Conditions for Bound States in a Superconductor with a Magnetic Impurity. II*

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The binding energy of the localized excitation at a magnetic impurity $JS\cdot\sigma$ in a superconductor is plotted as a function of J. Our previous work is improved by including nonsingular terms in the solution to Suhl's scattering equations. These are found to alter the criteria for bound states significantly. The theory predicts that bound states deep in the gap will only occur for negative J of the order of magnitude of the superconducting coupling constant g. For J outside this range, any bound states will be very close to the gap edge, and the Abrikosov-Gor'kov theory should be satisfactory.

I. INTRODUCTION

SEVERAL recent attempts[1–5] to find criteria for the occurrence of localized bound states around magnetic impurities in superconductors have produced a variety of results. Soda *et al.*[1] found bound states for arbitrary Kondo coupling constant J. In I, the present authors found a bound state for antiferromagnetic coupling $J<0$ and $|J|>|g|$, $|g|$ being the superconducting coupling constant. Takano and Matayoshi[4] found a bound state for arbitrary negative J. Shiba[5] proved that in the classical limit (infinite spin) a bound state exists for any sign of J, and the binding energy he found as a function of J corresponded to that predicted by Soda *et al.* in this limit.

The present authors used a technique analogous to that developed by one of us[6] to discuss Suhl's[7] equations for the normal-metal Kondo effect. Since that time, Zittartz and Muller-Hartmann[8,9] have shown that a rigorous solution of the normal-metal Kondo problem must include an analytic term ignored in I. Part of this term—the function χ of Zittartz[8]—is of order J^3 and thus constitutes a rather small correction in the normal metal. For the superconductor, however, χ is not negligible, for two reasons. First, the coefficient J^3 becomes $J^2\times J/g$, where g is the superconducting coupling constant. Thus χ is effectively of order J^2 if $J\sim g$, which is often the case in practice. Second, although χ is a very smooth function in a normal metal, its analytic structure does reflect to some extent that of the density of states, and in the superconductor it turns out to have a pole singularity at an energy corresponding to the top edge of the gap. Hence, in contrast to the normal-metal case, χ is extremely important in the superconducting problem. One might conjecture at this point that other regular terms, corresponding to multiparticle intermediate states, could also be significant. It becomes apparent from the discussion of Sec. II that this is not so, for χ turns out to be important only when the bound-state pole is close to the edge of the gap. The significance of this is that in evaluating the one-particle intermediate-state contribution to the energy of the bound state from a perturbation-theoretic point of view, one has a very large density of available states very close by, giving a small energy denominator and hence a large correction to the binding energy. Multiparticle intermediate states, on the other hand, would necessitate breaking a pair and so would always have a large energy denominator. Therefore, it is reasonable to neglect them throughout, a simplification which is not so evident in the normal state.

Unfortunately, we have not been able to evaluate the function χ exactly, because it involves an integral over the exact scattering t matrix which is not known. It is presumably possible to solve exactly the coupled equations for t and χ discussed in Sec. II. However, we find that the behavior of χ is not very sensitive to the value of t used in evaluating it. In Sec. III we find χ using Shiba's classical t matrix, and in Sec. IV we use Hamann's magnetic-impurity scattering t matrix. The final differences in general behavior of the bound-state energy as a function of coupling constant are reasonably small. Thus it appears that the results of Sec. IV should be rather close to those of a fully self-consistent theory.

When an analytic term is incorporated into the solution given in I, a different description of the bound state emerges. Here and in the following the "bound state" referred to is a pole in the scattering amplitude t_+.[3] The full scattering matrix t has poles both at these

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1 T. Soda, T. Matsuura, and Y. Nagaoka, Progr. Theoret. Phys. (Kyoto) **38**, 551 (1967).
2 K. Maki, Phys. Rev. **153**, 428 (1967).
3 M. Fowler and M. Maki, Phys. Rev. **164**, 484 (1967), referred to as I.
4 F. Takano and S. Matayoshi, Progr. Theoret. Phys. (Kyoto) **41**, 45 (1968).
5 H. Shiba, Progr. Theoret. Phys. (Kyoto) **40**, 435 (1968).
6 M. Fowler, Phys. Rev. **160**, 463 (1967).
7 H. Suhl, in *Rendiconti della Scuola Internazionale di fisica "Enrico Fermi" 1966* (Academic Press Inc., New York, 1967).
8 J. Zittartz and E. Muller-Hartmann, Z. Physik **212**, 380 (1968).
9 Y. Nagaoka, Phys. Rev. **138**, A1112 (1965).

energies and at minus these energies. This follows from the particle-hole symmetry of the Hamiltonian. On increasing the value of J from zero to positive (ferromagnetic) values, a bound-state pole moves into the gap from the top end. However, it always stays very close to the edge of the gap and for J very large compared to $|g|$ it tends to a value of order $|g|^2\Delta^{12}$ below the gap edge. Increasing J from zero antiferromagnetically gives very different behavior. In the range $J\sim g$ the pole sweeps arcoss the gap, then remains close to the bottom of the gap as $|J|$ becomes much larger than $|g|$. Thus for positive J and large negative J, the bound-state pole is close to the edge of the gap, and it might be expected that the density of states found by Abrikosov and Gor'kov (AG) using the Born approximation would be reasonably good. However, for negative J, $J\sim g$, the bound state is deep in the gap. It would appear in this case that the AG approximation should be inadequate, and this has indeed been observed in tunneling and other experiments. Of course, at the finite concentrations used experimentally, the bound states would overlap and form an impurity band, as discussed by Shiba. This should not alter the qualitative correctness of our solution.

In Sec. II, Ref. 3 is briefly reviewed and equations determining the pole positions as functions of J are derived. These equations depend on the function χ. In Sec. III an approximate form of χ based on Shiba's[5] (energy-independent) classical scattering amplitude is used, and the trajectories of the bound-state poles as functions of J and spin are found. In the limit of infinite spin, these go over to the results found by Shiba for a classical spin. In Sec. IV, Hamann's[10] t matrix for the normal Kondo problem is used to evaluate χ. Some interesting changes from the classical approximation of Sec. III are found, but we are unable to give a complete solution using Hamann's t matrix. Specifically, it is not clear for large negative J whether the pole is on the physical or unphysical sheet. However, it is, in any case, very close to the gap edge. In Sec. V, the physical significance of these results is discussed.

Note added in proof. This last point has now been resolved. Since submitting our revised manuscript, we have received a preprint from J. Zittartz and E. Müller-Hartmann solving the scattering equations exactly. Their final result is essentially indistinguishable from ours shown in Fig. 6.

II. STRUCTURE OF DISPERSION EQUATIONS

As in I, we discuss the coupled integral equations

$$t\pm(z)=J\int_{-D}^{D}\rho\frac{dx}{z-x}[|t_\pm|^2+\tfrac{1}{4}S(S+1)|\tau_\pm|^2]\times(g\pm f)+\sum\frac{a\pm i}{z-z_i},$$

$$\tau\pm(z)=-1+J\int_{-D}^{D}\rho\frac{dx}{z-x}(t_\pm{}^*\tau_\pm+t_\pm\tau_\pm{}^*-\tanh\tfrac{1}{2}\beta x|\tau_\pm|^2)(g\pm h)+\sum\frac{b\pm i}{z-z_i}. \quad (2.1)$$

Here D is a cutoff energy of the order of ϵ_F; ρ is the normal-metal density of states, assumed constant; $g(z)=\mathrm{Re}[z/(z^2-\Delta^2)^{1/2}]$; and $h(z)=\mathrm{Re}[\Delta/(z^2-\Delta^2)^{1/2}]$. J is taken positive for ferromagnetic coupling. (This is opposite to the convention used in I, but the present usage is more generally accepted.) The above t and τ matrices differ by a factor J from those in I. Writing the S matrix

$$S(x)=1+2\pi iJ\rho[(x+\Delta)/(x-\Delta)]^{1/2}t(x), \quad (2.2)$$

and defining the function $G(x)$ by

$$G(x)=S(x)/\tau(x), \quad (2.3)$$

we proved in I that $G(x)$ is a two-sheeted function with a discontinuity across the real-axis cut given by

$$G_2(x)-G_1(x)=-\pi i\rho[(x+\Delta)/(x-\Delta)]^{1/2}\times\tanh\tfrac{1}{2}\beta x, \quad (2.4a)$$

and in fact this same expression gives the difference between the values of G in the two sheets at any complex point z, by analytic continuation.

Putting $Y=-JG$, $J\rho=\gamma$ gives

$$Y_2(x)-Y_1(x)=\pi i\gamma[(x+\Delta)/x-\Delta]^{1/2}\tanh\tfrac{1}{2}\beta x. \quad (2.4b)$$

The equation is written in this form in a recent discussion by Zittartz.[11] The solution is

$$Y(z)=1+R(z)+f(z), \quad (2.5)$$

where

$$R(z)=-\tfrac{1}{2}\gamma\int_{-D}^{D}d\omega\tanh\tfrac{1}{2}\omega\,\mathrm{Re}\left(\frac{\omega+\Delta}{\omega-\Delta}\right)^{1/2}\frac{1}{z-\omega}$$

[in the notation of I, $R(z)=-\gamma A^{(+)}(z)$], and $f(z)$ is a function which does not reflect the square-root cuts along the real axis, i.e., it is the same on both sheets. Thus $f(z)$ does not affect Y_2-Y_1, but it must in general appear in $Y(z)$ for mathematical and physical consistency. In I we took $f(z)$ to be zero.

Zittartz[11] derives an explicit expression for $f(z)$ given an arbitrary density of states analytic in some neighborhood of the real axis. Although the BCS-like density of states in (2.1) has singularities at $\pm\Delta$, with slight modifications the same form for $f(z)$ can be used in this case. It is necessary to introduce several new functions to construct $f(z)$. The first one has a spectral representation given by the density of states appearing

[10] D. R. Hamann, Phys. Rev. **158**, 570 (1967).

[11] J. Zittartz, Z. Physik **217**, 43 (1968).

in Eqs. (2.1) and (2.2):

$$F(z)=\gamma\int_{-D}^{D} d\omega\frac{1}{z-\omega}\,\mathrm{Re}\left(\frac{z+\Delta}{z-\Delta}\right)^{1/2}. \qquad (2.6)$$

$F(z)$ is two-sheeted, and in the gap we can write

$$F_{\mathrm{I,II}}(z)=\pm\pi i\gamma[(z+\Delta)/(z-\Delta)]^{1/2}, \qquad (2.7)$$

neglecting as usual the singularities associated with the cutoff, which are only needed to ensure well-behaved functions at infinity.

The integral functions $I_n(z)$ of the t matrix are defined as

$$I_n(z)=\frac{1}{4\pi i}\int_C d\omega\,\tanh\frac{\frac{1}{2}\beta\omega}{z-\omega}F^n(\omega)t(\omega), \qquad (2.8)$$

where the contour is from $-D$ to D just above the real axis, then D to $-D$ below the real axis. Thus the integral includes not only the cut discontinuities in $\Delta<|\omega|<D$ but also the possibility of pole terms in the gap $|\omega|<\Delta$. In terms of these functions, it is shown in Ref. 8 that

$$f(z)=-\tfrac{1}{4}S(S+1)F_{\mathrm{I}}(z)F_{\mathrm{II}}(z)+\chi(z), \qquad (2.9)$$

where

$$\chi(z)=I_2(z)-[F_{\mathrm{I}}(z)+F_{\mathrm{II}}(z)]I_1(z)+F_{\mathrm{I}}(z)F_{\mathrm{II}}(z)I_0(z).$$

In the present case, this reduces to

$$\chi(z)=-\pi^2\gamma^2\frac{2\Delta}{\Delta-z}\frac{1}{4\pi i}\int_C \tanh\tfrac{1}{2}\beta\omega \times[t_2(\omega)-t_1(\omega)]\frac{d\omega}{\omega-\Delta}, \qquad (2.10\mathrm{a})$$

and hence

$$f(z)=-\tfrac{1}{4}S(S+1)\pi^2\gamma^2\frac{z+\Delta}{z-\Delta}-\pi^2\gamma^2\frac{2\Delta}{\Delta-z}\frac{1}{4\pi i} \times\int_C \tanh\tfrac{1}{2}\beta\omega[t_2(\omega)-t_1(\omega)]\frac{d\omega}{\omega-\Delta}. \qquad (2.10\mathrm{b})$$

Equation (2.10b) implies that $f(z)$ is a function known within a single constant depending on t. Thus an exact solution should involve only transcendental equations and be possible in principle. We have not been able to solve these equations. Note that from Refs. 8 and 11, one in general expects f to contain a regular integral operator acting on t. The simplification in (2.10) follows in a straightforward way from the assumption of the BCS density of states (2.7). Specifically, the term in $I_1(z)$ is zero because $F_{\mathrm{I}}+F_{\mathrm{II}}\equiv 0$, and the terms in $I_2(z)$, $I_0(z)$ combine easily as a result of the form of $F_{\mathrm{I}}F_{\mathrm{II}}$.

The final integral must include any pole terms on the physical sheet in the gap. Thus, it is necessary to solve for poles of t self-consistently.

Now in I it was shown that poles of the scattering matrix occur when

$$Y_1(z)Y_2(z)+4\alpha\gamma^2(z+\Delta)/(z-\Delta)=0, \qquad (2.11)$$

where $\alpha=\frac{1}{4}S(S+1)\pi^2$. Inserting $f(z)$ from (2.10) into (2.5) and then $Y(z)$ from (2.5) into (2.11) gives the pole positions as functions of the coupling constant, although in a rather implicit way. Further, it is not possible to say immediately whether a given pole is on the physical or unphysical sheet.

Equation (2.11) can be expressed more conveniently by putting

$$Y(z)=\gamma\pi[(\Delta+z)/(\Delta-z)]^{1/2}X(z)$$

(compare Ref. 4), which gives

$$X^2-X\tanh\beta\frac{z}{2}-S(S+1)=0. \qquad (2.12)$$

Hence solving the quadratic gives X as a function of z,

$$2X=\tanh\tfrac{1}{2}\beta z\pm[4S(S+1)+\tanh^2(\tfrac{1}{2}\beta z)]^{1/2}.$$

For $T=0$, this is just

$$X(z)=S,\ -(S+1),\quad \text{for } z<0$$
$$=S+1,\ -S,\quad \text{for } z>0. \qquad (2.13)$$

For nonzero temperatures, the step of unity at $z=0$ is smoothed.

Using the explicit expression for $R(z)$ $[=-\gamma A^+(z)]$ from I, and changing to the variable $y=\omega/\Delta$, the pole positions are given by

$$1+\frac{\gamma}{\rho|g|}+\gamma\left(\frac{1+y}{1-y}\right)^{1/2}\arcsin y+\alpha\gamma^2\frac{1+y}{1-y}+\chi(y) =\gamma\pi\left(\frac{1+y}{1-y}\right)^{1/2}X(y). \qquad (2.14)$$

At this point one should ideally evaluate χ self-consistently, using the exact t matrix. A formal solution for t in terms of f can in fact be constructed using standard techniques.[11] From (2.2) and (2.3), t can be expressed in terms of τ. The τ itself can be found by solving Eq. (2.8) of I:

$$\tau_{\mathrm{I}}^{-1}(z)\tau_2^{-1}(z)=Y_1(z)Y_2(z) +4\alpha\gamma^2(z+\Delta)/(z-\Delta). \qquad (2.15)$$

Following Zittartz,[11] the solution to this equation is

$$\tau_{1,2}(z)=-\exp\left[\pm\frac{1}{4\pi i}\left(\frac{z-\Delta}{z+\Delta}\right)^{1/2}\int_C\frac{d\omega}{z-\omega}\frac{\omega+\Delta}{\omega-\Delta} \times\ln\left(Y_1(z)Y_2(z)+4\alpha\gamma^2\frac{z+\Delta}{z-\Delta}\right)\right].$$

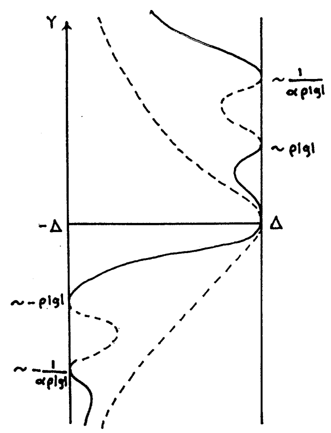

FIG. 1. Positions of bound-state poles in the gap as functions of $\gamma=\rho J$. This is not at all to scale. For any realistic spin, the second points of tangency occur at very high γ, and also the horizontal scale has been exaggerated for clarity in the range $0<J\ll 1$.

The contour c encloses the real axis and so includes the residues of any poles of the integrand in the gap.

Rather than solving these equations exactly, we have evaluated χ using approximate forms for t, then used the χ obtained to search for bound-state poles in t. This appears to be a reasonable procedure because from (2.10a), χ depends on t only through an integral over all energies of t, and is presumably fairly insensitive to the exact form of t. Thus, the simple classical approximation of Sec. III is quite close in essential physical behavior to Hamann's approximation discussed in Sec. IV.

III. CLASSICAL APPROXIMATION

From (2.10),

$$\chi(z)=-\pi^2\gamma^2[2\Delta/(\Delta-z)]I_0(\Delta)\,,$$

where

$$I_0(\Delta)=\frac{1}{4\pi i}\int_C \tanh\tfrac{1}{2}\beta\omega[t_2(\omega)-t_1(\omega)]\frac{d\omega}{\omega-\Delta}\,. \quad (3.1)$$

The t matrix here is actually t_+ (see I) and differs from the ordinary t matrix by an amplitude u, which is, however, rapidly decreasing away from the gap. Hence we assume that replacing t_+ by t in (3.1) is a good approximation.

Shiba[5] has shown that in the classical limit the t matrix is given by

$$t_{1,2}(\omega)=\pm i\alpha\gamma\left(\frac{\omega+\Delta}{\omega-\Delta}\right)^{1/2}\bigg/\left(1+\alpha\gamma^2\frac{\omega+\Delta}{\omega-\Delta}\right). \quad (3.2)$$

We shall evaluate χ using this t. It is important to note that this does not mean our results are identical to Shiba's. The final result of this section is a significant improvement on the classical limit, although it does of course go to that limit if the spin is made very large.

A useful property of $I_0(\Delta)$ in (3.1) is that ignoring the $\tanh\frac{1}{2}\beta\omega$ gives just $\frac{1}{2}t(\Delta)$ from Cauchy's theorem. Furthermore, from (2.4) of I, $|S(x)|<1$ for $x>\Delta$, so from (2.2) of the present paper, $t(\Delta)$ is zero. Thus

$$I_0(\Delta)=\frac{1}{4\pi i}\int_C(\tanh\tfrac{1}{2}\beta\omega-1)[t_2(\omega)-t_1(\omega)]\frac{d\omega}{\omega-\Delta}$$

$$=-\frac{1}{2\pi i}\int_{-D}^{-\Delta}[t_2(\omega)-t_1(\omega)]\frac{d\omega}{\omega-\Delta}-2P \quad (3.3)$$

at $T=0$, where P gives pole terms in $I_0(\Delta)$ arising from poles below the center of the gap. This formulation has the attraction of eliminating the very complex behavior of $t(\omega)$ for ω near Δ at small γ. It is a sufficiently good approximation to replace $(\omega+\Delta)/(\omega-\Delta)$ by unity in the range $(-D,\,-\Delta)$, giving

$$\chi(y)=-\frac{\alpha}{1+\alpha\gamma^2}\frac{2}{1-y}\frac{\gamma^3}{g}\,. \quad (3.4)$$

For high γ, in Shiba's approximation, the bound-state pole moves towards $-\Delta$ and should be included in $\chi(y)$, but in fact this turns out to give quite a small correction as the density-of-states factor $(\omega+\Delta)^{1/2}$ cuts down the contribution to the integral from this neighborhood.

The positions of the poles of the t matrix can be found in this approximation by inserting $\chi(y)$ given by (3.4) into (2.14). An important point is that for zero temperature the function $X(y)$ of (2.13) has a step discontinuity at $y=0$. This should be reflected in the y-γ curves defined by (2.14). However, the function $\chi(y)$ also has a step discontinuity at precisely the same point. This is easily seen from (3.3): The pole terms P have their residues multiplied by $\tanh\frac{1}{2}\beta\omega-1$, so the contribution to χ from a single pole changes discontinuously as that pole crosses the center of the gap, for zero temperature. The net result is that for the branches of curves on the physical sheet, there is no discontinuity at $y=0$. It is of course necessary to assume here that the exact self-consistent t matrix appears in χ, although the explicit form of the exact t is not required. Note that, in general, there are two possible pole positions for a given J and hence two trajectories. Thus as one pole crosses the gap center on the physical sheet the trajectory of the other pole, determined by the same equation (2.14), will suffer a discontinuity, for χ will change abruptly with no compensating change in $X(y)$, for the second pole will not be at $y=0$. However, in the cases of interest it turns out that the second pole is on the unphysical sheet, so these discontinuities are not of physical importance, and they will be ignored.

Using the approximate form of χ given above, the positions of poles of the scattering matrix in the gap are plotted as function of $\gamma=\rho J$ in Fig. 1. The explicit expressions determining pole positions at $T=0°$K are

$$1+\frac{\gamma}{\rho|g|}+\gamma\left(\frac{1+y}{1-y}\right)^{1/2}[\arcsin y-\pi(S+1)]+\alpha\gamma^2\frac{1+y}{1-y}-\frac{2\alpha}{1+\alpha\gamma^2}\frac{1}{1-y}\frac{\gamma^3}{\rho|g|}+\pi\gamma\left[\left(\frac{1+y}{1-y}\right)^{1/2}-\frac{1}{1-y}\right]\theta(-y)=0 \quad (3.5a)$$

and

$$1+\frac{\gamma}{\rho|g|}+\gamma\left(\frac{1+y}{1-y}\right)^{1/2}(\arcsin y+\pi S)+\alpha\gamma^2\frac{1+y}{1-y}-\frac{2\alpha}{1+\alpha\gamma^2}\frac{1}{1-y}\frac{\gamma^3}{\rho|g|}+\pi\gamma\left[\left(\frac{1+y}{1-y}\right)^{1/2}-\frac{1}{1-y}\right]\theta(-y)=0. \quad (3.5b)$$

Note that in terms of the variable $\eta=[(1+y)/(1-y)]^{1/2}$ these equations are quadratics with γ-dependent coefficients. Tangency of the γ-y trajectory to $z=+\Delta$ is given by the vanishing of the η-independent term.

To decide which branches of the curves are on the physical sheet it is important to notice that wherever the curve is tangent to $z=\pm\Delta$, it changes sheets. This is easy to check by examining the solution of the equation near one of these points. Thus a possible sheet assignment is as in Fig. 1. It is easy to draw the other three possibilities. However, if it is required that in the classical limit the curves go over to Shiba's result, the choice is between Fig. 1 and the same figure with the sheets interchanged. This is because as the spin is increased, the nonzero points of tangency to $z=\pm\Delta$ coalesce and further increase in spin causes the curves to stay on one sheet away from $z=\Delta$, as in Fig. 2. In the limit of large spin, the curves on the two sheets lie on top of each other. Thus there is in this limit a bound state for arbitrary J. The y-γ curves in this limit coincide precisely with those found by Shiba. Any other choice of sheet would give bound states for only one sign of J in the classical limit.

A sheet assignment similar to Fig. 1 was ruled out by Takano and Matayoshi[4] because of a step discontinuity on the physical sheet. However, from the discussion above, such steps do not actually occur and it appears now that Fig. 1 is in fact the correct sheet assignment. In the limit $|JS|\ll 1$, it gives precise agreement with the variational calculation of Soda

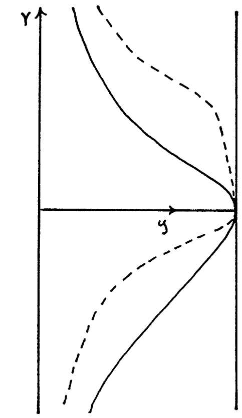

FIG. 2. Behavior of curves in Fig. 1 as the spin is increased through the region $\rho|g|S\sim 1$.

et al.[1] and in this limit their results should be very reliable. Another reason is that on comparing the pole trajectories with those of Shiba[5] in the classical limit, it appears that the Kondo effect enhances the binding strength for $J<0$ and lessens it for $J>0$ as might be expected. Note that for low spins the reappearance of the bound state at very high J is not to be taken seriously. For sufficiently high spins the reappearance takes place at reasonable values of the coupling strength.

To summarize: In this section we have used a simple energy-independent form of the t matrix as discussed by Shiba. However, in contrast to the classical case, we find bound-state energies quite different for different signs of J, reflecting the Kondo behavior of a normal metal. The results only become symmetrical with respect to the sign of J for the classical limit of infinite spin.

IV. EVALUATION OF χ USING HAMANN'S APPROXIMATION

Hamann's[10] approximate t matrix for scattering from a magnetic impurity is

$$t(\omega)=\frac{1}{2\pi i\rho}\left(\frac{\omega+\Delta}{\omega-\Delta}\right)^{1/2}\left(1-\frac{X(\omega)}{[|X(\omega)|^2+4\alpha]^{1/2}}\right), \quad (4.1)$$

with

$$X^{\pm}(\omega)=\frac{1}{\gamma}+\frac{1}{\rho|g|}-\left(\frac{\omega+\Delta}{\omega-\Delta}\right)^{1/2}\operatorname{arccosh}\frac{\omega}{\Delta}\pm\tfrac{1}{2}i\pi+\alpha\gamma\frac{\omega+\Delta}{\omega-\Delta}. \quad (4.2)$$

[The first three terms are just the function $R(z)$ of Eq. (2.5).] Since the definition of χ [see Eq. (3.3)] involves $t(\omega)$ in the range $-D<\omega<-\Delta$ (neglecting

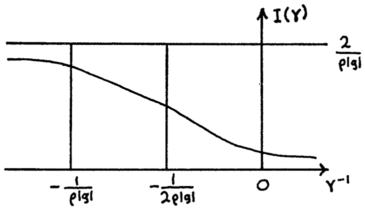

FIG. 3. Simplest (but incorrect) choice of square-root signs in $I(\gamma)$.

pole terms), it is a reasonable approximation to use

$$X(\omega)=1/\gamma+1/\rho|g|-\operatorname{arccosh}\omega/\Delta+\alpha\gamma \tag{4.3}$$

in place of (6.2).

Then the integral (3.3) can be performed exactly, and from (2.10) and (3.1),

$$\chi(y)=-\frac{\gamma}{1-y}\left\{\frac{1}{\rho|g|}+\left[\left(\frac{1}{\gamma}\right)^2+4\alpha\right]^{1/2}-\left[\left(\frac{1}{\gamma}+\frac{1}{\rho|g|}\right)^2+4\alpha\right]^{1/2}\right\}, \tag{4.4}$$

where

$$|g|^{-1}=\rho\ln(2D/\Delta).$$

Defining

$$K(\gamma)=\frac{1}{\rho|g|}+\left[\left(\frac{1}{\gamma}\right)^2+4\alpha\right]^{1/2}-\left[\left(\frac{1}{\gamma}+\frac{1}{\rho|g|}\right)^2+4\alpha\right]^{1/2}, \tag{4.5}$$

then

$$\chi(y)=-[\gamma/(1-y)]K(\gamma). \tag{4.6}$$

It is necessary to exercise some care in choosing the correct signs for the square-root terms in $K(\gamma)$. The simplest choice is as in Fig. 3. This is, however, incorrect, because the Kondo effect ensures that $K(\gamma)$ behaves quite differently in the regions $\gamma^{-1}<0$, $\gamma^{-1}>0$. For $\gamma^{-1}<0$, one should use

$$K(\gamma)=\frac{1}{\rho|g|}+\left[\left(\frac{1}{\gamma}+\frac{1}{\rho|g|}\right)^2+4\alpha\right]^{1/2}-\left(\frac{1}{\gamma^2}+4\alpha\right)^{1/2}, \tag{4.7}$$

as shown in Fig. 4. In Fig. 5, $K(\gamma)$ is plotted as a function of γ and is smooth.

One contribution to χ ignored in the above discussion is the residue of the bound-state pole itself. This contributes if the pole is on the physical sheet and in the lower half of the gap. The residue is precisely known for that value of γ at which the pole is in the middle of the gap, for at this point the pole contribution has to cancel the discontinuity in $X(y)$ [see Eqs. (2.13) and (2.14)]. In the classical case the residue varies slowly, going to zero as γ increases. It seems a reasonable approximation to take its contribution constant at the mid-gap value.

Thus the trajectories are determined by

$$0=1+\frac{\gamma}{\rho|g|}+\gamma\left(\frac{1+y}{1-y}\right)^{1/2}[\arcsin y-\pi(S+1)]+\alpha\gamma^2\frac{1+y}{1-y}-\frac{\gamma}{1-y}K(\gamma)+\pi\gamma\left[\left(\frac{1+y}{1-y}\right)^{1/2}-\frac{1}{1-y}\right]\theta(-y). \tag{4.8}$$

Typical curves are shown in Fig. 6.

The points of tangency of the trajectories to the lines $y=\pm1$ can be found in the standard fashion from (4.8) by equating the relevant coefficient to zero. Thus for tangency to $y=+1$

$$\gamma[2\alpha\gamma-K(\gamma)]=0. \tag{4.9a}$$

From Fig. 5 it follows immediately that this is only satisfied for $\gamma=0$. Hence in this approximation no sheet change occurs at $\gamma=+\rho|g|$.[12] A further possibility that has to be checked is that a pole in the lower half of the gap will contribute to χ and alter (4.9) sufficiently that the trajectory of the second pole will touch $y=+1$. The condition becomes

$$\gamma[2\alpha\gamma-K(\gamma)-\pi]=0. \tag{4.9b}$$

This would give tangency for very large positive γ but in that region all our approximations are invalid. Thus, provided $\gamma\ll1$, there is no tangency to $y=+1$ away from the origin.

Tangency to $y=-1$ is given by

$$1+\gamma/\rho|g|-\tfrac{1}{2}\gamma I(\gamma)-\tfrac{1}{2}\pi\gamma=0. \tag{4.10}$$

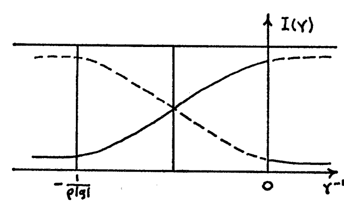

FIG. 4. Choice of square-root signs in $I(\gamma)$ consistent with the Kondo effect.

[12] J. Zittartz informed us that he had reached this same conclusion by a rather different path (private communication). This letter was the stimulus for the extension of our own technique in Sec. IV.

If the last term (the pole contribution) is dropped, tangency occurs at $\gamma=-2\rho|g|$. If it is included, tangency occurs at $\gamma\cong-\pi/4\alpha\cong-0.5$ for spin $\frac{1}{2}$. This would be outside the range of validity of the theory. Since the magnitude of the pole contribution is by no means clear in this high negative γ region, the point (if any) at which tangency takes place is hard to determine. In any case, for $|\gamma|\gg\rho|g|$ the pole is close to the edge of the gap. From (4.8) it can be shown that

$$\eta\cong\pi(S+\tfrac{1}{2})\frac{\gamma}{1+\gamma/\rho|g|} \quad (4.11)$$

for $-\gamma\gg\rho|g|$. Thus the pole tends asymptotically to a point of order $|g|^2\Delta$ above the gap edge.

For large positive γ, a similar procedure gives

$$\eta^{-1}\cong\tfrac{1}{2}\pi S\frac{\gamma}{1+\gamma/\rho|g|}. \quad (4.12)$$

In fact, this is a good approximation for all $\gamma>0$, corresponding to that of Soda *et al.*[1] for small positive γ. For small negative γ,

$$\eta^{-1}\cong\tfrac{1}{2}\pi(S+1)\frac{|\gamma|}{1+\gamma/\rho|g|}, \quad (4.13)$$

again coinciding with the results of Soda *et al.* In fact, these small $|\gamma|$ formulas are given correctly by the classical approximation of Sec. III.

V. DISCUSSION

We believe that the results of Sec. IV can be understood in terms of a simple physical picture. Rusinov[13] has shown that, neglecting Kondo-type complications, one can in straightforward fashion solve the Bogolyubov equation and write down the wave function describing the localized excitation (it spreads out over a distance of order the superconducting coherence length). The binding energy found by this technique agrees with Shiba's[5] result. It is, however, important to include the Kondo complication. For a normal metal at zero temperature, electrons within a characteristic energy

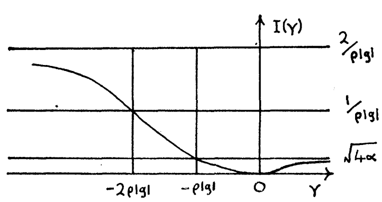

FIG. 5. Same as Fig. 4, but plotted as a function of γ rather than γ^{-1}.

[13] A. I. Rusinov, Zh. Eksperim. i Teor. Fiz. Pis'ma v Redaktsiyu **9**, 146 (1969) [English transl.: Soviet Phys.—JETP Letters **9**, 85 (1969)].

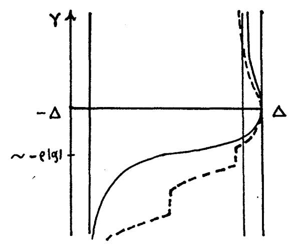

FIG. 6. Trajectories of bound-state poles in the gap as functions of γ. The full line is on the physical sheet, the dashed lines are on the unphysical sheet.

(denoted by T_K) of the Fermi surface are resonantly scattered in such a way that the local impurity spin is effectively screened, forming a singlet state. In a superconductor having a gap energy much less than T_K, this same "normal-metal" Kondo screening will still largely take place, because the vast majority of electrons involved have energies far from the Fermi surface and will be unaffected by the transition to the superconducting state. Thus, on the length scale associated with the Bogolyubov equation, there will be only a weak localized moment and hence a weakly bound excitation.

Suppose now that the coupling strength, and thus the Kondo temperature, is lowered through the region where it is comparable to the superconducting coupling. In the normal metal, this corresponds to the Kondo screening electrons being those belonging to a progressively narrower band about the Fermi level. In the superconductor this cannot go on indefinitely. The gap will eventually become important. As J becomes of order g, the shielding will begin to break down, and the localized excitation will become more tightly bound, i.e., it will move deep into the gap. For small values of J, the screening is no longer important, and the bound-state energy diminishes, going to zero with J.

These findings tie in rather well with Zuckermann's[14] result that the localized spin is most effective in lowering T_c when J is of order g.

For positive values of J, there is no Kondo resonance structure in the normal metal. That is, the localized spin scatters all electrons almost equally, not just those in a J-dependent energy range. Hence, the energy of the bound state does not change dramatically with increase in J.

For a finite concentration of impurities it is clear that the Bogolyubov wave functions of the localized excitations at each spin impurity will overlap and the localized states merge into an impurity band. Shiba[5] has given a detailed discussion of this point for classical impurity spins (no Kondo effect), showing how the density of states changes with increasing impurity concentration. The theory of AG[15] is a Born-approximation fit to the density-of-states function and is

[14] M. J. Zuckermann, Phys. Rev. **168**, 390 (1969).

clearly very poor at low concentrations, as it cannot show the separate impurity band in the gap. It is instructive to consider how the present results would alter Shiba's work. For positive J the bound state and the impurity band are very close to the edge of the gap, and one might expect the AG[15] density of states to be a good approximation in this situation. For negative J smaller than g, on the other hand, one would expect the AG theory to be very poor, as the impurity band will appear deep in the gap. Thus our model accounts (in very qualitative fashion) for the tunneling results of Woolf and Reif.[16]

It is straightforward to extend the work of Sec. II to finite temperatures. One finds trajectories qualitatively similar to those for $T=0$ (compare the discussion in I). However, for finite concentrations the picture is slightly altered—increasing the temperature decreases the gap and thus the whole energy scale of the system, so the wave function of the localized state spreads out further and further. Thus overlap with other localized states becomes more significant, and for low impurity concentrations the initially narrow impurity band will spread (relative to the gap size) as the temperature approaches T_c. In this model gaplessness occurs when the impurity band spreads over the center of the gap.[5] This will happen for arbitrarily low impurity concentrations provided the temperature is close enough to T_c.

ACKNOWLEDGMENT

We wish to thank J. Zittartz for a letter (in reply to our earlier manuscript) describing some of his unpublished work on the bound-state problem, using an approach different from ours. The extension of our method described in Sec. IV was stimulated by the discrepancy between our classical result and his work for positive J.

[15] A. A. Abrikosov and L. P. Gor'kov, Zh. Eksperim. i Teor. Fiz. **39**, 1781 (1960) [English transl.: Soviet Phys.—JETP **12**, 1243 (1961)].

[16] M. A. Woolf and F. Reif, Phys. Rev. **137**, A557 (1965).

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Specific Heat of Rhenium between 0.15 and 4.0 K*

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The specific heat of rhenium has been measured in the normal state between 0.15 and 4.0 K and in the superconducting state between 0.3 and 1.7 K. The specific heat in the normal state between 0.15 and 4.0 K was found to be $C_n=\gamma T+\alpha T^3+A/T^2$, where $\gamma=2290\pm20\,\mu$J/mole deg^2, $\alpha=27\pm2\,\mu$J/mole deg^4, and $A=49\pm2\,\mu$J deg/mole. Below $T_0=1.700$ K, the electronic contribution to the specific heat in the superconducting state was found to be $C_s=\gamma T_0 a e^{-bT_0/T}$, where $a=8.14$ and $b=1.413$. The above parameters were consistent with the vanishing of the entropy difference S_n-S_s at T_0. The value of the Debye temperature at absolute zero, $\Theta_0=416$ K, agrees with the value derived from measurement of elastic constants. The density of states at the Fermi level, $N(\zeta)$, derived from the measured value of γ, is 0.484 states of one spin per eV atom. The value for the superconducting energy gap derived from the value of b deduced in this work is $3.43kT_0$, compared to a value of $3.30kT_0$ deduced from thermal-conductivity measurements. The critical-field parameter H_0 was found to be 211 Oe, and the deviation of the critical-field curve from parabolic dependence was less than 3.7%. The resonant frequencies corresponding to the interaction between the nuclear quadrupole moment and the crystalline field are estimated to be 41 and 82 MHz.

1. INTRODUCTION

THE specific heat of rhenium has been measured previously by several workers[1–5] over various low-temperature ranges. Additional measurements of magnetic properties of this superconductor have been made,[6–11] which also yield some of the thermodynamic properties. Shepard and Smith[12] measured the elastic constants of rhenium single crystals down to 4.2 K,

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[1] N. M. Wolcott, *Conference de Physique des Basses Temperatures, Paris, Sept. 1955* (Centre National de la Recherche Scientifique et UNESCO, Paris, 1956), p. 286.

[2] R. Blanpain, Bull. Soc. Roy. Sci. Liege **26**, 182 (1957).

[3] P. H. Keesom and C. A. Bryant, Phys. Rev. Letters **2**, 519 (1959).

[4] R. Blanpain, Bull. Acad. Roy. Belg. Cl. Soc. **47**, 750 (1961).

[5] F. J. Morin and J. P. Maita, Phys. Rev. **129**, 1115 (1963).

[6] J. G. Daunt and T. S. Smith, Phys. Rev. **88**, 309 (1952).

[7] J. K. Hulm, Phys. Rev. **94**, 1390 (1954).

[8] G. K. White and S. B. Woods, Can. J. Phys. **35**, 656 (1957).

[9] J. K. Hulm and B. B. Goodman, Phys. Rev. **106**, 659 (1957).

[10] J. Doulat, B. B. Goodman, A. Lacaze, M. Renard, and L. Weil, Compt. Rend. **247**, 275 (1958).

[11] M. Renard, Physica **24**, S154 (1958).

[12] M. L. Shepard and J. F. Smith, J. Appl. Phys. **36**, 1447 (1965).