

Theory of Paramagnetic Impurity Spin Resonance in Metals*

M. B. WALKER

Department of Physics, University of Toronto, Toronto, Canada

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The frequency-dependent magnetic susceptibility describing the magnetic resonance of spin impurities in a metal is investigated theoretically, using thermodynamic Green functions and the Abrikosov diagram technique for spin operators. The single-particle pseudofermion propagator is shown to lead to formulas for the impurity spin energy-level shifts and widths which are identical, to all orders in perturbation theory, to those obtained in the standard quantum-mechanical theory of decaying states. The two-particle pseudofermion propagator describing impurity magnetic-resonance experiments is discussed, and it is shown that there are corrections to the interpretation of the magnetic resonance frequency shift and linewidth in terms of the individual level shifts and widths mentioned above. A perturbative evaluation of some of the formulas obtained shows that both the g shift and the linewidth of the impurity spin resonance exhibit Kondo-like corrections depending on $\ln T$ when $kT > \hbar\omega_0$, or on $\ln\omega_0$ when $kT < \hbar\omega_0$, ω_0 being the impurity spin-resonance frequency. The theory as developed is valid only when the conduction-electron spin-resonance frequency ω_c is sufficiently different from ω_0 , and it is shown that the contribution of the conduction-electron spin-magnetic moment to the absorption becomes increasingly important when this is not the case.

I. INTRODUCTION

THE results of paramagnetic-resonance experiments can be interpreted in terms of a frequency-dependent magnetic susceptibility¹ [see Eq. (1.1)]. This description is thought to be exact, provided the applied radio-frequency field is sufficiently small, and the problem is thus to evaluate such expressions in terms of the microscopic parameters contained in the Hamiltonian describing the system of interest. The model system to be discussed below consists of a low concentration of statistically independent impurity spins interacting with a sea of conduction electrons in a metal; a localized spin model for the impurities is assumed, and where explicit calculations are performed, the interaction between the conduction electrons and the impurities is taken to be the s - d interaction.² In order to exploit the methods of quantum field theory in the evaluation of the susceptibility, the spin operators associated with the magnetic impurities are expressed in terms of products of fictitious fermion operators, in a way which has been described by Abrikosov.³ The bulk of this paper will thus be concerned with the application of the Abrikosov diagram technique to the impurity magnetic-resonance problem.

The power absorbed by a sample from an oscillating magnetic field of frequency ω polarized along the x axis is proportional to the imaginary part of the frequency-dependent magnetic susceptibility, which is

given by¹

$$\chi''(\omega) \propto \int_{-\infty}^{\infty} dt e^{i\omega t} \langle [M_x(t), M_x] \rangle, \quad (1.1)$$

where M_x is the x component of the total (impurity spin plus conduction-electron spin) magnetic moment. The derivation of Eq. (1.1) assumes that the applied oscillatory magnetic field is spatially uniform across the sample, and all skin-depth problems are ignored.

When the paramagnetic impurities have a spin-only magnetic moment, and thus have the same g value as the conduction-electron spins, the total magnetic moment is proportional to the total spin. If one considers only interactions between the conduction electrons and impurity spins which are a result of electrostatic Coulomb interactions (such as the s - d exchange interaction) and which therefore commute with the total spin, it is clear that the motion of the total spin is determined entirely by the applied steady magnetic field (always assumed to be in the z direction) and is no different from what it would be if there were no interactions whatsoever. Any contributions to the resonance linewidth or line shift which are ascribed to the interaction of the conduction electrons with the impurities must therefore be due to the presence of some other interaction, such as the spin-orbit interaction, which does not commute with the total spin. This is not the only reason a microscopic theory of this particular case is difficult. The necessity of taking M_x in Eq. (1.1) to be the total moment (instead of simply the impurity spin moment) also adds to the complexity of the problem. Furthermore, when the conduction-electron spins contribute significantly to the absorption, a realistic assessment of the effects of skin depth and electron

* This research was supported in part by a grant from the National Research Council of Canada.

¹ R. Kubo and K. Tomita, *J. Phys. Soc. Japan* **9**, 888 (1954).

² T. Kasuya, in *Magnetism*, edited by G. T. Rado and H. Suhl (Academic Press Inc., New York, 1966), Vol. II B.

³ A. A. Abrikosov, *Physics* **2**, 5 (1965); see also S. D. Silverstein and C. B. Duke, *Phys. Rev.* **161**, 456 (1967); **161**, 470 (1967).

diffusion become necessary.⁴ For these reasons, this study will be devoted mainly to the simpler case discussed in the following paragraph.

When the conduction electrons and impurities have different g values, the susceptibility [Eq. (1.1)] can be separated into two parts, assuming that the interaction between the conduction electrons and impurities is sufficiently weak. This is easily seen by first assuming that there is no interaction at all. The susceptibility $\chi''(\omega)$, for positive ω , is then simply a sum of two δ functions, one at the impurity spin-resonance frequency ω_0 , and the other at the conduction-electron spin-resonance frequency ω_e . The presence of the interaction causes shifts of the resonance frequencies and a broadening of the δ functions into Lorentzians of nonzero width, but each resonance line can be considered separately provided they occur at sufficiently different frequencies. Thus, to study the impurity spin-resonance peak at ω_0 , it is sufficient to consider the formula for $\chi''(\omega)$ in which the total magnetic moment is replaced by the magnetic moment of the impurity spins only. A further simplification is introduced by making the assumption that the concentration of impurities is sufficiently low that they can be considered statistically independent. This means that

$$\sum_{ij} \langle M_{ix}(t) M_{jx} \rangle = N \langle M_{0x}(t) M_{0x} \rangle,$$

where i and j label the different impurity spins, N is the total number of impurities, and M_{0x} is the x component of the magnetic moment of any particular spin. In future calculations, it will therefore be assumed that the intensity of the impurity spin-resonance absorption signal is proportional to the function

$$A_{-+}'(\omega) = \int_{-\infty}^{\infty} dt e^{i\omega t} \langle [S_-(t), S_+] \rangle, \quad (1.2)$$

where the spin operators S_{\pm} refer to a single impurity spin, assumed to be at the origin of coordinates.

In Sec. V of this paper, corrections to the approximation (1.2) due to the incorporation of the conduction-electron spin moment in the formula for the susceptibility are treated, to lowest order in perturbation theory, and are shown to become increasingly important when ω_0 is close to ω_e . Also, at temperatures sufficiently far below the Kondo temperature, interactions between the impurity spins and the conduction electrons become exceptionally strong,^{5,6} and it is doubtful if (1.2) will remain a good approximation for the total absorption near ω_0 .

A method of evaluating the expression (1.2) in a

certain approximation has been suggested by Kubo and Tomita¹ in the section of their paper on motional narrowing. The basic assumption in their work is equivalent to assuming that the correlation function $\langle [S_-(t), S_+] \rangle$ has a time dependence which is given by

$$\langle [S_-(t), S_+] \rangle = \langle [S_-, S_+] \rangle \exp(i\tilde{\omega}_0 t - \Gamma t). \quad (1.3)$$

They then calculated $\tilde{\omega}_0$ (which differs from ω_0 because of the interaction) and Γ in terms of the microscopic parameters appearing in the Hamiltonian by expanding the left-hand side of (1.3) to second order in the interaction, and the right-hand side to first order in t , and comparing the coefficients of the terms linear in t . Such a procedure obviously depends very much on the assumption (1.3) of an exponential decay. It is perhaps possible to justify this assumption theoretically by expanding the left-hand side of (1.3) to all orders in the perturbation, and applying the Van Hove $\lambda^2 t$ limit⁷ to pick out the dominant terms. Terweil and Mazur,⁸ for example, have used Zwanzig's method⁹ to solve a related problem in the Van Hove $\lambda^2 t$ limit. Even if one could justify fully the formulas of Kubo and Tomita in this way, the results would be of limited usefulness because they still apply only in the weak-interaction limit. Moriya¹⁰ has applied the Kubo-Tomita approach to a particular nuclear-resonance problem, and Orbach and Spencer¹¹ have applied Moriya's results to the problem discussed in this paper. A fundamental paper on magnetic resonance which should also be mentioned is that of Wangsness and Bloch,¹² in which the Bloch equations¹³ are derived; the assumptions made in this paper appear closely related to those made by Kubo and Tomita.

The purpose of this paper is to study a method of evaluating the paramagnetic-resonance absorption line shape which can in principle be applied even to strongly interacting systems. It is now well known^{5,6} that the problem of spin impurities in a metal can not be attacked simply by applying lowest-order perturbation theory, and this is the reason for attacking it with the powerful Green-function techniques. These techniques can also be applied to the study of paramagnetic resonance in insulators; it is well known that the weak-interaction limit is not applicable even in this case, since a second-order process, namely the second-order Raman phonon process, is often more important than competing first-order processes. The method to be used below is to replace the spin operators by products

⁷ L. Van Hove, *Physica* **21**, 517 (1955).

⁸ R. H. Terweil and P. Mazur, *Physica* **32**, 1813 (1966).

⁹ R. Zwanzig, *Lectures Theoret. Phys.* **3**, 106 (1960).

¹⁰ T. Moriya, *Progr. Theoret. Phys. (Kyoto)* **28**, 371 (1962); *J. Phys. Soc. Japan* **18**, 516 (1963).

¹¹ R. Orbach and H. J. Spencer, *Phys. Letters* **26A**, 457 (1968).

¹² R. K. Wangsness and F. Bloch, *Phys. Rev.* **102**, 104 (1956).

¹³ F. Bloch, *Phys. Rev.* **70**, 468 (1946).

⁴ F. J. Dyson, *Phys. Rev.* **98**, 337 (1955).

⁵ J. Kondo, *Progr. Theoret. Phys. (Kyoto)* **32**, 37 (1964).

⁶ H. Suhl, in *Theory of Magnetism in the Transition Metals*, edited by W. Marshall (Academic Press Inc., New York, 1967).

of fictitious fermion operators in a way suggested by Abrikosov³ so that Wick's theorem and the standard methods¹⁴ of thermodynamic Green functions and diagram techniques can be exploited.

The single-particle pseudofermion propagators of the Abrikosov method can be interpreted as describing the time evolution of a system which has the impurity spin in a particular spin eigenstate (say $S_z = +\frac{1}{2}$) at the initial instant. The proper self-energy of this propagator thus describes the shift and width of this energy level due to the interaction of the impurity spin with the conduction electrons. The formulas obtained for the spin energy-level's shift and width are shown to be identical, to all orders of perturbation theory, to analogous expressions which arise in the standard quantum-mechanical theory¹⁵ of the lifetime and decay of virtual states.

Paramagnetic-resonance experiments are described in terms of the two-particle pseudofermion propagator. If the two-particle propagator is approximated by its free part, it is found that the resonance line shape is Lorentzian, and that the center frequency is equal to the difference in energy between the shifted spin energy levels, while the width is equal to the sum of the two level widths (spin $S = \frac{1}{2}$ is assumed); the individual energy-level shifts and widths referred to here are those mentioned in the preceding paragraph. It turns out, however, that the bound part of the two-particle Green function cannot be ignored, and when it is taken into account, corrections to the simple description in terms of the individual level shifts and linewidths are obtained.

Spencer and Doniach¹⁶ have also recently studied the magnetic-resonance problem using field-theoretic techniques, but using Kenan's¹⁷ drone fermion representation for the spin operators, rather than Abrikosov's³ technique. Although they explicitly carry out calculations only for the case $\omega_0 = \omega_e$, Spencer and Doniach assume that the total absorption can be approximated by the impurity spin contribution as calculated from (1.2); this is a controversial point and certainly requires further justification. Our results for the Kondo anomaly in the g shift agree with theirs, if we assume our formulas are valid when $\omega_0 = \omega_e$. Our explicit perturbative calculation of the single-particle propagator self-energy is also carried out to third order, at which point the Kondo-like contributions to the linewidth first appear; these contributions tend to narrow the resonance line below the Kondo temperature if the s - d exchange interaction is ferromagnetic, and broaden it if the interaction is antiferromagnetic. Also, our calculations

have been carried out in the temperature limit $T \ll \omega_0$ as well as the limit $T \gg \omega_0$, and it turns out that the results in the former limit can be obtained from those in the latter simply by replacing T by ω_0 . (Thus terms proportional to $\ln T$ become proportional to $\ln \omega_0$.)

The application of the Abrikosov technique to the theory of magnetic resonance in insulators, where the dominant interaction is between the impurity spins and phonons, is formally quite similar, as will be pointed out below.

II. SPIN GREEN FUNCTIONS AND THE ABRIKOSOV DIAGRAM TECHNIQUE

Thermodynamic Green functions¹⁴ and the Abrikosov diagram technique³ will be used to evaluate Eq. (1.2) for the paramagnetic-resonance absorption line shape. In this section the necessary preliminary definitions will be stated, and the notation established.

The temperature-dependent Green function $G_{-+}'(u)$ is defined by

$$G_{-+}'(u) = -\langle T\{S_-(u)S_+\} \rangle', \quad (2.1)$$

where $S_-(u) \equiv e^{uH} S_- e^{-uH}$, the spin operators are to be treated as bosons with respect to the time-ordering operation, and the primes have been included in G_{-+}' and the ensemble average $\langle \rangle'$ to distinguish them from similar quantities to be introduced later; the ensemble average of an operator A is defined as

$$\langle A \rangle' = \text{tr}'(e^{-\beta H} A) / \text{tr}'(e^{-\beta H}),$$

where tr' indicates a trace over a complete set of states describing the combined spin system and conduction-electron system. $G_{-+}'(u)$ can be expanded in a Fourier series, the expression being

$$G_{-+}'(u) = \beta^{-1} \sum_{x_\nu} e^{-x_\nu u} G_{-+}'(x_\nu), \quad (2.2)$$

where

$$G_{-+}'(x_\nu) = \int_0^\beta du e^{x_\nu u} G_{-+}'(u) \quad (2.3)$$

and $x_\nu = (2\pi\nu i/\beta)$ ($\nu = 0, \pm 1, \dots$). Now, define a new function $G_{-+}'(x)$ of the continuous complex variable x by the relation

$$G_{-+}'(x) = \frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega \frac{A_{-+}'(\omega)}{x - \omega}, \quad (2.4)$$

where $A_{-+}'(\omega)$ is given by Eq. (1.2); $G_{-+}'(x)$ can be shown to be the analytic continuation of $G_{-+}'(x_\nu)$. It will be shown below how $G_{-+}'(x_\nu)$ can be evaluated using diagram techniques, and once $G_{-+}'(x_\nu)$ has been determined, the resonance absorption intensity can be

¹⁴ A. A. Abrikosov, L. P. Gor'kov, and I. E. Dzialoshinski, *Methods of Quantum Field Theory in Statistical Physics* (Prentice-Hall, Inc., Englewood Cliffs, N.J., 1963).

¹⁵ M. L. Goldberger and K. M. Watson, *Collision Theory* (John Wiley & Sons, Inc., New York, 1964).

¹⁶ H. J. Spencer and S. D. Doniach, *Phys. Rev. Letters* **18**, 994 (1967).

¹⁷ R. P. Kenan, *J. Appl. Phys.* **37**, 1453 (1966).

found using the formula

$$\begin{aligned} A_{-+}'(\omega) &= i[G_{-+}'(\omega+i0^+) - G_{-+}'(\omega-i0^+)] \\ &= -2 \operatorname{Im} G_{-+}'(\omega+i0^+), \end{aligned} \quad (2.5)$$

which follows immediately from Eq. (2.4).

In order to make use of Wick's theorem to calculate Green functions arising in problems in which spin operators are involved, Abrikosov³ introduced a representation of the spin operators in terms of pseudofermion operators as follows. Let $|m\rangle$ be a complete set of states describing the impurity; for example, m can be taken to be an eigenvalue of S_z and has the $2S+1$ values $-S, \dots, S$. For each state $|m\rangle$ introduce a pair of pseudofermion creation and destruction operators a_m^\dagger and a_m ; these operators obey the usual fermion anticommutation relations $\{a_m, a_{m'}^\dagger\} = \delta_{mm'}$. The state $a_m^\dagger |0\rangle$ in the vector space in which the pseudofermion operators act is assumed to correspond to the state $|m\rangle$ in the space of the spin operators, and vice versa. The vacuum state $|0\rangle$ and states containing more than one pseudofermion are unphysical states with no counterparts in the space of the spin operators. Any operator f operating in the spin space can be written in the form $f = \sum_{m,n} |m\rangle f_{mn} \langle n|$; the operators $f' = \sum_{mn} f_{mn} a_m^\dagger a_n$ and f obviously have the same matrix elements between corresponding states and it is thus possible to use the pseudofermion representation of the spin operators in all calculations provided the unphysical states play no part. With reference to the calculation of the Green function (2.1), note that

$$\operatorname{tr}'[e^{-\beta H} T\{S_-(u)S_+\}] = e^{\beta\lambda} \operatorname{tr}[e^{-\beta(H_\lambda+H)} T\{S_-(u)S_+\}], \quad (2.6)$$

where it is understood that the limit $\lambda \rightarrow \infty$ is to be taken on the right-hand side of (2.6), $H_\lambda = \lambda \sum_m a_m^\dagger a_m$, and tr' is a trace over all spin states and conduction-electron states, whereas tr is a trace over all pseudofermion states and conduction-electron states; furthermore, all spin operators occurring on the right-hand side of (2.6) are to be written in the pseudofermion representation. For spin $S = \frac{1}{2}$ impurities, the pseudofermion representation of the spin operators is

$$S_- = a_\uparrow^\dagger a_\uparrow, \quad S_+ = a_\uparrow^\dagger a_\downarrow,$$

and

$$S_z = \frac{1}{2}(a_\uparrow^\dagger a_\uparrow - a_\downarrow^\dagger a_\downarrow). \quad (2.7)$$

The simplest way to see that Eq. (2.6) is true is to begin by writing it in the interaction representation. Since all spin operators contain a pseudofermion annihilation operator on the right, the vacuum state automatically gives zero contribution to a trace taken over a product of operators which contains spin operators. Also, by virtue of the fact that the term H_λ has been included in the Hamiltonian, each pseudofermion is given an additional energy λ , and the unphysical states containing two or more pseudofermions

will have a vanishingly small probability of being thermally excited. By making use of (2.6) and the definition (2.1), it can be shown that

$$G_{-+}'(u) = e^{\beta\lambda} \langle T\{S_-(u)S_+\}' \rangle \frac{\operatorname{tr} e^{-\beta(H_\lambda+H)}}{\operatorname{tr}' e^{-\beta H}}, \quad (2.8)$$

where the brackets $\langle \rangle$ without the prime imply a thermal average in the pseudofermion representation. Since the factor $\operatorname{tr} e^{-\beta(H_\lambda+H)}/\operatorname{tr}' e^{-\beta H}$ depends only on temperature and not on the variable u , it is not necessary to calculate it to determine the frequency dependence of $A_{-+}'(\omega)$; this factor thus enters into the interpretation of paramagnetic-resonance experiments only in that it affects the integrated intensity of the resonance line, which is not often measured. It is now convenient to define a new Green function $G_{-+}(u)$ (without the prime) by

$$G_{-+}(u) = e^{\beta\lambda} (1 + e^{-\beta\omega_0})^{-1} \langle T\{S_-(u)S_+\} \rangle, \quad (2.9)$$

where the normalizing factor has been chosen so that the spectral function $A_{-+}(\omega)$ calculated from this Green function using Eq. (2.5) is identical to $A_{-+}'(\omega)$ in the noninteracting limit, assuming spin $S = \frac{1}{2}$ impurities; λ_\downarrow is defined following Eq. (2.10). The Green function $G_{-+}(u)$ and the spectral function $A_{-+}(\omega)$ satisfy Eqs. (2.2)–(2.5), inclusive.

Although Abrikosov³ did not mention it, the conduction-electron Green function as defined by him also differs from the usual one by a factor of

$$\operatorname{tr} e^{-\beta(H+H_\lambda)}/\operatorname{tr}' e^{-\beta H}.$$

The temperature dependence of this factor should be taken into account when determining the temperature dependence of the electrical resistivity. There is, of course, no reason in principle why the pseudofermion representation should not also be used to evaluate factors such as $\operatorname{tr}' e^{-\beta H}$.

The explicit form of the Hamiltonian to be used below is, in the pseudofermion representation,

$$\begin{aligned} H_\lambda + H &= \sum_m \lambda_m a_m^\dagger a_m + \sum_p \epsilon_p c_p^\dagger c_p \\ &\quad + \sum_{mm'pp'} J_{mm'pp'} a_m^\dagger a_{m'} c_p^\dagger c_{p'}, \end{aligned} \quad (2.10)$$

where if the states $|m\rangle$ have energy ϵ_m , λ_m will be $\lambda + \epsilon_m$ (for spin $S = \frac{1}{2}$, $\lambda_\uparrow = \lambda + \frac{1}{2}\omega_0$ and $\lambda_\downarrow = \lambda - \frac{1}{2}\omega_0$) c_p^\dagger and c_p create and annihilate conduction electrons of momentum \mathbf{k} and spin σ , $p = (\mathbf{k}, \sigma)$, and $\epsilon_p = \epsilon_{\mathbf{k}} + \sigma\omega_e$, where $\sigma = \pm \frac{1}{2}$ and $\epsilon_{\mathbf{k}}$ is measured relative to the Fermi level. In explicit calculations $J_{mm'pp'}$ will be assumed independent of \mathbf{k} and \mathbf{k}' and denoted by $J_{mm'\sigma\sigma'}$; it will also be assumed that the only nonvanishing values of $J_{mm'\sigma\sigma'}$ are, for impurity spin $S = \frac{1}{2}$,

$$\begin{aligned} J_{\uparrow\uparrow\uparrow\uparrow} &= -J_{\downarrow\downarrow\downarrow\downarrow} = -J/2\Omega, \\ J_{\uparrow\downarrow\downarrow\uparrow} &= J_{\downarrow\uparrow\uparrow\downarrow} = -J'/\Omega, \end{aligned} \quad (2.11)$$

Ω being the quantization volume; the usual isotropic

s-d exchange interaction is thus obtained when J' is put equal to J . The Hamiltonian (2.10), with the restrictions implied by (2.11) and $J'=J$, may look more familiar if it is written in terms of the ordinary spin operators as

$$H = \sum_i (\mathbf{p}_i^2/2m) - 2JS \cdot \sum_i \mathbf{s}_i \delta(\mathbf{r}_i) + \omega_0 S_z + \omega_s \sum_i S_{iz}, \tag{2.12}$$

where \mathbf{p}_i , \mathbf{r}_i , and \mathbf{s}_i are the momentum, position and spin of the i th electron.

Finally, before going on to discuss the propagator formalism in detail, it should be noted that the integrated intensity is related to the expectation value of the z component of the impurity spin by the formula

$$\int_{-\infty}^{\infty} d\omega A_{-+}'(\omega) = 2\pi \langle S_z \rangle. \tag{2.13}$$

The influence of the *s-d* exchange interaction on $\langle S_z \rangle$ has been calculated by Everts and Ganguly¹⁸ to second order in perturbation theory. When $\langle S_z \rangle$ is written in the form $g_i \mu_B \langle S_z \rangle = \chi_i \hbar$, they find

$$\chi_i = \frac{g_i^2 \mu_B^2 S(S+1)}{3kT} \left[1 + \frac{g_e}{g_i} J_\rho - \frac{g_e}{g_i} (J_\rho)^2 \ln \left(\frac{D}{T} \right) \right]. \tag{2.14}$$

It should be noted that the total area under the curve $A_{-+}'(\omega)$ is composed of a contribution from the resonance peak, and a contribution from the wings of the resonance curve. The experimentally observed resonance intensity depends, however, only on the area under the resonance peak, and thus the relation of the observed intensity to $\langle S_z \rangle$ is not well defined.

III. SINGLE-PARTICLE PROPAGATORS

The single-particle pseudofermion propagators are defined by

$$G_m(u) = -\langle T \{ a_m(u) a_m^\dagger \} \rangle, \tag{3.1}$$

and the functions $G_m(z)$ and $A_m(\omega)$ are defined by relations identical to (2.2)–(2.5) with the exception that $x_\nu = 2\pi i_\nu/\beta$ is replaced by $z_\nu = (2\nu+1)\pi i/\beta$; this distinction between the meaning of x_ν and z_ν will be retained throughout. For completeness, the Green functions $G_{mm'}(u) = -\langle T \{ a_m(u) a_{m'}^\dagger \} \rangle$, $m \neq m'$, should also be introduced, but the diagonal elements $G_m(z)$ are much larger than the off-diagonal elements $G_{mm'}(z)$, $m \neq m'$ when z is close to a resonance of $G(z)$, provided the energy levels m are nondegenerate. Future calculations will only make use of the value of $G(z)$ when z is near a resonance, so the off-diagonal elements will be ignored. Furthermore, if the interaction is assumed to be simply the *s-d* exchange interaction, which conserves the

z component of the total spin, the off-diagonal elements are identically zero.

The zero-order propagators are given by

$$G_m^{(0)}(z_\nu) = (z_\nu - \lambda_m)^{-1}. \tag{3.2}$$

The full Green function can be evaluated formally by standard diagrammatic methods¹⁴ and is given by

$$G_m(z_\nu) = [z_\nu - \lambda_m - M_m(z_\nu)]^{-1}, \tag{3.3}$$

where $M_m(z_\nu)$ is the sum of all proper self-energy diagrams.

It can be shown that a self-energy diagram containing n pseudofermion closed loops is of order $\exp(-n\beta\lambda)$, and therefore all diagrams containing one or more closed pseudofermion loops can be ignored. Consider, for example, the diagram shown in Fig. 1, which is actually part of a larger self-energy diagram. The closed pseudofermion loop contributes a factor

$$F = \beta^{-1} \sum_{z_0} G_m^{(0)}(z_0) G_{m'}^{(0)}(z_0 + z_1 - z_2). \tag{3.4}$$

The sum over z_0 can be performed by converting it to a contour integral; thus

$$F = -(2\pi i)^{-1} \int_C \frac{dz_0}{e^{\beta z_0} + 1} (z_0 - \lambda_m)^{-1} (z_0 + z_1 - z_2 - \lambda_{m'})^{-1}, \tag{3.5}$$

where C is a contour which runs up the right-hand side and down the left-hand side of the imaginary axis. The contour running up the right-hand side of the imaginary axis can be closed at infinity in the right half-plane and can thus be considered to enclose the entire right half-plane; similarly, the contour running down the left-hand side of the imaginary axis can be considered to enclose the entire left-hand plane. The integrand in (3.5) has two poles in the right half-plane and the residue to each is proportional to $e^{-\beta\lambda}$. In general, associated with each closed pseudofermion loop is an independent energy variable (such as z_0 in the above example) which appears in the argument of each pseudofermion Green function associated with the loop, and nowhere else; the sum over this energy variable can be performed giving a contribution proportional to $e^{-\beta\lambda}$ as above. Thus all diagrams containing closed pseudofermion loops can be neglected.

The rules for calculating the contributions of the various self-energy diagrams will now be stated explicitly. Examples of such diagrams are shown in Fig. 2

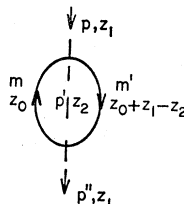


FIG. 1. A diagram containing a closed pseudofermion loop; the dashed (full) lines represent conduction-electron (pseudofermion) propagators.

¹⁸ H. U. Everts and B. N. Ganguly, Phys. Rev. **174**, 594 (1968). (This paper also contains references to earlier calculations of $\langle S_z \rangle$.)

where all first-, second-, and third-order diagrams are displayed. The full lines representing the pseudofermion propagators are always connected to the various vertices so as to form a single line running straight up (that is, without kinks); since in the n th order, there are $n!$ other ways connecting these lines, each of which gives an identical contribution to the self-energy, the procedure of considering only the diagrams indicated cancels out the factor $(n!)^{-1}$ appearing in the expansion of the S matrix. The contributions of the self-energy diagrams are calculated as follows:

- (1) With each n th-order diagram associate a factor $(-1)^{n+f}\beta^{-n}$, where f is the number of closed conduction-electron loops.
- (2) With each vertex associate a factor $J_{mm'pp'}$ as indicated in Fig. 2(a).
- (3) With each (dashed) conduction-electron line labeled by z_p, p associate a factor $g_p^{(0)}(z_p) = (z_p - \epsilon_p)^{-1}$; if the line leaves and enters the same vertex, a factor $\exp(z_p 0^+)$ should be included.
- (4) With each (full) pseudofermion line labeled by z_p, m associate a factor $G_m^{(0)}(z_p) = (z_p - \lambda_m)^{-1}$.
- (5) Restrict the number of independent z 's by putting the total z in lines leaving the interaction equal to the total z in lines entering the interaction.
- (6) Sum over all p 's, internal m 's, and independent z 's.

As an example, the second-order self-energy corresponding to the diagram of Fig. 2(c) is given by

$$M_m^{(2)}(z_p) = -(1/\beta^2) \sum_{z_1 z_2} \sum_{m' p p'} |J_{mm'pp'}|^2 \times G_{m'}^{(0)}(z_p + z_1 + z_2) g_p^{(0)}(z_1) g_{p'}^{(0)}(-z_2). \quad (3.6)$$

The sums over z_1 and z_2 may be performed by contour integration as was done in going from (3.4) to (3.5),

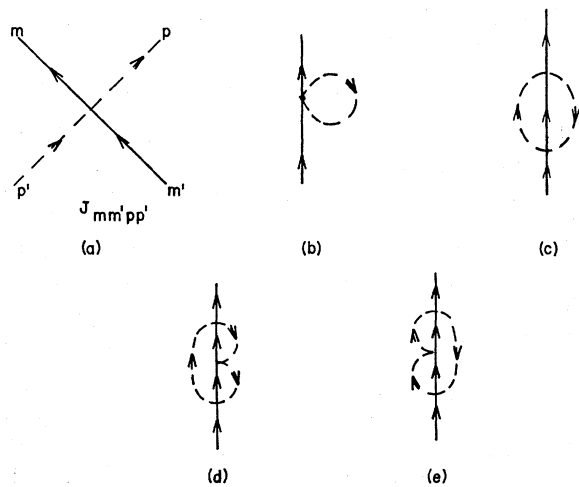


FIG. 2. Illustrating (a) the labeling of the interaction vertex; and (b) the first-order, (c) the second-order, and (d) and (e) the third-order pseudofermion proper self-energy diagrams.

giving

$$M_m^{(2)}(z_p) = \sum_{m' p p'} |J_{mm'pp'}|^2 \times G_{m'}^{(0)}(z_p + \epsilon_p - \epsilon_{p'}) f^+(\epsilon_p) f^-(\epsilon_{p'}), \quad (3.7)$$

where

$$f^\pm(\epsilon_p) = [e^{\pm\beta\epsilon_p} + 1]^{-1}.$$

The sums over the z 's can be performed for a general diagram with no greater difficulty if the following points are noted. The variables z associated with each conduction-electron line [z_1 and z_2 in the example (3.6)] can be chosen independently as can the variable associated with the external pseudofermion line (z_p in the above example) and this choice completely determines the z variables associated with the internal pseudofermion lines. It is convenient to label all electron lines (hereafter the term electron line refers to an upward directed line) by a positive z variable [e.g., $+z_1$ as in (3.6)] and all hole lines by a negative z variable [e.g., $-z_2$ as in (3.6)]; all z variables in the arguments of pseudofermion Green functions are then prefixed by a positive sign. The sums over the z variables are now performed using the relations

$$-\beta^{-1} \sum_z g_p(z) F(z) = (2\pi i)^{-1} \int_C \frac{dz}{e^{\beta z} + 1} g_p(z) F(z) = -f^+(\epsilon_p) F(\epsilon_p)$$

and

$$-\beta^{-1} \sum_z g_p(-z) F(z) = (2\pi i)^{-1} \int_C \frac{dz}{e^{\beta z} + 1} g_p(-z) F(z) = -f^-(\epsilon_p) F(-\epsilon_p), \quad (3.8)$$

where C is the contour referred to following Eq. (3.5) and $F(z)$ is a product of all G_m 's whose arguments contain the variable z associated with the particular electron or hole line under consideration. Because z occurs with a positive sign in the arguments of all of the G_m 's, the poles of $F(z)$ will be in the right half-plane and at a distance of the order λ from the imaginary axis, and can thus be ignored in performing the contour integration since their residues will be of order $e^{-\beta\lambda}$.

In the quasiparticle approximation for $G_m(z)$ as given by Eq. (3.3), $M_m(z)$ is replaced by $M_m(\lambda_m + i0^+)$ when z is in the upper half-plane [G in the lower half-plane can be determined by noting that $G^*(z) = G(z^*)$ and $M^*(z) = M(z^*)$]. Following the above arguments through to their logical conclusion leads to a convenient set of rules for the calculation of $M_m(\lambda_m + i0^+)$, which will be simply called M_m from now on. The contribution of a particular diagram to M_m is thus found by associating a factor (-1) with each closed electron hole loop, a factor $f^-(\epsilon_p)$ with each electron line, a factor $(-1)f^+(\epsilon_p)$ with each hole line (conduction-electron lines leaving and entering the same vertex are to be treated as hole lines in this respect), a factor $J_{mm'pp'}$ with each vertex as shown in Fig. 2(a), and a factor $G_{m'}^{(0)}$ with each pseudofermion line. The factors $G_{m'}^{(0)}$ are

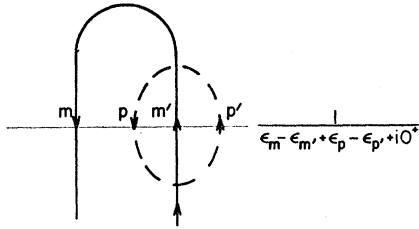


FIG. 3. Illustrating the determination of the energy denominators in the expression for M_m .

determined in the same way as energy denominators are in ordinary perturbation theory; a horizontal line is drawn between two vertices and a line crossing it in an upward direction contributes an energy $+\epsilon$, whereas a line crossing it in the downward direction contributes an energy $-\epsilon$; an example is given in Fig. 3.

The self-energy M_m can thus also be calculated from the formula

$$M_m = \sum_f P_f \langle mf | V + V(\epsilon_m + \epsilon_f - H + i0^+)^{-1} V | mf \rangle_P, \tag{3.9}$$

where H is given by Eq. (2.10) with $\lambda=0$ and the operators $a_m^\dagger a_{m'}$ replaced by $|m\rangle\langle m'|$ since the operators in (3.8) are meant to act in the original spin space, and not the pseudofermion space; $|m\rangle$ is an impurity spin eigenstate of energy ϵ_m , $|f\rangle$ is an eigenstate of the unperturbed conduction-electron system with energy E_f , and $P_f = e^{-\beta E_f} / \sum_f e^{-\beta E_f}$ is the probability that the state $|f\rangle$ is occupied if the conduction-electron system is assumed to be in thermal equilibrium. It is a straightforward matter to construct a diagram technique to evaluate the perturbation series implied by Eq. (3.9) (the subscript P attached to the final ket means that only proper self-energy diagrams are to be included) and to show that the rules one obtains in this way are identical to the rules for M_m discussed in the preceding paragraph.

The result (3.9) can also be derived in the same way for a spin interacting with a system of harmonic phonons, $|f\rangle$ being in this case an eigenstate of the harmonic lattice Hamiltonian, and V being the spin-phonon interaction.

Equation (3.9) is important because it establishes contact between Abrikosov technique and ordinary scattering theory. The matrix element appearing in (3.9) is the diagonal matrix element of a matrix R defined by

$$R_{mf, m'f'} = \langle mf | V + V(\epsilon_m + E_f - H + i0^+)^{-1} V | m'f' \rangle_P. \tag{3.10}$$

The definition (3.10) of R corresponds to that used by Goldberger and Watson¹⁵ in their general quantum-mechanical discussion of the lifetime and decay of virtual states. The main difference between our discussion and ordinary quantum-mechanical discussions

is that the system is assumed to be in thermal equilibrium at a nonzero temperature, a condition which means that a thermal average over the conduction-electron states must be taken, as in (3.9).

M_m can be written in the form

$$M_m = \Delta_m - i\Gamma_m, \tag{3.11}$$

where Δ_m and Γ_m are real. It is evident from (3.3) that Δ_m corresponds to a shift of the energy level m induced by the interaction, and Γ_m corresponds to the level's width. The expression

$$\Gamma_m = \frac{1}{2} \sum_{m'} w_{m \rightarrow m'}, \tag{3.12}$$

where

$$w_{m \rightarrow m'} = 2\pi \sum_{ff'} P_f |R_{mf, m'f'}|^2 \delta(\epsilon_m + E_f - \epsilon_{m'} - E_{f'}), \tag{3.13}$$

is simply a statement of the optical theorem.¹⁵ The existence of the transition probability $w_{m \rightarrow m'}$ for $m \neq m'$ implies that the spin system will jump from state m to state m' after a certain time and this gives rise to a lifetime broadening of the level m . The term $w_{m \rightarrow m}$ describes a broadening of the level m which does not result from a decay process, but is due to the fact that thermal fluctuations in the conduction-electron concentration near the impurity cause a modulation of the phase of the precessional motion of the spin around the external magnetic field.

Consider now a paramagnetic-resonance experiment performed on a system of spin- $\frac{1}{2}$ impurities. In the absence of the interaction the paramagnetic-resonance line is a δ function centered at the frequency $\omega_0 = \epsilon_\uparrow - \epsilon_\downarrow$. Intuitively one might expect that the presence of the interaction would shift the resonance frequency by an amount Δ equal to the difference of the level shifts, i.e., $\Delta = \Delta_\uparrow - \Delta_\downarrow$, and would give the line a width Γ equal to the sum of the two level widths, i.e., $\Gamma = \Gamma_\uparrow + \Gamma_\downarrow$. There are corrections to this simple-minded picture, as will be shown in the next section, but at the moment Δ and Γ as defined by

$$\Delta = \Delta_\uparrow - \Delta_\downarrow \quad \text{and} \quad \Gamma = \Gamma_\uparrow + \Gamma_\downarrow \tag{3.14}$$

will be computed to second and third order in the interaction, respectively, in order to exhibit the Kondo-like divergences occurring in these quantities. In these explicit calculations, the simplified interaction (2.11) will be assumed. Also, it should be emphasized that the following explicit calculations apply only to ions characterized by an effective spin $\frac{1}{2}$; e.g., iron-group or rare-earth ions having a Kramers doublet lying lowest in energy.

The contributions of the various diagrams can easily be written down using the general rules outlined above. The self-energy of the spin-up level to first order in the interaction, is represented by Fig. 3(b) and is given by

$$M_\uparrow^{(1)} = (J/2\Omega) \sum_k [f^+(\epsilon_{k\downarrow}) - f^+(\epsilon_{k\uparrow})]. \tag{3.15}$$

Also $M_{\downarrow}^{(1)} = -M_{\uparrow}^{(1)}$. The expression (3.14), and all subsequent expressions will be evaluated assuming a density of states per unit energy range per unit volume which is a constant ρ in the interval $-D < \epsilon_k < D$ and zero outside this interval. There is no contribution to the linewidth in first order, but the resonance is shifted by an amount

$$\Delta^{(1)} = J\rho\omega_e, \quad (3.16)$$

a result which is valid both when $T \gg \omega_e$ and when $T \ll \omega_e$. This shift of the resonance frequency is a familiar experimentally verifiable effect in nuclear resonance in metals,¹⁹ where it is called the Knight shift.

The second-order contribution to the self-energy can be obtained from (3.7) by letting $z_r = \lambda_m + i0^+$ and using (2.11). At temperatures such that $T \gg \omega_0$, the net level shift Δ [given by Eq. (3.13)] is given by

$$\Delta^{(2)} = -2(J'\rho)^2 \{ T[\ln(D/T) + C] - \delta\omega \ln 2 \}, \quad (3.17)$$

where C is a constant roughly equal to unity and $\delta\omega = \omega_0 - \omega_e$. At temperatures such that $T \ll \omega_0$, the shift is

$$\Delta^{(2)} = -2(J'\rho)^2 \{ \omega_0[\ln(D/\omega_0) + 1] - \delta\omega \ln 2 \}. \quad (3.18)$$

The second-order contribution to the linewidth Γ [given by Eq. (3.13)] is

$$\Gamma^{(2)} = \pi[(J\rho)^2 + 2(J'\rho)^2]T, \quad T \gg \omega_0 \quad (3.19)$$

and

$$\Gamma^{(2)} = \pi(J'\rho)^2\omega_0, \quad T \gg \omega_0. \quad (3.20)$$

Our result (3.17) reduces to that recently obtained by Spencer and Doniach¹⁶ when $\omega_0 = \omega_e$. The interesting feature of (3.17) is the Kondo-like⁵ dependence on $\ln(D/T)$ which will have the effect of reducing the paramagnetic-resonance frequency when the temperature falls below the Kondo temperature T_k [defined by $T_k \equiv D \exp(-1/J\rho)$]. In the case of nuclear resonance, where $\omega_0 \ll \omega_e$, it is interesting that the logarithmic terms in (3.17) and (3.18) are completely negligible in comparison with the terms proportional to $\delta\omega$ and the sec-

ond-order correction to the g shift is thus essentially temperature-independent; this is of little practical importance, as $J\rho$ is so small that the first-order correction (3.16) is by far the most important one. At high temperatures, the linewidth [Eq. (3.19)] has contributions both from the lifetime broadening and the phase modulation processes described following (3.12); these are proportional to J^2 and J'^2 , respectively. As one would expect, in the low-temperature limit, the lower level remains perfectly sharp (i.e., $\Gamma_{\downarrow}^{(2)} = 0$); the upper level is, however, broadened by the spin making a spontaneous transition to the lower level and emitting an electron-hole pair.

It is in third order that logarithmic terms first appear in the expression for the linewidth. The third-order terms [Figs. 3(d) and 3(e)] can be divided into two classes, those which contain the spin-flip interaction J' and those which do not. The contribution of the terms in which J' does not appear to the spin-up self-energy is

$$M_{\uparrow} = 2(J/2\Omega)^3 \sum_{\mathbf{k}_1 \mathbf{k}_2 \mathbf{k}_3 \sigma} (-1)^{1/2-\sigma} \times \frac{f^+(\epsilon_{\mathbf{k}_1 \sigma}) f^+(\epsilon_{\mathbf{k}_2 \sigma}) f^-(\epsilon_{\mathbf{k}_3 \sigma})}{(\epsilon_{\mathbf{k}_1} - \epsilon_{\mathbf{k}_2} + i0^+) (\epsilon_{\mathbf{k}_2} - \epsilon_{\mathbf{k}_3} + i0^+)}, \quad (3.21)$$

whereas their contribution to the spin-down self-energy is $M_{\downarrow} = -M_{\uparrow}$. Since $M_{\uparrow} = -M_{\downarrow}$, these terms cannot contribute to the linewidth. They will therefore be ignored, as we intend to evaluate only the linewidth, and not the shift, in third order.

The assumption that the density of states is an even function of energy (energy is measured relative to the Fermi surface) will often be used to simplify expressions from here on, and in fact has already been used in writing (3.20).

The terms in third-order perturbation theory containing spin-flip processes give contributions to the self-energies of

$$M_{\uparrow}^{(3)} = 2 \left(\frac{J'}{\Omega} \right)^2 \frac{J}{\Omega} \sum_{\mathbf{k}_1 \mathbf{k}_2 \mathbf{k}_3} \frac{f^+(\epsilon_{\mathbf{k}_1 \downarrow}) f^+(\epsilon_{\mathbf{k}_2 \uparrow}) f^-(\epsilon_{\mathbf{k}_3 \downarrow})}{(\epsilon_{\mathbf{k}_1} - \epsilon_{\mathbf{k}_3} + \delta\omega + i0^+) (\epsilon_{\mathbf{k}_2} - \epsilon_{\mathbf{k}_3} + i0^+)} + \left(\frac{J'}{\Omega} \right)^2 \frac{J}{\Omega} \sum_{\mathbf{k}_1 \mathbf{k}_2 \mathbf{k}_3} \frac{f^+(\epsilon_{\mathbf{k}_1 \downarrow}) f^+(\epsilon_{\mathbf{k}_2 \downarrow}) f^-(\epsilon_{\mathbf{k}_3 \uparrow})}{(\epsilon_{\mathbf{k}_1} - \epsilon_{\mathbf{k}_3} + \delta\omega + i0^+) (\epsilon_{\mathbf{k}_2} - \epsilon_{\mathbf{k}_3} + \delta\omega + i0^+)} \quad (3.22)$$

and

$$M_{\downarrow}^{(3)} = 2 \left(\frac{J'}{\Omega} \right)^2 \frac{J}{\Omega} \sum_{\mathbf{k}_1 \mathbf{k}_2 \mathbf{k}_3} \frac{f^+(\epsilon_{\mathbf{k}_1 \downarrow}) f^+(\epsilon_{\mathbf{k}_2 \uparrow}) f^-(\epsilon_{\mathbf{k}_3 \uparrow})}{(\epsilon_{\mathbf{k}_1} - \epsilon_{\mathbf{k}_3} + i0^+) (\epsilon_{\mathbf{k}_2} - \epsilon_{\mathbf{k}_3} - \delta\omega + i0^+)} + \left(\frac{J'}{\Omega} \right)^2 \frac{J}{\Omega} \sum_{\mathbf{k}_1 \mathbf{k}_2 \mathbf{k}_3} \frac{f^+(\epsilon_{\mathbf{k}_1 \uparrow}) f^+(\epsilon_{\mathbf{k}_2 \uparrow}) f^-(\epsilon_{\mathbf{k}_3 \downarrow})}{(\epsilon_{\mathbf{k}_1} - \epsilon_{\mathbf{k}_3} - \delta\omega + i0^+) (\epsilon_{\mathbf{k}_2} - \epsilon_{\mathbf{k}_3} - \delta\omega + i0^+)}. \quad (3.23)$$

The evaluation of Γ using (3.13), (3.22), and (3.23) gives

$$\Gamma^{(3)} = -12\pi J'^2 J \rho^3 [\ln(D/T) + C] T, \quad T \gg \omega_0 \quad (3.24)$$

and

$$\Gamma^{(3)} = -4\pi J'^2 J \rho^3 [\ln(D/\omega_0) + 1] \omega_0, \quad T \ll \omega_0 \quad (3.25)$$

where C is the same constant as appeared in (3.17).

¹⁹ A. Abragam, *Principles of Nuclear Magnetism* (Clarendon Press, Oxford, 1961).

Notice that the correction (3.24) to the linewidth tends to narrow the line below the Kondo temperature if the s - d exchange interaction is ferromagnetic and broaden it if the interaction is antiferromagnetic; thus an experimental measurement of the linewidth as the temperature is lowered below the Kondo temperature allows the sign of the exchange integral to be determined. Also, a detailed study of the individual level widths in the low-temperature limit shows that the lower level

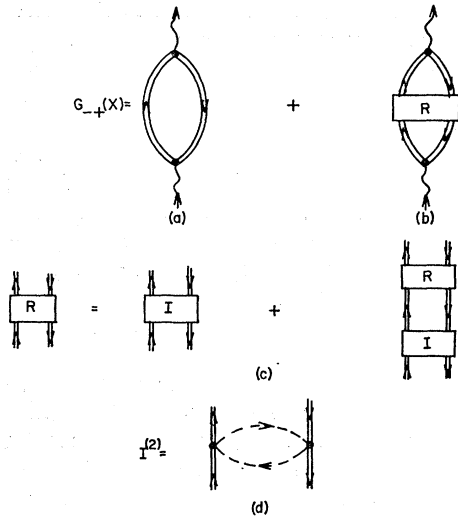


FIG. 4. The full two-particle correlation function is represented by (a) plus (b); the Bethe-Salpeter equation (c) determines the reducible particle-hole interaction R in terms of the irreducible interaction I ; the second-order irreducible interaction is shown in (d).

remains perfectly sharp, and that the broadening of the upper level is a purely lifetime broadening which is a result of the spin making a spontaneous transition from the upper level to the lower one.

It is an interesting fact [see Eqs. (3.17)–(3.19), and (3.25)] that results which are applicable in the limit $T \ll \omega_0$ are obtained from those applicable in the limit $T \gg \omega_0$ simply by replacing T by ω_0 .^{19a} Further inspection of the above results shows that at temperatures greater than the Kondo temperature T_k , the higher-order corrections to the perturbation series appear to be getting smaller; this is also the case if the magnetic field is strong enough that $\omega_0 > T_k$. If $\omega_0 < T_k$ and $T < T_k$, however, a nonperturbative approach to the problem is required. This situation is to be expected, as it is analogous to the one which arises in the study of the electrical resistivity^{5,6} and many other properties of dilute magnetic alloys.

IV. TWO-PARTICLE PROPAGATOR

A rigorous theory of paramagnetic resonance should not be based on the intuitive speculations concerning the significance of M_m which were presented in the previous section, but should be based on a study of the two-particle propagator with the aim of evaluating $A_{-+}(\omega)$ [cf. Eq. (1.2)]. In this section, the impurity will be assumed to have a spin $S = \frac{1}{2}$, and the propagator to be studied is $G_{-+}(u)$ which is defined by Eqs. (2.9) and (2.7). The function $G_{-+}(x_\nu)$ is related to $G_{-+}(u)$ by Eq. (2.3) and can be evaluated diagrammatically; $A_{-+}(\omega)$ is then obtained from $G_{-+}(x_\nu)$ by using (2.5).

^{19a} Note added in proof. Y. L. Wang and D. J. Scalapino (unpublished). These authors have derived similar formulas for the line shift and linewidth in the zero-temperature high-field limit.

The full Green function, represented diagrammatically in Fig. 4, is a sum of two terms, the free part [Fig. 4(a)] and the bound part [Fig. 4(b)]. The rules for evaluating $G_{-+}(x_\nu)$ are the same as the rules for evaluating $G_m(x_\nu)$ except that an extra factor $e^{\beta\lambda} (1 + e^{-\beta\omega_0})^{-1} \beta^{-1}$ must be added; also, double solid lines are used to represent the full pseudofermion Green function $G_m(z_\nu)$. The wiggly lines at the top and bottom of each diagram are associated with the external microwave field and labeled by x_ν ; this is merely to ensure the proper energy conservation relations between the z variables associated with the pseudofermion propagators and there are no additional factors associated with these wiggly lines or the uppermost and lowermost vertices. All pseudofermion lines shown in Figs. 4(a), 4(b), and 4(c) directed upwards (downwards) are associated with spin-up (-down) propagators; other labelings may be possible, but their corresponding contributions to $G_{-+}(x)$ near $x = \omega_0$ will be negligible if the spin energy levels are nondegenerate. The bound part of $G_{-+}(x_\nu)$ illustrated in Fig. 4(b) is a product of four single-particle propagators and the reducible particle-hole interaction R which is given in terms of the irreducible interaction I by the Bethe-Salpeter equation illustrated in Fig. 4(c). Thus $G_{-+}(x_\nu)$ is given by

$$e^{-\beta\lambda} (1 + e^{-\beta\omega_0}) G_{-+}(x_\nu) = \beta^{-1} \sum_{z_1} F_\nu(z_2) + \beta^{-2} \sum_{z_1, z_2} F_\nu(z_1) R_\nu(z_1, z_2) F_\nu(z_2), \quad (4.1)$$

where

$$R_\nu(z_1, z_2) = I_\nu(z_1, z_2) + \beta^{-1} \sum_{z_3} I_\nu(z_1, z_3) F_\nu(z_3) R_\nu(z_3, z_2) \quad (4.2)$$

and

$$F_\nu(z_3) = G_\uparrow(z_3) G_\downarrow(z_3 - x_\nu). \quad (4.3)$$

As a first step in the evaluation of $G_{-+}(x_\nu)$, consider only the free part, $G_{-+}^F(x_\nu)$, which is given by the first term on the right-hand side of Eq. (4.1), together with Eq. (4.3). The sum over z_1 can be carried out most easily by making use of the spectral representation (2.4) of the G_m 's, with the result that

$$G_{-+}^F(x_\nu) = \tanh\left(\frac{1}{2}\beta\omega_0\right) \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \frac{d\omega d\omega'}{2\pi 2\pi} \frac{A_\uparrow(\omega) A_\downarrow(\omega')}{x_\nu - \omega + \omega'}, \quad (4.4)$$

where the factor $e^{-\beta\omega'} - e^{-\beta\omega}$ which had appeared under the double integral sign in Eq. (4.4) has been replaced by $e^{-\beta\lambda} (1 - e^{-\beta\omega_0})$. The spectral functions are determined using (2.5) and (3.3) and are found to be

$$A_m(\omega) = 2\Gamma_m [(\omega - \lambda_m - \Delta_m)^2 + \Gamma_m^2]^{-1}, \quad (4.5)$$

where Γ_m and Δ_m are functions of ω determined from the self-energy by the relations $M_m(\omega \pm i0^+) = \Delta_m(\omega) \mp i\Gamma_m(\omega)$. Since the major contributions to the double integral over ω and ω' in Eq. (4.4) come from the

regions of the maxima of $A_{\uparrow}(\omega)$ and $A_{\downarrow}(\omega')$ at $\omega \approx \lambda_{\uparrow}$ and $\omega' \approx \lambda_{\downarrow}$, and since the variation of the self-energy with frequency is small over the width of the spectral functions (this can be easily checked in the low orders of perturbation theory), $\Delta_m(\omega)$ and $\Gamma_m(\omega)$ can be assumed constant and equal to $\Delta_m(\lambda_m)$. The integrations over the frequency variables in (4.4) are now easily performed by contour integration, with the result that

$$\tilde{G}_{-+}(x) = \tanh \frac{1}{2}(\beta\omega_0) (x - \omega_R + i\Gamma)^{-1}, \quad (4.6)$$

where $\omega_R = \omega_0 + \Delta$, Δ and Γ are given by Eq. (3.13), and x is assumed to be in the upper half-plane (the tilde on \tilde{G} means that \tilde{G} is identical to G only when x is in the upper half-plane). The spectral function associated with (4.6) is

$$A_{-+}^F(\omega) = \tanh \frac{1}{2}(\beta\omega_0) 2\Gamma [(\omega - \omega_R)^2 + \Gamma^2]^{-1}. \quad (4.7)$$

Thus, in this approximation, the absorption line is a Lorentzian centered at the frequency $\omega_R = \omega_0 + \Delta$ and having a half-intensity half-width equal to Γ , which is just what was predicted on intuitive grounds in the preceding section.

There are significant corrections to (4.7), however, which come from the bound part of the two-particle propagator. As a first step in attempting to estimate these corrections, it is assumed that the irreducible interaction I is given by its lowest-order contribution, namely, the second-order contribution shown in Fig. 4(d). Furthermore, the simplified interaction (2.11) will be assumed throughout this section. Explicitly, I is given by

$$I(z_1, z_2) = (J/2\Omega)^2 (1/\beta) \sum_{p_1 p_2 z_3} \delta_{\sigma_1 \sigma_2} g_{p_1}(z_3) g_{p_2}(z_3 + z_2 - z_1). \quad (4.8)$$

The sum over z_3 is easily performed. An important property of $I(z_1, z_2)$ is that it is a function of $z_1 - z_2$ only, which allows it to be written in the form

$$I(z_1 - z_2) = (2\pi)^{-1} \int_{-\infty}^{\infty} d\omega I(\omega) (z_1 - z_2 - \omega)^{-1}, \quad (4.9)$$

where

$$I(\omega) = -(2\pi) (1 - e^{\beta\omega}) (J/2\Omega)^2 \times \sum_{p_1 p_2} \delta_{\sigma_1 \sigma_2} f^+(\epsilon_{p_1}) f^-(\epsilon_{p_2}) \delta(\omega - \epsilon_{p_1} + \epsilon_{p_2}). \quad (4.10)$$

When Eq. (4.2) for R is iterated and substituted into Eq. (4.1), it is found that the contribution to $G_{-+}(x_\nu)$ of the term which is of the n th order in the irreducible interaction is given by

$$G_{-+}^{(n)}(x_\nu) = e^{\beta\lambda_{\downarrow}} (1 + e^{-\beta\omega_0})^{-1} \beta^{-(n+1)} \sum_{z'_s} F_\nu(z_1) I(z_1 - z_2) \times F_\nu(z_2) I(z_2 - z_3) \cdots F_\nu(z_{n+1}). \quad (4.11)$$

The introduction of the representation (4.9) of $I(z_1, z_2)$ makes it possible to do easily all but one of the sums

over the z variables, with the result that

$$G_{-+}^{(n)}(x_\nu) = \frac{e^{\beta\lambda_{\downarrow}}}{1 + e^{-\beta\omega_0}} \prod_{i=1}^n \left(\int \frac{d\omega_i}{2\pi} \frac{I(\omega_i)}{1 - e^{\beta\omega_i}} \right) \beta^{-1} \times \sum_z F_\nu(z + \sum_{i=1}^n \omega_i) F_\nu(z + \sum_{i=2}^n \omega_i) \cdots F_\nu(z + \omega_n) F_\nu(z). \quad (4.12)$$

To proceed further, the approximate expression,

$$\tilde{F}_\nu(z) = (x_\nu - \omega_R + i\Gamma)^{-1} [(z - x_\nu - \lambda_{\downarrow})^{-1} - (z - \lambda_{\uparrow})^{-1}], \quad (4.13)$$

is used (the tilde again indicating that x_ν is in the upper half-plane). This can be derived by introducing the spectral representation for the G_m 's into Eq. (4.3) and proceeding in much the same way as was done in going from (4.4) to (4.6). Equation (4.13) is now substituted into (4.12) and the final sum over z is performed by contour integration. When evaluating the residues, the approximation

$$\tilde{F}_\nu(\lambda_{\downarrow} + x_\nu + \omega) \approx \tilde{F}_\nu(\lambda_{\uparrow} + \omega) \approx i\pi \delta(\omega) (x_\nu - \omega_R + i\Gamma)^{-1} \quad (4.14)$$

will be used. In arriving at (4.14), x_ν has been put equal to $\omega_0 + i0^+$ in the square bracket in (4.13), since when the sum over z in (4.12) is performed, the square bracket referred to gives a factor which is slowly varying near $x_\nu \approx \omega_0 + i0^+$. In the way just indicated, one finally arrives at the expression

$$\tilde{G}_{-+}^{(n)}(x) = \tanh \frac{1}{2}(\beta\omega_0) (n+1) (-i\Gamma')^n (x - \omega_R + i\Gamma)^{-(n+1)}, \quad (4.15)$$

where

$$\Gamma' = -\frac{1}{2} \int_{-\infty}^{\infty} d\omega \frac{I(\omega)}{1 - e^{\beta\omega}} \delta(\omega) = \frac{1}{2} \pi (J\rho)^2 T, \quad (4.16)$$

which is to be compared with Eqs. (3.19) and (3.20) for Γ . The series defined by (4.16) can be recognized as the derivative of a geometric series which, when summed, gives

$$\tilde{G}_{-+}(x) = \tanh \frac{1}{2}(\beta\omega_0) (x - \omega_R + i\Gamma) [x - \omega_R + i(\Gamma + \Gamma')]^{-2}. \quad (4.17)$$

The spectral function corresponding to (4.17) is

$$A_{-+}(\omega) = \tanh \frac{1}{2}(\beta\omega_0) \times \frac{2(\Gamma + 2\Gamma')(\omega - \omega_R)^2 + 2\Gamma(\Gamma + \Gamma')^2}{[(\omega - \omega_R)^2 + (\Gamma + \Gamma')^2]^2}, \quad (4.18)$$

where, to be consistent, ω_R and Γ should be calculated only to second order in J . Equation (4.18) can be seen to describe a line which is approximately Lorentzian in shape and which has a half-intensity half-width roughly equal to $\Gamma + \Gamma'$. The inclusion of the bound part of

the two-particle propagator in the theory thus makes little difference to the qualitative features of the resonance line shape, but is necessary to obtain accurate quantitative results.

It should be emphasized here that the mathematical methods used above are somewhat lacking in rigor, and a more thorough investigation of the behavior of Eq. (4.1) is certainly necessary. A worrying feature of the above work is that while the approximation (4.14) appears to be a reasonable one to use when calculating the individual terms of the perturbation series, the presence of the δ function is a crucial factor in determining the fact that (4.15) is simply the derivative of a geometric series, which is the result that allows us to sum the infinite series explicitly. It would be more satisfactory to have been able to effectively sum the perturbation series before making any approximations, but this appears to be much more difficult and we have not succeeded in doing this so far. In spite of these deficiencies, however, there can be no doubt that the magnitude of each individual term in the perturbation series is estimated correctly by (4.15), and that to obtain $G_{-+}(x)$ when x is near ω_0 requires a study of $G_{-+}(x)$ to all orders in the irreducible interaction.

The theory of Kubo and Tomita^{1,11} assumes a Lorentzian line shape, for which they calculate a width which is given by $\Gamma+2\Gamma'$, where Γ and Γ' are given by Eqs. (3.19), (3.20), and (4.16) above. Our lowest-order results agree approximately with Kubo and Tomita's results, but a detailed comparison is not possible until a rigorous solution of the Bethe-Salpeter equation is obtained.

V. EFFECT OF THE CONDUCTION-ELECTRON MOMENTS

The lowest-order contribution of the conduction-electron moments to the total susceptibility will be calculated here to show that these terms become increasingly important when the conduction-electron spin-resonance frequency ω_e is sufficiently close to the spin-resonance frequency ω_0 . This contribution can be obtained from the propagator

$$G_{\times}(u) = e^{\beta\lambda} (1 + e^{-\beta\omega_0})^{-1} \langle T \{ S_{-}(u) S_{+} \} \rangle, \quad (5.1)$$

where 0 is the total conduction-electron spin. Equation (5.1) describes one of the cross terms which occurs in the susceptibility [Eq. (1.1)] when M_x is taken to be the moment of the impurity spin plus the total conduction-electron spin moment. The zero-order contribution to (5.1) vanishes, and the first-order contribution, illustrated in Fig. 5(a), gives

$$G_{\times}^{(1)}(x_p) = - (J'/\Omega) \tanh \frac{1}{2} (\beta\omega_0) \frac{\sum_{\mathbf{k}} [f^{\uparrow}(\epsilon_{\mathbf{k}\downarrow}) - f^{\uparrow}(\epsilon_{\mathbf{k}\uparrow})]}{(x_p - \omega_0)(x_p - \omega_e)} \quad (5.2)$$

when the sums over the internal z variables are performed. The contribution of the other cross term can

be obtained from $G(u) = e^{\beta\lambda} (1 + e^{-\beta\omega_0})^{-1} \langle T \{ s_{-}(u) S_{+} \} \rangle$; its lowest-order contribution is illustrated in Fig. 5(b) and turns out also to be given by Eq. (5.2). The absorption as calculated from (5.2) is

$$A_{\times}^{(1)}(\omega) = -2\pi J' \rho(\omega_e/\delta\omega) \times \tanh \frac{1}{2} (\beta\omega_0) [\delta(\omega - \omega_0) - \delta(\omega - \omega_e)], \quad (5.3)$$

where $\delta\omega = \omega_0 - \omega_e$. Absorption at the impurity spin-resonance frequency is indicated by the δ function $\delta(\omega - \omega_0)$ in (5.3), and its intensity can be seen to be a factor $J' \rho(\omega_e/\delta\omega)$ weaker than that given in Eq. (4.6). This term becomes increasingly important as ω_0 becomes close to ω_e , and when $J' \rho(\omega_e/\delta\omega)$ is sufficiently large, contributions of the conduction-electron moments to the total susceptibility can not be ignored. It appears that this could be the case even when $\delta\omega$ is greater than the width of either of the resonance lines.

These considerations define the limits of validity of the work in the previous sections only at sufficiently high temperatures. Below the Kondo temperature, the interaction of the conduction electrons and impurity spins is strong,⁶ and it is unlikely that a separation of the susceptibility into parts will be meaningful even if $\delta\omega$ is relatively large.

In phenomenological studies of magnetic resonance in dilute magnetic alloys using a modified Bloch equation approach²⁰⁻²² the fact that the conduction-electron spin motion and the impurity spin motion cannot be considered separately has long been recognized. There one studies a set of coupled equations describing the motion of the combined impurity-conduction-electron system.

VI. APPLICATION TO EXPERIMENT

The majority of impurity spin-resonance experiments performed so far in metals have been performed on Gd, Mn, or Eu impurities,^{21,23} and resonances corresponding to $g \approx 2$ are observed. The fact that $g \approx 2$ is interpreted

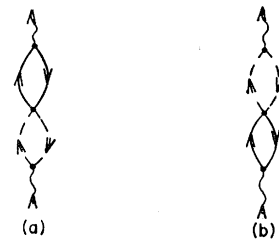


Fig. 5. Lowest-order diagrams contributing to the cross terms (between conduction-electron spins and impurity spins) appearing in the total susceptibility.

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²³ J. Owen, M. E. Browne, V. Arp, and A. F. Kip, J. Phys. Chem. Solids **2**, 85 (1957); D. Shaltiel and J. H. Wernick, Phys. Rev. **136**, 245 (1964); M. Peter, D. Shaltiel, J. H. Wernick, H. J. Williams, J. B. Mock, and R. C. Sherwood, *ibid.* **126**, 1395 (1962), and others.

to mean that the impurity moment is essentially a spin-only (no orbital contribution) magnetic moment. As noted above, our theory does not apply to the $g \approx 2$ case.

A few experiments have been performed on other rare-earth impurities in metals²⁴ and g values differing greatly from two (e.g., $g \approx 3$ to 9) have been observed. Our theory applies directly to this case. In particular, Burr and Orbach²⁴ have measured the linewidth of Er impurities in Mg from 2 to 4°K and found good agreement with the lowest-order Kubo-Tomita¹ theory. The Kondo temperature associated with Er impurities in Mg is thus presumably lower than 2°K.

Since iron-group impurities are in general expected to have higher Kondo temperatures than rare-earth impurities, it would be interesting to study the resonance of iron-group ions having $g \neq 2$ at low temperatures. For example, cobalt resonances at $g \approx 5$ have been

²⁴ C. R. Burr and R. Orbach, *Phys. Rev. Letters* **19**, 1133 (1967); L. L. Hirst, G. Williams, D. Griffiths, and B. R. Coles, *J. Appl. Phys.* **39**, 844 (1968).

observed²⁵ in ScCo₂ and YCo₂, but the linewidth increases as the temperature is lowered due to the strong Co-Co interactions. It would be interesting to try similar experiments on these compounds, but with all but a small fraction of the cobalt atoms replaced by another diamagnetic metallic atom. Also, other dilute alloys of paramagnetic ions having $g \neq 2$ will no doubt be found in the near future; should these ions have Kondo temperatures in a practically attainable temperature range, they will serve as a good test of our theory of the Kondo-like anomalies (3.17) and (3.24). It should also be noted [Eqs. (3.18) and (3.25)] that when $\omega_0 > T$, increasing the magnetic field tends to suppress the Kondo anomalies.

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Electron Spin Resonance of Free Radicals Formed from Group-IV and Group-V Hydrides in Inert Matrices at Low Temperature*

GEORGE S. JACKEL AND WALTER GORDY

Department of Physics, Duke University, Durham, North Carolina

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The electron-spin-resonance spectra of molecular free radicals formed from the group-IV and group-V hydrides at 4.2°K in the xenon matrix have been observed and compared with those observed in krypton and other matrices. From these spectra, certain properties of the free radicals and certain matrix effects have been derived. Molecular free radicals formed by γ irradiation of a matrix containing PH₃ or AsH₃ are PH₂ and AsH₂, respectively. From analysis of the hyperfine structure, the P-bonding orbitals of PH₂ were found to have 20.6% 3s character in the Xe matrix, compared with 19% in the Kr matrix. Because of anisotropies in the coupling and in the g tensor the hyperfine structure of AsH₂ could not be measured. In the Xe matrix the average g is 2.0050 for PH₂, and 2.034 for AsH₂. No spectra could be observed for SbH₂, although evidence for dissociation of SbH₂ was indicated by the strong H-atom lines observed for a γ -irradiated sample of SbH₃ in the Xe matrix. Molecular free radicals formed by γ irradiation of the group-IV hydrides are CH₃, SiH₃, GeH₃, and SnH₃. The observed hyperfine structure caused by the isotopes ²⁹Si, ⁷³Ge, and ^{117,119}Sn indicate that the radicals SiH₃, GeH₃, and SnH₃ are not planar like CH₃, but are pyramidal in structure. Noticeable difference in the isotropic coupling of ²⁹Si for the Kr matrix, 240 G, and for the Xe matrix, 190 G, indicates strong interaction of the matrix with the SiH₃ radicals.

I. INTRODUCTION

ENERGY absorbed from a γ -ray source by a rare-gas matrix at low temperature is efficiently transferred¹ to dissociate certain simple molecules trapped in dilute solution in the matrix. This process provides an effective method for production of trapped atoms and

simple molecular free radicals at isolated points in the inert matrix which can then be studied effectively with electron spin resonance (ESR).^{2,3} For many substances this method is simpler to apply than the method of producing the free radicals in the gaseous state and then trapping⁴ them at low temperatures. From this laboratory we have reported studies of radicals formed

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