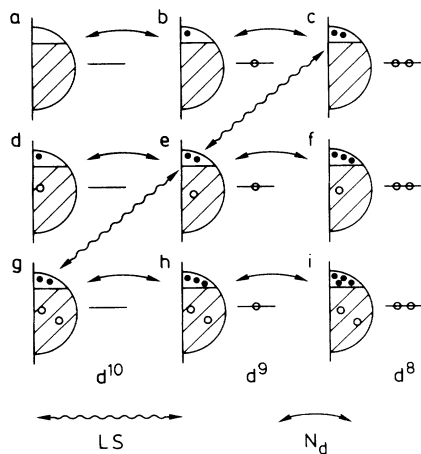


FIG. 1. Basis states for a Cu impurity. The solid lines indicate hopping of leading order in  $1/N_d$  and the wavy lines indicate hopping leading to the local singlet.

tion is rather accurate, even for  $N_d$  as small as 2, as comparisons with exact calculations show.<sup>13,15</sup> In this order the Kondo temperature vanishes if  $T_F \rightarrow 0$ . However, it is easy to show that for sufficiently strong hybridization the LS gets bound at zero doping (e.g., Sec. III), and apparently *the LS cannot be described in this order*. As discussed in Sec. III, in the field theoretical formulation the noncrossing approximation (NCA) (Ref. 16) suffers from the same pathology.<sup>14</sup> To obtain the LS in the variational approach, we have to include the states  $g$  in Fig. 1.

The reason for the problems in these  $1/N_d$  expansions at low doping is obvious; although the  $a$ - $b$  hybridization is  $N_d$  times stronger than the  $b$ - $d$  hopping, only a fraction  $\sim \delta$  (doping) of the valence-band states are involved, while processes like  $b$ - $d$  profit from the large phase space  $1 - \delta$ , and are dominant despite their weaker coupling. This suggests an alternative expansion, using  $\delta$  as the small parameter. Taking the states  $c$ ,  $g$ , and  $e$  of Fig. 1,

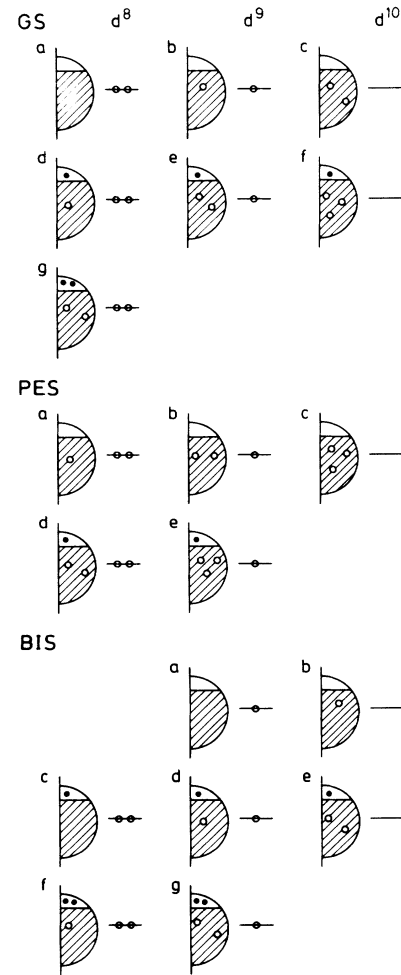


FIG. 2. Basis states emphasizing the local singlet character and using the doping as a small parameter. The coupling between states in different rows goes to zero with the doping. States used in the ground-state, photoemission, and BIS calculations are shown.

one obtains an exact solution for the local singlet in the case that only two holes are present.<sup>3,12,11</sup> We note that for large  $U$  the LS binding has a rather subtle origin; in fact, it originates from constraints implied on states  $g$  to avoid linear dependence, which translate into spin-flip processes in the strong-coupling limit (Sec. III). Thus we use the following small- $\delta$  expansion: take the states  $g$ ,  $e$ , and  $c$  in Fig. 1 and fix the two conduction electrons at the Fermi energy. This then leads to the states in the top row of Fig. 2, which describe the local singlet. For finite doping, there is hopping to the states in the second row. This hopping is of zeroth order in  $1/N_d$ , but of first order in  $\delta$ . Thus this basis set provides an expansion for small values of  $\delta$ . By comparing the two figures, one expects that at a certain carrier concentration the phase-space restrictions and the coupling parameter difference will balance, and it is no longer possible to identify a small parameter.

As mentioned above, a particularly simple case is a nearly filled impurity interacting with an almost empty conduction band. In that case we use a basis state  $a$  with a  $d^{10}$  configuration and a basis state  $b$  with a  $d^9$  configuration and a conduction electron in Fig. 1. The coupling between these states is of order  $(1/N_d)^0$ . If  $U = \infty$  the coupling to all other states is of the order  $\delta/N_d$ . The reason this works so well is in fact straightforward. A  $d^{10}$  impurity plus an empty conduction band is a one-particle problem for  $U = \infty$  and the states  $a$ - $b$  form a complete basis. Obviously, if  $\delta$  is small one can expand around this limit.

In Sec. IV we will work out the spectroscopic properties as a function of doping in the nearly empty impurity  $p$ -type case and study the LS-KS crossover. We also calculate the local susceptibility, using a basis set which at the same time accounts for the LS as well as the KS. The results for both the local susceptibility and the spectroscopic properties indicate a rather smooth crossover from the LS to the KS. Before we turn to these problems, we first characterize the low-energy properties of the low doping limit. After introducing the model in Sec. II, we focus on the strong-coupling, low- $\delta$  limit which can be studied by exploiting few-particle problems (Sec. III). We find that in contrast to the usual Kondo problem,

where the mass enhancement is  $\sim 1/T_K$ , the effective mass is in fact *reduced* due to the presence of the local singlet.

## II. MODEL

We consider the Anderson impurity model

$$H = \sum_{\nu} \left\{ \sum_i \varepsilon_i c_{i\nu}^{\dagger} c_{i\nu} + \varepsilon_d c_{\nu}^{\dagger} c_{\nu} + \frac{1}{\sqrt{N}} \sum_i [(V_{\nu}(\varepsilon_i) c_{\nu}^{\dagger} c_{i\nu} + \text{H.c.}] \right\} + U \sum_{\nu < \mu} n_{\nu} n_{\mu}, \quad (3)$$

where  $\varepsilon_d$  is the energy of the  $3d$  level on the impurity site. The  $3d$  states are labeled by an orbital index  $m$  and a spin index  $\sigma$ , and  $\nu = (m, \sigma)$  is a combined index. The index  $\nu$  runs between 1 and  $N_d = 10$ . The delocalized electrons are described by the first term, where the sum is over the  $N$  itinerant states. The hopping between the conduction states and the  $3d$  state is described by the third term, where  $V_{\nu}(\varepsilon_i)$  is a hopping matrix element. The last term describes the Coulomb interaction between the  $3d$  electrons.

Since the  $x^2 - y^2$  orbital plays a particularly important role for Cu impurities, one often considers a model with only a spin-degenerate  $3d$  level, i.e.,  $N_d = 2$ . In the limit of a small doping, i.e., few holes, it is convenient to make an electron-hole transformation, i.e., the configurations with 0, 1, or 2  $3d$  holes are mapped onto the  $d^0$ ,  $d^1$ , and  $d^2$  configurations, respectively, for  $N_d = 2$ , and the limit of few electrons is considered. Typically, the  $d^8$  ( $d^2$ ) configuration lies energetically much higher than the  $d^9$  ( $d^1$ ) configuration, due to the large value of  $U$ . For low-energy properties, this configuration can therefore be projected out. If, in addition, we make the less justified assumption, for Cu systems, that the  $d^{10}$  ( $d^0$ ) configuration is much higher than the  $d^9$  ( $d^1$ ) configuration, a simple Hamiltonian can be derived, containing only the Cu spin ( $S$ ) (Refs. 17 and 18)

$$H = \sum_{\sigma} \sum_i \varepsilon_i c_{i\sigma}^{\dagger} c_{i\sigma} + \frac{1}{N} \left( \frac{1}{\Delta} + \frac{1}{U - \Delta} \right) \sum_{ij} V_i V_j [S^z (c_{i\uparrow}^{\dagger} c_{j\uparrow} - c_{i\downarrow}^{\dagger} c_{j\downarrow}) + S^+ c_{i\downarrow}^{\dagger} c_{j\uparrow} + S^- c_{i\uparrow}^{\dagger} c_{j\downarrow}] + \frac{1}{2N} \left( \frac{1}{\Delta} - \frac{1}{U - \Delta} \right) \sum_{\sigma} \sum_{ij} V_i V_j c_{i\sigma}^{\dagger} c_{j\sigma}. \quad (4)$$

Here  $\Delta$  is the energy separation between the  $d^0$  and  $d^1$  configuration and  $U - \Delta$  is the energy separation between the  $d^2$  and  $d^1$  configurations. We have also introduced the abbreviation  $V_i = V_{\nu}(\varepsilon_i)$ , since  $V$  is independent of  $\nu$  in this  $N_d = 2$  limit. In the applications below, we assume either that  $V(\varepsilon) \equiv V$  is a constant, or that

$$|V_i|^2 = 2V^2 [B^2 - (\varepsilon_i - \varepsilon_0)^2]^{1/2} / (\pi B), \quad (5)$$

i.e., that  $|V(\varepsilon)|^2$  has a semielliptical shape. Here  $2B$  is the total bandwidth and  $\varepsilon_0$  is the center of the band.

## III. LOW DENSITY AND STRONG COUPLING

Starting out with a full valence band, the first hole added might bind to the Cu spin, forming the local sin-

glet. This problem can be mapped on an effective single-particle problem in the strong coupling  $N_d = 2$  limit [Eq. (4)], from which it is easy to determine the LS binding energy and wave function. It seems intuitively clear that only a single hole can bind to the impurity spin, and this is also the outcome of our numerical calculations. Therefore, at low-carrier densities, the question is how the Fermi-liquid renormalizes due to the scattering of the quasiparticles against the LS bound state, which is robust as long as the Fermi energy (measured relative to the top of the valence band) is much smaller than the LS binding energy. As in the Kondo problem, one expects that this leads to modification of the quasiparticle energies (mass enhancement), as well as quasiparticle-quasiparticle interactions. With respect to the latter, the low-carrier density again helps, because it follows from well-known  $T$ -matrix arguments<sup>19</sup> that these interactions approach a constant in this limit. The effect of the interactions on the quasiparticle energies therefore vanishes in the limit of a small carrier density. The changes in the quasiparticle energies due to the Cu spin can now be determined by monitoring the changes in level structure of an additional hole added in the presence of the LS. We deduce a very accurate ansatz wave function for this case, which shows that the effective mass decreases for decreasing LS binding energy, in striking contrast to the usual Kondo effect.

For notational simplicity, we use the electron-hole transformation mentioned in the preceding section, and study the Cu spin interacting with one conduction electron. The exact local singlet solution, starting from Eq. (4), is derived by introducing the basis functions<sup>20</sup>

$$|i\rangle = \frac{1}{\sqrt{2}}(|\uparrow i \downarrow\rangle - |\downarrow i \uparrow\rangle), \quad (6)$$

where  $\uparrow$  indicates that the Cu spin points upwards and  $i \downarrow$  gives the energy  $\varepsilon_i$  and spin of the conduction electron. The state (6) is constructed to be a singlet. We can also introduce triplet states

$$|\tilde{i}\rangle = \frac{1}{\sqrt{2}}(|\uparrow i \downarrow\rangle + |\downarrow i \uparrow\rangle). \quad (7)$$

The states (6) and (7) form a complete set for this one-electron plus spin problem. The singlet and triplet states do not couple to each other and the lowest state is formed in the singlet channel. The exact ground-state wave function can therefore be written as<sup>20</sup>

$$|\phi\rangle = \sum_i \alpha_i |i\rangle. \quad (8)$$

We have

$$H|i\rangle = \varepsilon_i |i\rangle - \frac{I}{N} V_i \sum_j V_j |j\rangle, \quad (9)$$

where  $I = 1/\Delta + 2/(U - \Delta)$ . We note the importance of the spin-flip term in Eq. (4), since the coupling to the  $d^0$  configuration would otherwise be zero. This also illustrates that there is an asymmetry between the couplings to the  $d^0$  and  $d^2$  configurations. Due to the separable form of the interaction in (9), the solution can be found analytically. One obtains the implicit equation

$$\frac{I}{N} \sum_i \frac{|V_i|^2}{\varepsilon_i - E_0} = 1 \quad (10)$$

for the ground-state energy  $E_0$ . We let the band extend between 0 and  $2B$  ( $0 \leq \varepsilon_i \leq 2B$ ). If  $V_i \equiv V$ , Eq. (10) always has a solution with  $E_0 < 0$ . If  $|E_0| \ll 2B$ , we obtain  $E_0 \approx -2B \exp(-1/J)$ , where  $J = IV^2/(2B)$ . This result shows striking similarities with the result to lowest order in  $(1/N_d)$  for the Kondo problem, using the Anderson impurity model. We note, however, that in that case the prefactor refers to the occupied part of the band and that there is a degeneracy factor in the exponent. For the semielliptical shape (5) of  $|V(\varepsilon)|^2$  there is a solution  $E_0 < 0$  if  $2V^2I/B > 1$ , i.e., if the hopping matrix elements are large enough. This bound solution is the local singlet. We further obtain

$$\alpha_i = \frac{CI}{N} \frac{V_i}{(\varepsilon_i - E_0)}, \quad (11)$$

where

$$C = \left[ \frac{I^2}{N} \sum_i \frac{|V_i|^2}{(\varepsilon_i - E_0)^2} \right]^{-1/2} \quad (12)$$

is a normalization constant.

We now turn to the three-particle (two holes plus spin) problem, which will give the quasiparticle spectrum for small  $\delta$ . In contrast to the two-particle problem this is no longer simple to solve. We first study this problem numerically by discretizing the energies of the holes in a finite number ( $N$ ) of points. The spectrum of eigenvalues obtained in this way is rather complicated at energies larger than 0 (excitation energies larger than  $|E_0|$ ). However, in the interval  $E_0 < E < 0$ , the spectrum looks like that of the unperturbed hole, with corrections scaling with  $1/N$ . This shows that only a single hole binds to the spin, and the other holes experience a phase shift due to the presence of the LS bound state. The eigenenergies for  $N = 31$  are given by  $E_i^{\text{ex}}$  in Table I. The inverse

TABLE I. Result for the two-holes plus spin problem.  $E_i^{\text{ex}}$  are exact total energies,  $E_i^{\text{an}}$  are results for the analytical ansatz (13), and  $\Delta\varepsilon_i^{\text{ex}}$  are the spacing of the excitation energies. The parameters are  $V = 1.8$ ,  $\Delta = 1$ ,  $U = \infty$ , and  $2B = 2$ . The form (5) was used for  $|V(\varepsilon)|^2$  and the energy was discretized in 31 equidistant points.

	1	2	3	4	5	6	7	8	9	10
$E_i^{\text{ex}}$	-0.7149	-0.6386	-0.5681	-0.4987	-0.4298	-0.3611	-0.2927	-0.2244	-0.1562	-0.0881
$E_i^{\text{an}}$	-0.7149	-0.6386	-0.5681	-0.4987	-0.4297	-0.3611	-0.2926	-0.2243	-0.1561	-0.0880
$\Delta\varepsilon_i^{\text{ex}}$		0.0763	0.0705	0.0694	0.0689	0.0687	0.0684	0.0683	0.0682	0.0681

of the spacing ( $\Delta\varepsilon_i^{\text{ex}}$ ) of these energies gives the density of states. This should be compared with the density of states in the absence of an impurity. In that case the spacing is simply given by the energy interval (0.0667) in our discretization of the mesh. We can see that the density of states is reduced due to the interaction with the impurity, i.e., there is a mass reduction. Alternatively, one could compare the mass with that obtained for the noninteracting ( $U = 0$ ) impurity system; although the mass is also reduced in the noninteracting case, we observed that the interactions lead to a further reduction.

To understand this mass reduction, we want to obtain an approximate analytical solution. We introduce the basis functions for the two conduction electrons plus spin problem

$$|i2\rangle = \frac{1}{\sqrt{2}} \left[ \sum_k \alpha_k |\uparrow k \downarrow i \uparrow\rangle - \sum_{k \neq i} \alpha_k |\downarrow k \uparrow i \uparrow\rangle \right], \quad (13)$$

where  $\alpha_k$  is the coefficient in Eq. (11). The state (13) is built up from the local singlet ground state with the electron  $i$  added. To avoid the violation of the Pauli principle the restriction  $k \neq i$  is introduced. This can be expected to be a good basis set for the study of states with an excitation energy which is smaller than the local singlet binding energy, while for larger energies one expects states where the local singlet is broken up to be important. The states  $|i2\rangle$  are not orthogonal

$$\langle i2|j2\rangle = \delta_{ij} - \frac{1}{2}\alpha_i\alpha_j. \quad (14)$$

Although the calculations can be carried out for a finite  $U$ , the expressions are simpler for  $U = \infty$  and therefore we consider this limit below. The matrix elements of the Hamiltonian are

$$\langle i2|H|j2\rangle = (\varepsilon_i + E_0)\delta_{ij} - E_0\alpha_i\alpha_j + \frac{1}{2N\Delta}V_iV_j. \quad (15)$$

To perform calculations we change to an orthogonal basis set

$$|\tilde{i}2\rangle = |i2\rangle + \frac{1}{2}\beta\alpha_i \sum_k \alpha_k |k2\rangle, \quad (16)$$

where  $\beta = 2(\sqrt{2} - 1)$ . Then we obtain

$$\delta\rho(\varepsilon) = \frac{1}{\pi} \frac{d}{d\varepsilon} \text{Im} \ln \left[ \left( 1 + \frac{\delta}{z - 2E_0} \right) \left( \frac{1}{2N\Delta} \right) \sum_i \frac{|V_i|^2}{E_0 + \varepsilon_i - z} + 1 - \frac{3\delta/2}{z - 2E_0 + \delta} \right], \quad (22)$$

where  $z = \varepsilon - i0^+$  and  $\delta = 3\beta(4 + \beta)C^2/(4N\Delta)$ . The expression inside the brackets does not change its phase as  $\varepsilon$  goes through  $2E_0$ , due to opposite changes in the phases of the two factors. Thus there is no contribution to the density of states at  $2E_0$ , which is correct, since the lowest state of the system is located at  $E_0$ . If we only consider  $\varepsilon \geq E_0$  we can then drop the first factor. This leads to the expression

$$\delta\rho(\varepsilon) = \frac{1}{\pi} \frac{d}{d\varepsilon} \varphi(\varepsilon), \quad (23)$$

where

$$\begin{aligned} \langle \tilde{i}2|H|\tilde{j}2\rangle &= (\varepsilon_i + E_0)\delta_{ij} \\ &+ \frac{1}{2N\Delta}(V_iV_j + V_iX_j + X_iV_j + \frac{1}{3}X_iX_j), \end{aligned} \quad (17)$$

where  $X_i = 3\beta C\alpha_i/2$ . We observe that the second term of Eq. (17) describes a repulsive energy-dependent scattering potential. The repulsive character of the potential suggests a mass reduction, at least over some energy range. The states of the system are now obtained by diagonalizing the matrix (17). The results are compared in Table I with the results of the exact numerical solution. The agreement is excellent, and it is therefore justified to try to understand the results based on the analytical ansatz (13). Thus we study the change of the density of states due to the coupling between the impurity and the conduction band

$$\delta\rho(\varepsilon) = \frac{1}{\pi} \text{Im}[\text{Tr}(z - H)^{-1} - \text{Tr}(z - H_0 - E_0)^{-1}], \quad (18)$$

where  $z = \varepsilon + i0^+$  and  $\text{Tr}(z - H)^{-1}$  is evaluated in the space (13).  $H_0$  is the first term in Eq. (4), and corresponds to a system where the interaction between the local spin and the conduction electrons has been turned off. We first observe that the matrix (17) is separable and can be diagonalized analytically. We obtain

$$\begin{aligned} [(z - H)^{-1}]_{ij} &= \frac{\delta_{ij}}{z - E_0 - \varepsilon_i} \\ &+ \frac{F_iV_j + F_iX_j + G_iV_j + \frac{1}{3}G_iX_j}{z - E_0 - \varepsilon_j}, \end{aligned} \quad (19)$$

where

$$F_i = \frac{1}{2N\Delta} \sum_k [(z - H)^{-1}]_{ik} V_k \quad (20)$$

and

$$G_i = \frac{1}{2N\Delta} \sum_k [(z - H)^{-1}]_{ik} X_k. \quad (21)$$

By inserting the expression (19) for  $(z - H)^{-1}$  in Eqs. (20) and (21) we obtain two equations for the unknown  $F_i$  and  $G_i$ , which are solved. After lengthy calculations we obtain

$$\varphi(\varepsilon) = \text{Im} \ln \left[ \frac{1}{2N\Delta} \sum_i \frac{|V_i|^2}{E_0 + \varepsilon_i - z} + 1 - \frac{3\delta/2}{z - 2E_0 + \delta} \right] \quad (24)$$

is a phase shift. We now assume that  $V_i = V$  and that  $|E_0| \ll 2B$ , which leads to

$$\delta\rho(\varepsilon) = \frac{2B}{(E_0 - \varepsilon)(E_0 + 2B - \varepsilon)} + \frac{4B\Delta}{V^2} \frac{3\delta/2}{(\varepsilon - 2E_0 + \delta)^2} \left\{ \left[ \ln \left| \frac{2B + E_0 - \varepsilon}{\varepsilon - E_0} \right| + \frac{4B\Delta}{V^2} \left( 1 - \frac{3\delta/2}{\varepsilon - 2E_0 + \delta} \right)^2 \right]^2 + \pi^2 \right\}^{-1}. \quad (25)$$

The second term gives a contribution which is proportional to  $1/|E_0|$ . This is similar to the Kondo problem, where the density of states is  $\sim 1/T_K$  close to the Fermi energy. Somewhat surprisingly there is, however, a prefactor  $(V^2/2B\Delta)^2$  in the present problem. The first term in the numerator is a correction due to the band edges. This correction is large and negative if  $\varepsilon$  is close to one of the band edges  $E_0$  or  $E_0 + 2B$ . Such corrections also appear in the treatment of the Kondo problem, but are usually neglected, since the band edges are assumed to be far away. Close to the band edges this term dominates over the contribution from the second term, and there is a reduction in the density of states. This explains the mass reduction observed in the numerical calculations. We note that these band-edge corrections are intimately connected to the local singlet, since the local singlet type of hopping is important exactly when the Fermi energy is close to one of the band edges. However, even for Ce compounds the neglect of this type of effects is probably not justified, since the conduction density of states often has a strong variation. As we will show in Sec. V, the local susceptibility  $\chi_{\text{local}}$  is, not surprisingly,  $\sim 1/E_0$  in this limit. The change  $\delta\chi$  in the global susceptibility  $\chi$ , on the other hand, is proportional to the density of

states, and it decreases for decreasing  $E_0$ , while the local susceptibility increases. This is in striking contrast with the usual assumption, which is based on a constant density of states (DOS) over an energy interval much greater than  $T_K$ , that  $\chi_{\text{local}} = \delta\chi$ . In the constant DOS limit the system is characterized by a single energy scale  $T_k$ , while in the limit studied above the system cannot be characterized by the local singlet binding energy only.

Above we have discussed the cases of two particles and three particles. If the number of particles is larger but the system still is in the low-density limit it is useful to use a  $T$ -matrix approach. Here we use the formalism of Keiter and Kimball<sup>21</sup> applied to the Anderson impurity model. We consider the processes shown in Fig. 3, which describe the scattering of a localized  $3d$  electron (dashed line) with the quantum number  $M'$  and a conduction electron (solid line) with the quantum number  $M$  ( $\neq M'$ ) and the energy  $E$ . The scattering takes place via the excitation of the  $3d$  electron into a conduction state ( $E_1 M'$ ), leaving the  $3d$  level empty (denoted by a wavy line). We consider processes where at the end the  $3d$  electron has the initial quantum number  $M'$  again. The  $T$  matrix satisfies the following equation:

$$T_{MM'}(E, E', z) = \int dE_1 \frac{\bar{V}(E)\bar{V}(E_1)^2\bar{V}(E')}{(z - E - E_1)(z - \varepsilon_d - E_1)(z - E_1 - E')} + \int dE_1 \int dE_2 \frac{\bar{V}(E)\bar{V}(E_1)^2\bar{V}(E_2)T_{MM'}(E_2, E', z)}{(z - E - E_1)(z - \varepsilon_d - E_1)(z - E_1 - E_2)(z - \varepsilon_d - E_2)}, \quad (26)$$

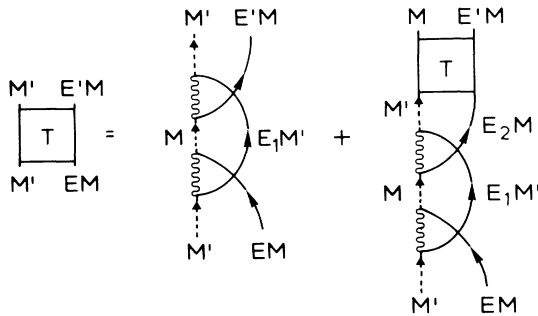


FIG. 3. Diagrams describing the  $T$  matrix  $T_{MM'}(E, E', z)$ . Here the  $T$  matrix is described by the square, a  $3d$  electron by a dashed line, a conduction electron by a solid line, and an empty  $3d$  level by a wavy line.

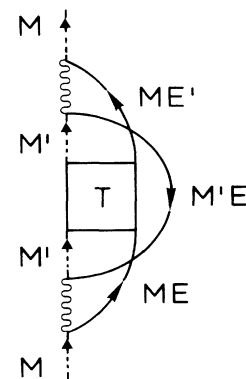


FIG. 4. Diagram contributing to the partition function. The notations are the same as in Fig. 3.

where

$$\bar{V}(E) = V(E)\sqrt{[1 - f(E)]} \quad (27)$$

and  $f(E)$  is the Fermi function. We now consider the limit  $\Delta \gg 2B$ . For  $z$  close to the ground-state energy, we can then replace the denominators  $(z - E - E_1)$  and  $(z - E_1 - E_2)$  by  $z$ . The equation for the  $T$  matrix is then separable and can be solved analytically. We further assume that the local singlet binding energy is small compared with  $\Delta$ .

Solving Eq. (26), we obtain the  $T$  matrix

$$T_{MM'}(E, E', z) = \frac{F(z)\bar{V}(E)\bar{V}(E')}{z} + F(z)^2 \int dE_2 \frac{\bar{V}(E)\bar{V}(E_2)^2\bar{V}(E')}{z^2(z - \varepsilon_d - E_2)A(z)}, \quad (28)$$

where

$$F(z) = \int dE \frac{\bar{V}(E)^2}{z(z - \varepsilon_d - E)} \quad (29)$$

and

$$A(z) = 1 - F(z) \int dE \frac{\bar{V}(E)^2}{z(z - \varepsilon_d - E)}. \quad (30)$$

$A(z)$  has a zero at  $z = \varepsilon_d + E_0$ , where  $E_0$  is the local singlet binding energy. This follows from Eq. (10), since  $I = 1/|\varepsilon_d| \approx 1/|\varepsilon_d + E_0|$ . Thus the  $T$  matrix has a pole at  $z = \varepsilon_d + E_0$ .

We now calculate contributions to the partition function  $Z$ . First we consider the diagram in Fig. 4 which contains an incoming line describing a  $3d$  electron and the  $T$  matrix just discussed. For  $M \neq M'$  we obtain the contribution

$$Z_1 = \sum_{M \neq M'} \int \frac{dz}{2\pi i} e^{-\beta z} \frac{1}{(z - \varepsilon_d)^2} \int dE dE' dE_1 \frac{\bar{V}(E)\bar{V}(E')V(E_1)^2 f(E_1)T_{MM'}(E, E', z + E_1)}{(z - E)(z - \varepsilon_d - E + E_1)(z - \varepsilon_d - E' + E_1)(z - E')}. \quad (31)$$

For  $T \rightarrow 0$  the contribution from the pole in the  $T$  matrix dominates. Using the assumptions above [ $|\varepsilon_d| \gg 2B$  and  $(V/\varepsilon_d)^2 \ll 1$ ] we obtain

$$Z_1 = \frac{1}{2} N_d (N_d - 1) e^{-\beta(\varepsilon_d + E_0)}, \quad (32)$$

which is the correct result in this limit. For  $M = M'$  we can replace the  $T$  matrix in Fig. 3 by a simpler  $T$  matrix where the basic scattering process only involves the conversion of the incoming  $3d$  electron into a conduction electron  $EM$  and the conversion of the incoming conduction electron into a  $3d$  electron. The corresponding  $T$  matrix has a rather similar structure as Eq. (28), but due to a sign change in the expression for  $A(z)$  there is no pole. We can also consider a diagram with an incoming empty state which is otherwise equivalent to Fig. 4. In the approximation considered here, such a diagram gives a contribution which is reduced by a factor  $(V/\varepsilon_d)^2$  and which can therefore be neglected.

We can first notice that the most important diagram in this limit (Figs. 3 and 4) is not included in the noncrossing approximation (NCA).<sup>16</sup> In situations where the local singlet is important it is therefore crucial to go beyond the NCA. We further notice that the pole in the  $T$  matrix should lead to a pole in the vertex function. It is interesting to ask for the implications of this in terms of the recent work on the linear energy dependence of the imaginary part of the self-energy for the high- $T_c$  systems.<sup>22</sup>

#### IV. THE CROSSOVER FROM THE LOCAL TO KONDO SINGLET

Above we have discussed the low doping limit and the local singlet (LS). Below we consider finite dopings and the crossover to the Kondo singlet (KS), which dominates for large dopings. As the doping is increased, there

should be a crossover from the situation with more than one energy scale, illustrated by the results for the effective mass in Sec. III, to the universal behavior in the Kondo limit. We also expect the singularity in the vertex function in Sec. III to lose importance, since the Kondo limit is well described in theories neglecting vertex corrections. Intermediate dopings are also interesting, since there is no small parameter available in this doping regime, as discussed in the Introduction. We calculate the spectral function and the local susceptibility.

We first focus on the spectral function. In the Introduction we argued that the basis states in Fig. 2 provide a good basis set if the doping  $\delta$  is much smaller than  $1/N_d$ . In the following we consider for simplicity the case when  $N_d = 2$ . The state  $a$  then corresponds to a  $d^0$  state and the state  $c$  to a  $d^2$  state. We recall that the physical situation for the high- $T_c$  compounds is that  $E(d^9) < E(d^{10}) < E(d^8)$ . In our  $N_d = 2$  model, this corresponds to  $E(d^1) < E(d^2) < E(d^0)$ . The coupling between the states  $a$ - $b$  is  $\sim N_d = 2$  and the coupling  $b$ - $c$  is  $\sim N_d - 1 = 1$ . For the coupling to the second row we have that the coupling  $b$ - $d$  is  $\sim 1$  and the coupling  $c$ - $e$  is  $\sim 2 = N_d$ . If the energy of  $d^0$  configuration is much larger than other energies, the degeneracy factor then favors the coupling between the first and second row ( $c$ - $e$ ), while the doping favors the coupling in the first row ( $b$ - $c$ ). This is the competition between the two small parameters  $1/N_d$  and  $\delta$  we have discussed before. On the other hand, if the  $d^2$  state is much higher than other states, both the degeneracy and the doping favor the coupling ( $a$ - $b$ ) in the first row. This is a simple situation and, as discussed in the Introduction, the case  $E(d^2) = \infty$  and  $\delta = 0$  can be mapped on a one-particle problem. In this limit it is sufficient to use the states  $a$  and  $b$  in the ground-state calculation. We shall first consider this physically

unlikely situation, since it allows us to solve the problem analytically. We shall show how in this limit a peak is formed on the bremsstrahlung isochromat spectroscopy (BIS) side. This peak is interesting, since it goes over to a LS peak when we lower the  $d^2$  configuration. We then consider the case when the  $d^0$  and  $d^2$  configurations are degenerate. This symmetric case is a good test case, because as the doping is increased to  $\delta = 0.5$ , i.e., the Fermi energy is in the middle of the band, the spectrum should be symmetric. This provides a way of checking the accuracy of our calculation for  $\delta \gg 0$ , where we have no small parameter. We then focus on the crossover between the LS and KS peaks by increasing the doping from  $\delta \approx 0$  to 0.5.

We first consider the low doping case and with  $E(d^2) = \infty$ , mentioned above. Thus we work to lowest order in the doping, and include the states  $a$  and  $b$  at the top of Fig. 2 for the ground-state calculation, which gives a zero-order calculation. For the BIS calculation we include the states  $a$ ,  $c$ , and  $d$  at the bottom of Fig. 2. Although the states  $c$  and  $d$  are of first order in the doping, they are needed since the intensity just above the Fermi energy is otherwise zero. This does not contradict the statement

that these states are of first order in the doping, since the integrated intensity just above the Fermi energy is of first order due to the small energy range over which this intensity appears. The calculation shows great similarities with the corresponding calculation for Ce (Ref. 13), but also some differences. The ground state is written as

$$|\phi\rangle = A \left[ |0\rangle + \int_{-2B}^{\epsilon_F} a(\epsilon) |\epsilon\rangle d\epsilon \right], \quad (33)$$

where  $|0\rangle$  is the state  $a$  and  $|\epsilon\rangle$  is the state  $b$  in Fig. 2. The band extends from  $-2B$  to 0. The coefficient  $a(\epsilon)$  is determined variationally. The BIS spectrum is now expressed in terms of the Green's function

$$g_\nu^>(z) = \left\langle \phi \left| \psi_\nu \frac{1}{z + E_0 + E_0^0 - H} \psi_\nu^\dagger \right| \phi \right\rangle, \quad (34)$$

where  $E_0^0$  is the energy of the state  $|0\rangle$  and  $E_0 + E_0^0$  is the ground-state energy. The matrix elements of  $(z + E_0 + E_0^0 - H)$  are calculated for the basis states  $a$ ,  $c$ , and  $d$ , and the corresponding matrix is inverted. For  $N_d = 2$  we obtain

$$g^>(z) = A^2 \left[ z + E_0 - \epsilon_d - \int_{\epsilon_F}^0 dE \frac{|V(E)|^2}{z + E_0 - E - 2 \int_{-2B}^{\epsilon_F} d\epsilon \frac{|V(\epsilon)|^2}{z + E_0 - E - \epsilon_d + \epsilon}} \right]^{-1}, \quad (35)$$

where  $\epsilon_d$  is the energy of the  $3d$  level. We can now write

$$\text{Im} \frac{1}{z + E_0 - E - \int_{-2B}^{\epsilon_F} \frac{2|V(\epsilon)|^2}{z + E_0 - E - \epsilon_d + \epsilon} d\epsilon} = \pi A^2 \delta(\epsilon - E) + \mu(\epsilon - E), \quad (36)$$

where  $z = \epsilon - i0^+$  and  $\text{Im} \mu(E - i0^+) = 0$  for  $E < \epsilon_d - E_0$ . In the small doping limit the real part of the integral of  $E$  goes to zero and can be neglected. The imaginary part has to be kept, however, since it leads to a finite contribution to the spectrum in the range  $\epsilon_F$  to 0. Also in the Ce calculation the real part of (36) is neglected, but in that case the justification is based on a  $1/N_d$  argument. We obtain

$$\rho(E) = \frac{1}{\pi} \text{Im} g^>(E - i0^+) = \frac{A^2 |V(E)|^2}{(E + E_0 - \epsilon_d)^2} \quad (37)$$

for  $\epsilon_F \leq E < 0$ . The spectrum essentially reflects the shape of  $|V(E)|^2$ , but it is enhanced by the factor  $(E + E_0 - \epsilon_d)^{-2}$ , which grows as the energy increases and would diverge at  $\epsilon = \epsilon_d - E_0$ . At this energy Eq. (37) is not valid, but from Eq. (35) it follows that the system has a  $\delta$  function at this energy. As discussed at the beginning of this section, in the present case [ $E(d^2) = \infty$ ] this peak is a particlelike peak. As  $E(d^2)$  is lowered this peak goes over to the LS peak, corresponding to the situation where the system has lost the LS binding energy. This case requires a numerical treatment and it is discussed below. For small dopings, the theory above gives a gap between the continuum (37) and the  $\delta$  function.

If the calculation were performed to higher order in the doping this gap would disappear, but the intensity would be very small for a small doping, and we would be left with a pseudogap.

We now consider numerical results for the spectrum. We focus on the case  $N_d = 2$  and consider arbitrary doping  $\delta < 0.5$ . The case  $\delta > 0.5$  is uninteresting, since in this  $N_d = 2$  case we can use an electron-hole transformation together with the results for  $\delta < 0.5$  to obtain the results for  $\delta > 0.5$ . For the photoemission spectroscopy (PES) calculation we use the ground-state basis functions  $a$  to  $e$  in Fig. 2 and the PES basis functions  $a$  to  $e$ . This calculation is correct to leading order in  $\delta$  and includes some of the important next-order contributions. The choice of ground-state basis functions and final-state basis functions is consistent in the sense that the PES spectrum starts at the Fermi energy, as it should. For the BIS calculation we use the ground-state basis functions  $a$  to  $g$  and the BIS basis functions  $a$  to  $g$ . In this case we are not aware of a consistent way of choosing the basis states so that the BIS spectrum starts exactly at the Fermi energy for this type of basis function, appropriate in the small- $\delta$  limit. However, inconsistencies rapidly decrease as the size of the basis set is increased, and for the basis set used here the spectrum starts very close to the Fermi energy.

In Fig. 5 we show results for the combined PES and BIS spectra as a function of doping. The top spectrum is for  $\delta = 0.5$ . This is the most unfavorable case for the expansion used here and it serves as a test of the accuracy. The parameters are chosen in such a way that this cor-

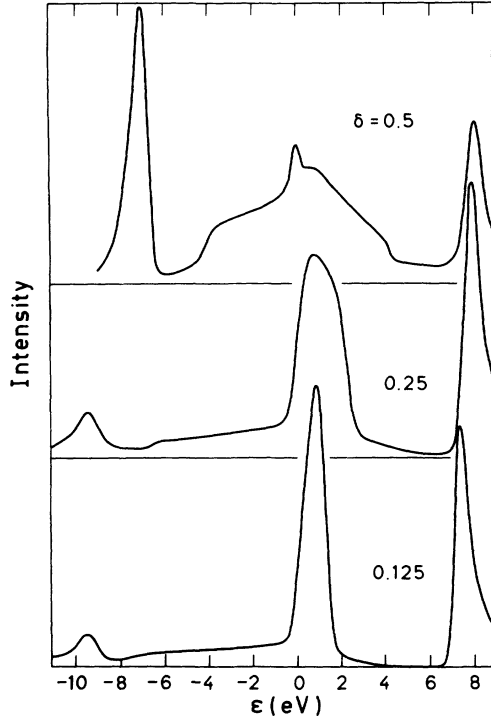


FIG. 5. The PES and BIS spectrum for  $N_d = 2$  for different dopings  $\delta = 0.5, 0.25,$  and  $0.125$ . The form (5) was used for  $|V(\epsilon)|^2$  and the parameters were  $2B = 8, \epsilon_d = -5, U = 10,$  and  $V = 2.6$ . A Gaussian broadening of 0.7-eV full width at half maximum (FWHM) has been introduced. All energies are in eV and the Fermi energy is set to zero.

responds to the symmetric Anderson model. The spectrum should therefore be symmetric around the Fermi energy. In the calculation this is not quite the case, since we have used basis sets appropriate for the small doping limit. The PES and BIS sets are therefore not equivalent for  $\delta = 0.5$ . The deviation from a symmetric behavior is therefore a test of the accuracy. The ground state should have the  $3d$  occupancy 1.0 in this symmetric case. The calculations give the result 0.99 in good agreement with the exact result. The peak at  $-8$  eV corresponds to a  $d^0$  final state and the peak at  $8$  eV corresponds to a  $d^2$  final state. In the full  $N_d = 10$  calculation these peaks would instead correspond to final  $d^8$  and  $d^{10}$  states, respectively. The Kondo peak can be seen at the Fermi energy. The structures at  $-4$  and  $+4$  eV correspond to the band edges. We can see that the spectrum is essentially symmetric. The peaks at  $-8$  and  $8$  eV are at the same distance to the Fermi energy, although the peak on the BIS side has a somewhat smaller weight. The KS peak is located at  $\epsilon = 0$  and the weight in the range  $-4$  to  $4$  eV is essentially symmetric, although on the BIS side there is more weight at  $1$  eV and less weight between  $3$  and  $4$  eV than on the PES side. BIS calculations with fewer basis states gives a more pronounced structure at  $1$  eV, suggesting that this structure may disappear in a more accurate calculation. Figure 5 also shows results for smaller dopings, which means that the unoccupied part

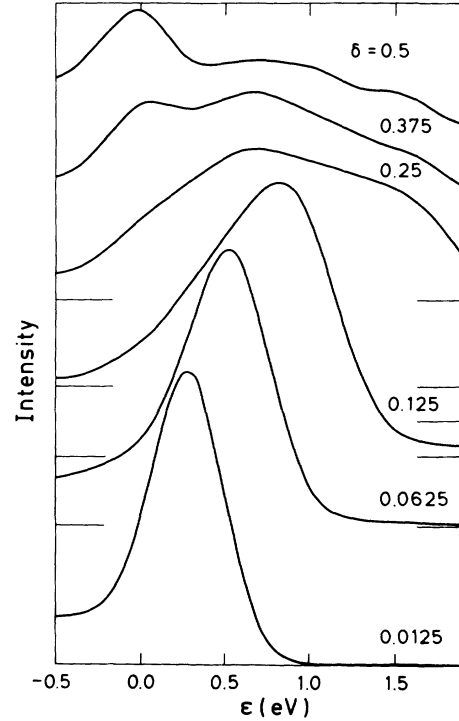


FIG. 6. The same as Fig. 5 but over a smaller energy scale and also for smaller dopings. A Gaussian broadening with a FWHM of 0.5 eV has been introduced.

of the band is reduced. On the BIS side weight is then transferred from the broad continuum in the range  $2-4$  eV to the split off state at about  $7-8$  eV as well as to the peak close to the Fermi energy. At the same time the occupied part of the band becomes broader and the broad continuum on the PES side takes weight from both the split off state at about  $8-9$  eV and from the emission close to the Fermi energy.

In Fig. 6 we show the spectrum over a smaller energy range, with a smaller broadening and also for smaller dopings. The lowest curve shows results for  $\delta = 0.0125$ . The figure shows very clearly the local singlet (LS) peak discussed above, which here appears at about  $\epsilon = 0.3$  eV. In Fig. 7 we also show a calculation with a smaller broadening. We can here clearly see the spectral weight according to Eq. (37), which ends at the top of the band,  $0.1$  eV above the Fermi energy. Above this energy there is a pseudogap up to the LS peak at about  $0.3$  eV.

As the doping is increased, the LS peak may be expected to be tied to the Fermi energy and not to the top of the band, since it is a many-body resonance. Figure 6 shows that this is only partly true. The LS peak moves down relative to the top of the band, but it moves up relative to the Fermi energy, which is the energy zero in the figure. The reason is the interaction with the states corresponding to Eq. (37), which push the LS peak upwards. Since the weight of these states increases with the doping, the LS peak moves upwards with doping relative to the Fermi energy. The figure, however, also shows that for the doping  $\delta = 0.0625$ , for which the top of the

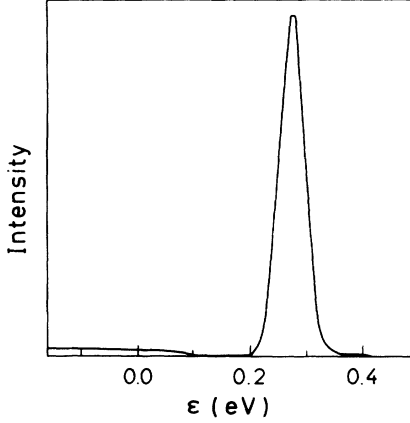


FIG. 7. The same as Fig. 6 but over a smaller energy scale and with a smaller broadening for  $\delta = 0.0125$ . A Gaussian broadening with a FWHM of 0.05 eV has been introduced.

band is 0.5 eV above the Fermi energy, the top of band essentially reaches up to the LS peak, which leads to a rather asymmetric broadening. As the doping is further increased to  $\delta = 0.125$  the top of the band extends above the LS peak. At this point the LS peak starts to go over to a traditional KS peak, where the KS lies in a continuum. As the doping is further increased, the peak starts to move towards the Fermi energy, and for the symmetric case there is a Kondo peak at the Fermi energy. As discussed above, the calculation becomes less accurate for larger doping, and it is not clear if the structure at about 0.7 eV for  $\delta = 0.375$  and 0.5 is real or not. We also notice that the Kondo peak is rather broad compared with the Ce case, due to the small degeneracy used here and due to the large value of  $N_d V^2$  compared with typical values for Ce compounds.

$$[(H - E_0)^{-1}]_{ij} = \frac{\delta_{ij}}{\varepsilon_i - E_0} - \frac{V_i V_j}{N\Delta(\varepsilon_i - E_0)(\varepsilon_j - E_0) \left(1 + \frac{1}{N\Delta} \sum_k \frac{|V_k|^2}{\varepsilon_k - E_0}\right)}. \quad (41)$$

If we assume, for simplicity, that  $V(\varepsilon) \equiv V$  the integrals can be performed analytically. If we further assume that  $|E_0| \ll B$ , we obtain

$$\chi_l = \frac{1}{3} j(j+1) \frac{1}{|E_0|}. \quad (42)$$

We note that this form for the susceptibility looks like the result obtained in the Kondo limit, except that the Kondo binding energy is replaced by the local singlet binding energy  $E_0$ . The origin is also similar. In both cases the splitting between the lowest singlet and triplet states is given by  $T_K$  and  $E_0$ , respectively, if we work to lowest order in  $1/N_d$  for the Kondo problem and to lowest order in the doping for the present problem. In the local singlet case this follows, since the triplet states  $|\tilde{\varepsilon}\rangle$  in Eq. (7) lose the local singlet binding energy due to the presence of a plus sign in Eq. (40).

Although it is not clear if a finite order  $1/N_d$  type of

We now turn to the local susceptibility. Above we argued that for  $N_d = 2$  the interesting case is  $E(d^1) < E(d^2) \ll E(d^0)$  and an almost full valence band. Due to an electron-hole transformation, we can as well consider the case  $E(d^1) < E(d^0) \ll E(d^2)$  and an almost empty valence band. Here we therefore study  $E(d^2) = \infty$  and small fillings of the band,  $E_f = \delta(2B)$ , where  $2B$  is the bandwidth.

The local susceptibility is defined by  $\chi_l = m/H$ , where  $m$  is the moment induced on the impurity by the external field  $H$  acting on the Cu spin only. Let us first consider this quantity in the low doping limit, as described by the strong-coupling  $N_d = 2$  model (4).

The static susceptibility can be written as

$$\chi_l = 2 \left\langle \phi \left| S^z \frac{1}{H - E_0} S^z \right| \phi \right\rangle. \quad (38)$$

The operator  $S^z$  turns the singlet states (6) into triplet states and couples to the states  $|\tilde{i}\rangle$  in Eq. (7). We have that  $\langle \tilde{i} | S^z | j \rangle = \frac{1}{2} \delta_{ij}$ . The susceptibility can then be written as

$$\chi_l = \frac{2}{3} j(j+1) \sum_{ij} \alpha_i [(H - E_0)^{-1}]_{ij} \alpha_j, \quad (39)$$

where  $j = \frac{1}{2}$  and the matrix elements of  $(H - E_0)^{-1}$  are taken between the states Eq. (7). We obtain

$$H|\tilde{i}\rangle = \varepsilon_i |\tilde{i}\rangle + \frac{1}{N\Delta} V(\varepsilon_i) \sum_j V_j |\tilde{j}\rangle. \quad (40)$$

We note that compared with Eq. (9) the second term has a plus sign instead of a minus sign. As a result, a bound state cannot form independently of the strength of the coupling. Furthermore, the coupling is determined by  $1/\Delta$  instead of  $I$ . As before the matrix corresponding to Eq. (40) is separable and can be inverted analytically. We obtain

expansion makes sense in the present situation, the fast convergence in the  $N_d = 2$ , large- $\delta$  case indicates that something might be learned. In order to obtain both the KS and LS, one should at least take into account states  $a, b, d, e$ , and  $g$  (Fig. 1), and in this basis the local susceptibility can be calculated numerically along lines described in detail elsewhere.<sup>23</sup> The susceptibility is calculated using a resolvent approach as in Eq. (38) and the Hamiltonian is inverted using triplet-basis functions equivalent to the singlet-basis functions in the ground-state calculations. This is a  $U = \infty$  calculation, including all states of order  $(1/N_d)^0$  and  $(1/N_d)^1$  in a  $1/N_d$  expansion as well as the coupling between the states  $e$  and  $g$  leading to the local singlet. In the limit of small doping and for a large value of  $E(d^0) - E(d^1)$  the calculation reproduces the susceptibility calculated above, and for large dopings the states  $a, b, d$ , and  $e$  give the Kondo susceptibility calculated to order  $(1/N_d)^1$ .

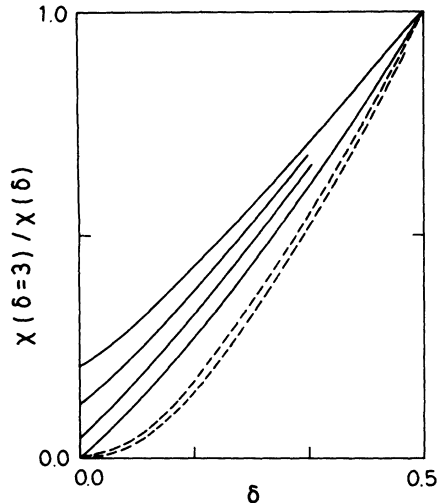


FIG. 8. The local susceptibility  $\chi_l$  as a function of doping  $\delta$ . The solid lines were calculated using the states  $a$ ,  $b$ ,  $d$ ,  $e$ , and  $g$  in Fig. 1 and the dashed lines without the states  $g$ . The form (5) was used for  $|V(\epsilon)|^2$  and the  $\epsilon_d = -2.5$  and  $2B = 6$  were used, and the width of the occupied part of the band was  $\delta(2B)$ . The solid lines were calculated for  $V = 3.5, 4, 4.5$  and  $5$ , with the lowest curve for the lowest value, and the dashed lines were obtained for  $V = 3.5$  (lower line) and  $V = 5$  (upper line).

The results are presented in Fig. 8 as a function of the doping  $\delta = T_F/(2B)$ , where  $T_F$  is the Fermi energy relative to the bottom of the band and  $2B$  is the total bandwidth. We have used the model (5) for  $|V(\epsilon)|^2$ . In Fig. 8 we show results for different values of the hopping strength  $V$ . Although  $N_d = 2$ , the susceptibility is not symmetric around  $\delta = 0.5$ , since  $U = \infty$ . The local singlet can form for  $V \geq 4$  but does not form for  $V \leq 3.5$ . In the zero-doping limit,  $1/\chi_l$  is therefore zero for  $V = 3.5$  while it is finite for  $V \geq 4$ . In Fig. 8 we also show results (dashed curves) obtained without the basis states  $g$ . Although the calculation is still correct to order  $(1/N_d)^1$  in a  $1/N_d$  expansion, it is qualitatively wrong for small dopings and for  $V \geq 4$ , since the calculation neglects the formation of a local singlet. The figure also illustrates

how the local singlet formation loses importance as the doping is increased. However, even for  $\delta \sim \frac{1}{4}$  the local singlet still plays an appreciable role. The figure also illustrates that in terms of the local susceptibility there is a smooth crossover from the situation where the local singlet dominates to the situation where the Kondo effect dominates.

## V. SUMMARY

We have discussed the problem of a magnetic impurity in a strongly doped semiconductor. This system turns out to have several interesting features. We find that there is mass reduction due to scattering of carriers against multiple charged impurity states and due to the closeness of a band edge. We expect this to be quite a generic feature of these systems.

We also discovered that the properties of these systems can be strikingly different depending on the type of doping. We studied the extreme cases of a nearly empty and a nearly filled impurity, hybridizing with a nearly filled valence band. In the former situation for  $U = \infty$ , the gap state is a single-particle bound state in the undoped system, which gradually turns into a Kondo resonance for increasing doping. For a nearly filled impurity interacting with a nearly filled valence band, there is a local singlet gap state resulting from the binding of a carrier to the impurity spin. The treatment of the LS requires the inclusion of vertex corrections in the NCA type of approach. As the doping is increased we get the Kondo type of effects. We have studied the crossover for the one-particle spectral function and the local susceptibility, and found that these properties suggest a smooth crossover. More theoretical (and experimental) work is needed to fully characterize the crossover.

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<sup>1</sup>J.W. Allen, S.J. Oh, O. Gunnarsson, K. K. Schönhammer, M.B. Maple, M.S. Torikachvili, and I. Lindau, *Adv. Phys.* **35**, 275 (1986).

<sup>2</sup>D.C. Langreth, *Phys. Rev.* **150**, 516 (1966).

<sup>3</sup>J. Zaanen, G.A. Sawatzky, and J.W. Allen, *Phys. Rev. Lett.* **55**, 418 (1985).

<sup>4</sup>J. Zaanen, in *Unoccupied Electronic States*, edited by J.C. Fuggle and J.E. Inglesfield, Topics in Applied Physics (Springer, Heidelberg, in press), Chap. 4.

<sup>5</sup>O. Gunnarsson, O. Jepsen, and Z.-X. Shen, *Phys. Rev. B* **42**, 8707 (1990).

<sup>6</sup>O. Gunnarsson, O.K. Andersen, O. Jepsen, and J. Zaanen, *Phys. Rev. B* **39**, 1708 (1989).

<sup>7</sup>J. Zaanen and G.A. Sawatzky, *Can. J. Phys.* **65**, 1262 (1987).

<sup>8</sup>J.F. Annett, R.M. Martin, A.K. McMahan, and S. Satpa-

thy, *Phys. Rev. B* **40**, 2620 (1989).

<sup>9</sup>C.M. Varma, S. Schmitt-Rink, and E. Abrahams, *Solid State Commun.* **62**, 681 (1987).

<sup>10</sup>V.J. Emery, *Phys. Rev. Lett.* **58**, 2794 (1987).

<sup>11</sup>H. Eskes and G.A. Sawatzky, *Phys. Rev. Lett.* **61**, 1415 (1988).

<sup>12</sup>F.C. Zhang and T.M. Rice, *Phys. Rev. B* **37**, 3759 (1988).

<sup>13</sup>O. Gunnarsson and K. Schönhammer, *Phys. Rev. Lett.* **50**, 604 (1983); *Phys. Rev. B* **28**, 4315 (1983); in *Handbook on the Physics and Chemistry of Rare Earths*, edited by K.A. Gschneider, Jr., L. Eyring, and S. Hüfner (Elsevier, Amsterdam, 1987), Vol. 10, p. 103.

<sup>14</sup>J. Zaanen and O. Gunnarsson, *Physica C* **162-164**, 821 (1989).

<sup>15</sup>J.W. Rasul and A.C. Hewson, *J. Phys. C* **17**, 3337 (1984).

<sup>16</sup>Y. Kuramoto, *Z. Phys. B* **53**, 37 (1983); P. Coleman, *Phys.*

- Rev. B **29**, 3035 (1984).
- <sup>17</sup>J.R. Schrieffer and P.A. Wolff, Phys. Rev. **149**, 491 (1966).
- <sup>18</sup>J. Zaanen and A.M. Oleś, Phys. Rev. B **37**, 9423 (1988).
- <sup>19</sup>J. Kanamori, Prog. Theor. Phys. **30**, 275 (1963).
- <sup>20</sup>K. Yosida, Phys. Rev. **147**, 223 (1966).
- <sup>21</sup>H. Keiter and J.C. Kimball, Int. J. Magn. **1**, 233 (1971); H. Keiter and G. Morandi, Phys. Rep. **109**, 227 (1984).
- <sup>22</sup>P.W. Anderson, in *Frontiers and Borderlines in Many Particle Physics*, International School of Physics "Enrico Fermi," Course CIV, edited by R.A. Broglia and J.R. Schrieffer (North-Holland, Amsterdam, 1988); C.M. Varma, P.B. Littlewood, S. Schmitt-Rink, E. Abrahams, and A.E. Ruckenstein, Phys. Rev. Lett. **63**, 1996 (1989).
- <sup>23</sup>O. Gunnarsson and K. Schönhammer, J. Magn. Magn. Mater. **52**, 141 (1985); in *Theory of Heavy Fermions and Valence Fluctuations*, edited by T. Kasuya and T. Saso (Springer, Berlin, 1985), p. 100.