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Path Integral Theory of Magnetic Alloys

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The theory of dilute magnetic alloys is studied using Anderson's model. The Coulomb interaction is represented by the fluctuating potential acting on single electrons at the impurity site, and the partition function is rigorously formulated as a path integral over all possible time histories of this potential. For any particular path, the response of the electron gas is calculated using a method introduced by Nozières and De Dominicis, which is exact in the limit that the potential fluctuations are slow. From this, the contribution of any particular path to the partition function is obtained as an explicit and rather simple functional. When the Coulomb interaction is large compared to the width of the virtual bound state, a particular group of paths are singled out on the basis that they make the largest contributions. The functional is evaluated for this set of paths, and gives an expression which can be interpreted as the grand partition function for a one-dimensional gas of classical particles interacting through a logarithmic pair potential. This is identical to the result of a recent study of the $s-d$ exchange model by Anderson and Yuval. An analysis of this result has been given earlier, and it yields a satisfactory description of the Kondo effect. The resistivity is estimated, and found to approach the unitarity limit below the Kondo temperature and the Hartree-Fock value above the Kondo temperature. The correspondence between the Anderson and $s-d$ exchange models is shown to break down when the former is only weakly magnetic.

I. INTRODUCTION

This paper describes a new approach to the theory of dilute magnetic alloys.[1] The approach employs the Anderson model,[2] and bases its only approximations on a single widely held assumption: Spin polarization on the impurity persists much longer than it would in the absence of the Coulomb interaction. The goal of the investigation is to make firmly based predictions about the behavior of dilute alloys below the Kondo temperature, where perturbation expansions diverge.[3] Because the physical mechanism of the Kondo effect is not well understood, it is very difficult to give *a priori* justification to any approximation procedure. For this reason we have avoided the standard gambits of modern many-body theory, such as partial summation of perturbation expansions and decoupling equations of motion. While such schemes have the ability to continue the leading terms in high-temperature expansions to low temperatures, this ability is not a genuine criterion for their quality as low-temperature approximations. The key approximation in this study is purely mathematical; no class of diagram or type of correlation is excluded. Furthermore, the validity of the approximation can be established self-consistently from the behavior of the solution.

The approach is the outgrowth of several lines of investigation. Anderson showed that a spin-polarized state is energetically favorable for his model when the Coulomb repulsion U on the impurity becomes larger than the width Δ of its virtually bound d state.[2] This result was derived within the Hartree-Fock approximation, and the mechanism involved is generally accepted as the correct one for local moment formation. There is a serious difficulty, however. The polarized state is a "broken-symmetry" solution of the model. While such solutions are acceptable approximations in the case of large systems that undergo phase transitions, it is very difficult to believe that a single atom could induce such an effect. The operational definition of the existence of a local moment is that the excess susceptibility (of the alloy over the pure host) approximates a Curie law, at least above some temperature.[4] This requires that the spin polarization on the impurity be long lived, but not infinitely long lived as in the Hartree-Fock approximation.

Theoretical treatments yielding such long-lived spin fluctuations were put forward by several workers using the linearized time-dependent Hartree-Fock (or random-phase) approximation.[5] This approximation has the disadvantage of breaking down just at the value of U at which Anderson's broken-symmetry solution becomes possible. To yield the desired long lifetimes, the value of U must be just under this threshold, a condition which could only be expected in isolated instances. Furthermore, the intrinsic linearity of the approximation precludes saturation of the moment in an applied field and a Curie-law temperature dependence.[6]

This theory was substantially improved and "nonlinearized" by Suhl, who retained the random-phase approximation but included the fluctuation-induced broadening of the local single-particle spectrum.[7] The resulting renormalized random-phase approximation was valid for arbitrarily large values of U. Detailed calculations showed that the temperature dependence of the susceptibility and resistivity resembled experimental results.[8] Unfortunately, the characteristic temperature found within this approximation is proportional to $\exp[-(U/\Delta)^2]$, instead of $\exp[-(U/\Delta)]$ as expected from the Kondo-effect mechanism.[9] This suggests that many processes contributing to the Kondo anomaly, including the leading ones, are omitted.

The local spin-fluctuation description of magnetic alloys is not the exclusive property of these particular approximations. Since the spin-up and spin-down electron gases are coupled only through the impurity d state, each system must see the other as a localized fluctuating potential. Recent developments in another problem suggest that the Kondo-effect divergences are all connected with the response of each electron gas to the low-frequency components of the fluctuating potential. Furthermore, the newly developed techniques can be adapted to a suitably formulated version of the spin problem.

In studying x-ray absorption in metals, Mahan found that the interaction between the conduction electrons and the localized deep hole created by the x ray could not be treated by perturbation theory. Each term in the series diverged as some power of $\ln|\omega-\omega_0|$ as the x-ray energy ω approached the absorption threshold ω_0.[10] The singularities are associated with the Fermi-surface cutoff of the conduction-electron distribution, as are the divergent coefficients found by Kondo in the perturbation series for the s-d exchange model.[3] Nozières, Gavoret, and Roulet[11] were able to sum an extremely complicated set of diagrams corresponding to the most and next-most divergent terms in perturbation theory, which accurately describe the threshold behavior for a weak electron-hole interaction.

A far simpler treatment of the same problem was given by Nozières and De Dominicis (ND).[12] They observed that the deep hole and its interaction with the electrons could be rigorously replaced by a time-dependent potential. For absorption near the threshold, this potential could be considered slowly varying, and the response of the electrons could be calculated exactly. The key step in the calculation was to replace the free-electron Green's function by the function it approaches asymptotically at large times. The equation for scattering by the potential then becomes a soluble singular integral equation of the type studied by Muskhelishvili.[13] We shall refer to the step of replacing the Green's function by its asymptotic form as the ND approximation.

The solution calculated by this simplified method is valid for an arbitrarily strong electron-hole interaction. It only depends on the scattering phase shifts at the Fermi surface produced by a time-independent potential of the same value. Expanding the phase shift for a weak potential reproduces the result obtained by diagrammatic summation.

To use the ND method on the Anderson model, it is necessary to consider the fluctuating potential explicitly. This can be accomplished using a rigorous transformation introduced by Stratonovich[14] and generalized by Hubbard.[15] The transformation replaces instantaneous two-particle interactions with interactions mediated by a c-number field. Unlike the familiar problems with interactions mediated by a quantum field, this c-number field has no intrinsic dynamics. Its values at separate

space-time points are independent random variables with Gaussian distribution. However, it acquires a nontrivial "dynamics" through its coupling to the particles.

In the case of the Anderson model, the fluctuating field only acts on the d state and is a function of time alone. Any particular such function will subsequently be called a path. The ND approximation can be used to calculate the electron-gas response for each path, and we expect it to do so with sufficient accuracy. High-frequency fluctuations are not treated accurately, and are not expected to be important to the magnetic properties of the impurity. The Stratonovich-Hubbard transformation gives the partition function as a sum of contributions from all paths.[14,15] We shall be interested in identifying the most important paths and calculating their contributions.

The main result of this paper is to show that for large U/Δ a simple set of paths makes the dominant contribution. The average of the partition function over these paths corresponds precisely to an expression recently found by Anderson and Yuval for the s-d exchange model.[16] Their method applies the ND approximation to a rearranged form of perturbation theory for that model, and has little in common with the method used here except the result. This may be interpreted as a classical partition function for a one-dimensional gas, and an approximate evaluation of its properties has been carried out.[17]

A further result is that the case of $U/\Delta \sim 1$ is found to be qualitatively different from the large U case. The interpretation of weakly magnetic impurities as Kondo-compensated states with high Kondo temperatures[18] is therefore inappropriate.

A crude calculation of the resistivity is also given. The unitarity limit (for orbital s-wave scattering) is found for temperatures well below the Kondo temperature. The scattering rate falls to the value found in the Hartree-Fock approximation at high temperatures or magnetic fields.

In Sec. II, our use of the Hubbard transformation is discussed, and the eigenstates of the single-particle part of the Hamiltonian are derived. In Sec. III, the ND approximation for this problem, the Green's function for an arbitrary path, and the contribution to the partition function from an arbitrary path are derived. In Sec. IV, the partition function is evaluated for the appropriate paths in the weak- and strong-coupling limits, and the correspondence with the Anderson-Yuval expression is shown. In Sec. V, the resistivity is calculated. In Sec. VI, the main results and key steps in achieving them are summarized and discussed critically in the context of the complete calculation.

In Sec. III, the ND approximation is used in its original form, which is strictly applicable only well below the Kondo temperature. A generalization valid for all temperatures is relegated to the Appendix, since it requires more complicated and less familiar mathematics. The result, however, is an extremely simple modification of the low-temperature expression.

II. FORMULATION OF PARTITION FUNCTION

A. Single-Particle Solutions of Anderson Model

The Hamiltonian of the Anderson model is the sum of two terms[2]:

$$H_0 = \sum_{k\sigma} \epsilon_{k\sigma} n_{k\sigma} + \sum_{\sigma} \epsilon_{d\sigma} n_{d\sigma} + \sum_{k\sigma} (V_{kd} C^{\dagger}_{k\sigma} C_{d\sigma} + V^{*}_{kd} C^{\dagger}_{d\sigma} C_{k\sigma}), \tag{2.1}$$

$$H_1 = U n_{d+} n_{d-} . \tag{2.2}$$

The creation operator for the eigenstates of H_0 may be written, in general, as a linear combination of those for the unperturbed states:

$$C^{\dagger}_{\lambda\sigma} = a^{*}_{\lambda d} C^{\dagger}_{d\sigma} + \sum_k a^{*}_{\lambda k} C^{\dagger}_{k\sigma} . \tag{2.3}$$

Schrödinger's equation then yields two coupled equations for the coefficients:

$$(\epsilon_d - \epsilon_\lambda) a^{*}_{\lambda d} + \sum_k V^{*}_{kd} a^{*}_{\lambda k} = 0 , \tag{2.4}$$

$$(\epsilon_k - \epsilon_\lambda) a^{*}_{\lambda k} + V_{kd} a^{*}_{\lambda d} = 0 . \tag{2.5}$$

Eliminating the coefficients gives the eigenvalue equation

$$\epsilon_{d\sigma} - \epsilon_{\lambda\sigma} - \sum_k [|V_{kd}|^2/(\epsilon_k - \epsilon_\lambda)] = 0 . \tag{2.6}$$

Now let us assume that the free-electron states are given in a spherical-harmonic decomposition around the impurity, and that V_{kd} is nonzero for only one harmonic. The set of these ϵ_k then forms a one-dimensional mesh which is evenly spaced in the neighborhood of any energy. The value of the sum in (2.6) varies from $-\infty$ to $+\infty$, as ϵ_λ varies between two neighboring mesh points, so there is a solution ϵ_λ between every pair ϵ_k, ϵ_{k+1}. We can write

$$\epsilon_{\lambda\sigma} = \epsilon_{k\sigma} - \eta(\epsilon_{\lambda\sigma})/\pi\rho(\epsilon_{\lambda\sigma}) , \tag{2.7}$$

where ρ is the density of k states and η can be identified as the scattering phase shift. Away from ϵ_λ the sum in (2.6) may be replaced by an integral:

$$\epsilon_d - \epsilon_\lambda - \rho(\epsilon_\lambda)|V(\epsilon_\lambda)|^2 \sum_{l=-L}^{L} [l + \eta(\epsilon_\lambda)/\pi]^{-1} - P\int_{-\infty}^{\infty} d\epsilon \, \frac{\rho(\epsilon)|V(\epsilon)|^2}{\epsilon - \epsilon_\lambda} = 0 , \tag{2.8}$$

where L is a large integer (but much smaller than the number of states N). P denotes principal

value, and $V(\epsilon) = V_{kd}$ at $\epsilon_k = \epsilon$. Using the formula[19]

$$\sum_{l=-\infty}^{\infty} (l + \eta/\pi)^{-1} = \pi \cot\eta \ , \tag{2.9}$$

we find

$$\eta(\epsilon_\lambda) = \tan^{-1}\left[\pi\rho(\epsilon_\lambda)\,|V(\epsilon_\lambda)|^2 \times\left(\epsilon_d - \epsilon_\lambda - P\int_{-\infty}^{\infty} \frac{\rho(\epsilon)\,|V(\epsilon)|^2}{\epsilon - \epsilon_\lambda}\, d\epsilon\right)^{-1}\right] . \tag{2.10}$$

If the usual convention of treating ρ and V as constants is followed, this simplifies to

$$\eta(\epsilon) = \tan^{-1}[\Delta/(\epsilon_d - \epsilon)] \ , \tag{2.11}$$

where Δ is the resonance width given by the numerator in (2.10).

We will also need the matrix element $a_{\lambda d}$ which is determined from the normalization requirement

$$|a_{\lambda d}|^2 + \textstyle\sum_k |a_{\lambda k}|^2 = 1 \ . \tag{2.12}$$

Substituting (2.5) in (2.12) yields

$$|a_{\lambda d}|^2 = \{1 + \textstyle\sum_k [\,|V_{kd}|^2/(\epsilon_k - \epsilon_\lambda)^2\,]\}^{-1} \ . \tag{2.13}$$

The sum in (2.13) is so singular that it is equal to the contribution from the vicinity of ϵ_λ alone,

$$|a_{\lambda d}|^2 = \{1 + \rho^2(\epsilon_\lambda)\,|V(\epsilon_\lambda)|^2 \times \sum_{l=-L}^{L} [l + \eta(\epsilon_\lambda)/\pi]^{-2}\}^{-1} . \tag{2.14}$$

The sum is evaluated using the formula[19]

$$\sum_{l=-\infty}^{\infty} (l + \eta/\pi)^{-2} = \pi^2 \csc^2\eta \ . \tag{2.15}$$

Since $\rho^2 V^2$ is of order N, unity may be neglected by comparison and

$$|a_{\lambda d}|^2 = \sin^2\eta(\epsilon_\lambda)/\pi^2\rho^2(\epsilon_\lambda)\,|V(\epsilon_\lambda)|^2 \ , \tag{2.16}$$

which for (2.11) reduces to

$$|a_{\lambda d}|^2 = (\Delta/\pi\rho)[(\epsilon_\lambda - \epsilon_d)^2 + \Delta^2\,]^{-1} \ . \tag{2.17}$$

This unusually extensive treatment of H_0 has been undertaken for several reasons. First, identification of the phase shift is important for interpretation of later results. Second, the ND approximation for this problem can be derived very easily using (2.17). Third, by starting with the exact eigenstates of H_0 we avoid a double expansion in V_{kd} and the interaction, which might well lead to ambiguities as we tried to embed it properly in an already quite involved many-body theory.

B. Hubbard Formulation

The partition function can be expressed as

$$Z = Z_0 \langle\, T_\tau \exp[\,-\textstyle\int_0^\beta d\tau\, H_1(\tau)\,]\,\rangle \ , \tag{2.18}$$

where Z_0 is the partition function for H_0, $\beta = 1/kT$, H_1 is in the interaction representation defined by H_0, T_τ is the ordering operator with respect to τ, and $\langle\ \rangle$ is the thermal average with respect to H_0. The transformation requires that H_1 be a diagonal quadratic form of operators. This can be accomplished in an infinite variety of ways by making use of the identity

$$n_{d\sigma}^2 = n_{d\sigma} \tag{2.19}$$

and moving the $n_{d\sigma}$ terms into H_0. We shall choose the particular form

$$H_1 = \tfrac{1}{4} U(n_{d+} + n_{d-})^2 - \tfrac{1}{4} U(n_{d+} - n_{d-})^2 \ , \tag{2.20}$$

for reasons discussed later. In (2.18), the operators in H_1 may be treated as independent c numbers for each τ as long as they are within the domain of T_τ. Therefore, for each τ we may use the identity

$$e^{a^2} = \int_{-\infty}^{\infty} dx \exp(-\pi x^2 - 2\pi^{1/2} a x) \tag{2.21}$$

to replace the exponential of the squared operators, represented by a, by an integral in which the operators only appear linearly in the exponent. This yields

$$Z = Z_0 \int \delta x\, \delta y\, \langle\, T_\tau \exp[\,-\textstyle\int_0^\beta d\tau\, (\pi x^2/\beta + \pi y^2/\beta + \tilde{H}_1)]\,\rangle \ , \tag{2.22}$$

where

$$\tilde{H}_1 = (\pi U/\beta)^{1/2}\{\,x(\tau)[n_{d+}(\tau) - n_{d-}(\tau)\,] + iy(\tau)[n_{d+}(\tau) + n_{d-}(\tau)]\} \ . \tag{2.23}$$

In (2.23), x and y are explicitly τ-dependent c-number functions, and $n_{d\sigma}$ are time dependent through the interaction representation. The integrals in (2.22) run over all functions $x(\tau)$ and $y(\tau)$.

The above derivation parallels that given by Hubbard except in introducing the interaction representation at the outset.[15] For any given path, explicitly represented here by a particular pair of functions x and y, the quantum-mechanical average in (2.22) factors into a product of two terms of the form

$$Z_\sigma = \langle\, T_\tau \exp[\,-\textstyle\int_0^\beta d\tau\, v_\sigma(\tau) n_{d\sigma}(\tau)\,]\,\rangle \ , \tag{2.24}$$

one for each spin system. The explicit form of the spin-dependent potential v_σ is easily obtained from (2.23).

The exponential in (2.24) is the same as the S matrix introduced in the usual derivation of Feynman diagrams for finite-temperature Green's

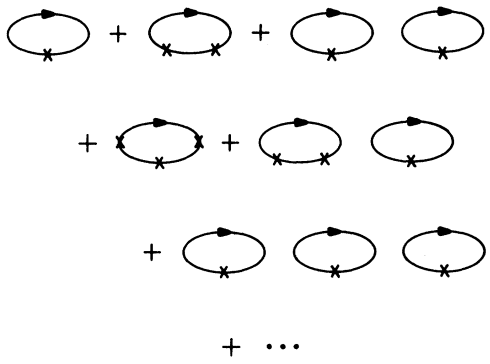

FIG. 1. Feynman diagrammatic expansion of (2.24). Each line corresponds to the Green's function G^0_λ, and each x to the potential $v_\sigma(\tau)$ times the matrix elements $a_{\lambda d}a^*_{\lambda' d}$.

functions. Therefore, it is given by the sum of closed-loop diagrams shown in Fig. 1.[20] Each vertex represents the external potential v_σ acting at the time τ. The sum is much simpler than usually encountered, since each vertex is attached to just two lines representing the Green's functions G^0_λ, where λ is one of the previously derived eigenstates of H_0. The diagrams may be simplified further by the usual device of grouping connected parts. The actual sum we will calculate is just the simple series shown in Fig. 2, which is the logarithm of the complete sum in Fig. 1. In counting closed-loop diagrams, a factor of $1/n$ (where n is the number of vertices) must be included to reflect the "rotational" invariance of each diagram. This is easily accomplished for the present simple series. Each vertex is multiplied by the fictitious coupling constant g, the series is divided by g, and an integral is performed from $g=0$ to $g=1$.

Before proceeding, we pause to note the relationship between this formalism and the conventional diagrammatics. The complete perturbation series for Z has a product of two sums of the type shown in Fig. 1. If we write out any single term in that product, it will be a polynomial in the classical fields x and y. The Gaussian functional average over such a polynomial is easily carried out, and will give a contribution only when each x and y can be paired with another x and y, respectively, with an equal time argument. In other words, the x and y fields contribute lines which connect pairs of vertices in Fig. 1, and the "propagator" of each line is, trivially, δ function in time. The square root of U enters as a factor at each vertex, so each line contributes a factor U. Thus, we could recover the usual diagrammatic sum with two-particle interactions.

To carry out the sum in Fig. 2, we first note that each vertex carries the factor $v_\sigma(\tau)a_{\lambda d}a^*_{\lambda' d}$, where λ and λ' label the Green's functions flanking that vertex, and $a_{\lambda d}$ is the matrix element introduced in (2.3). Since each vertex is separable in λ and λ', the λ sums are all independent. With each G^0_λ we can group the matrix element factors from its ends and introduce the quantity

$$G^0_{d\sigma}(\tau-\tau')=\sum_\lambda |a_{\lambda d}|^2 G^0_{\lambda\sigma}(\tau-\tau') . \tag{2.25}$$

If we open each loop at one point, the resulting sum of lines with ends labeled by two times τ and τ' can be called the complete d-state Green's function for the path under consideration. It can be generated by iterating the integral equation

$$G_{d\sigma}(\tau,\tau')=G^0_{d\sigma}(\tau,\tau') + g\int_0^\beta d\tau'' G^0_{d\sigma}(\tau,\tau'')v_\sigma(\tau'')G_{d\sigma}(\tau'',\tau'), \tag{2.26}$$

where we have included the coupling constant g. In terms of the solution of (2.26), the average (2.24) is given by

$$Z_\sigma=\exp\left[-\int_0^g dg\int_0^\beta d\tau\, v_\sigma(\tau)G_{d\sigma}(\tau,\tau^+)\right] . \tag{2.27}$$

The complete partition function is obtained by taking the product Z_+Z_- for a particular path times the Gaussian weighting factor for that path, and integrating over all paths.

At this point it is convenient to introduce a simplifying approximation. The potential v_σ has two independent components arising from the two fields x and y. The x field is coupled to the z component of the spin in the d state, while the y field is coupled to the particle number. If we recall the manner in which this formalism generates the ordinary diagrams discussed above, we can argue that the interaction lines generated by the y field typically carry large energies. This should be true because density fluctuations have high characteristic energies (like the plasmon energy), and because there is no particular instability or near-instability associated with density fluctuations in this model. We expect the density fluctuations to have a little effect on, or interaction with, the large long-lived spin-density fluctuations which we wish to treat accurately. Furthermore, the ND approximation we shall use is not capable of treating the response of the electrons to a rapidly

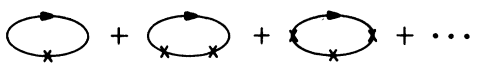

FIG. 2. Linked-cluster diagrams corresponding to the complete sum in Fig. 1, and equal to its logarithm.

fluctuating field. Therefore, we shall make the simplest possible approximation for the integral over the y field, which is to replace it by its integrand evaluated for the extremal y function.

Hubbard states that the extremal approximation to the functional-integral form of the partition function is equivalent to the Hartree-Fock approximation, and that the extremal paths are τ independent.[15] Our expressions (2.26) and (2.27) are easily evaluated for constant x and y, and we verify that they reproduce Anderson's Hartree-Fock calculation.[2] For $\epsilon_d = -\frac{1}{2}U$, in which case the Anderson model becomes symmetric under the interchange of electrons and holes, the equations determining the best values of x and y are independent and we find

$$y_0 = -\tfrac{1}{2} i(U\beta/\pi)^{1/2} . \tag{2.28}$$

After this value is substituted in (2.23), it may be combined with the ϵ_d term in H_0, which it exactly cancels. This puts the effective d-state resonance at the Fermi surface in the absence of the interaction effects carried by the x field, and greatly simplifies the algebra of the rest of our calculation. We shall specialize to the symmetric case, which we have previously argued is not only representative but physically the most realistic.[9]

Some readers may object at this point that the extremal approximation for the y field is unnecessary. Wang, Evenson, and Schrieffer have applied the Hubbard transformation to the Anderson model in developing a theory of itinerant ferromagnetism.[21] However, they wrote H_1 as the diagonal quadratic form

$$H_1 = -\tfrac{1}{2}U(n_{d+} - n_{d-})^2 + \tfrac{1}{2}U(n_{d+} + n_{d-}) , \tag{2.29}$$

combined the linear term with H_0, and introduced only a single field to carry out the Hubbard transformation.

While either form is equivalent and must give the same results if the electron-gas response and the functional average are carried out exactly, this is certainly not true in any particular approximation. The extremal approximation to the functional derived from (2.29) acquires spin-polarized solutions at $U = \frac{1}{2}\pi\Delta$, which is only half the critical interaction strength found by Anderson. Formally maximizing Hubbard's general expression indicates that the extremal approximation corresponds to the Hartree-Fock approximation if

$$\sum_\alpha \lambda_\alpha \langle \rho_\alpha^2 \rangle = \sum_\alpha \lambda_\alpha [\langle \rho_\alpha \rangle]^2 , \tag{2.30}$$

where the ρ_α are the operators and λ_α the matrix elements in the selected diagonal quadratic form of H_1.[15] The form we have chosen, (2.20), satisfies this condition, while (2.29) does not. The lack of correspondence between the Hartree-Fock approximation and the extremal approximation based on (2.29) does not appear to be important in the work of Wang *et al.*[21]

In the present work, where our eventual aim will be to select important paths, the identification of the Hartree-Fock solution will be of prime importance. Therefore, we believe that the gains to our complete program are well worth the cost in formal neatness of introducing the y field and treating it in what we believe to be a physically well-justified approximation.[22] The importance of having an independent criterion for selecting the diagonal quadratic form becomes more obvious when one realizes that any normalized linear combination of (2.20) and (2.29) could also be used, as well as many other possibilities.

III. EVALUATION OF FUNCTIONAL

A. Asymptotic G^0

To solve (2.26) in a manner paralleling ND, we must first find the asymptotic form of $G_d^0(\tau)$ for large τ.[12] The unperturbed propagators for H^0 are diagonal in the λ representation of Sec. II A and are given by[23]

$$\begin{aligned} G_\lambda^0(\tau) &= -e^{-\epsilon_\lambda \tau}[1 - f(\epsilon_\lambda)], \quad \tau > 0 \\ G_\lambda^0(\tau) &= e^{-\epsilon_\lambda \tau} f(\epsilon_\lambda) , \qquad \tau < 0 \end{aligned} \tag{3.1}$$

where f is the Fermi function. Substituting this and (2.21) in (2.25) and recognizing that the density of λ states and k states may be taken as equal in converting this sum to an integral yields

$$G_d^0(\tau) = \int_{-\infty}^{\infty} \frac{d\epsilon}{\pi} \frac{\Delta}{(\epsilon - \epsilon_d)^2 + \Delta^2} e^{-\epsilon\tau}[f(\epsilon) - \theta(\tau)] , \tag{3.2}$$

where θ is the unit step function. The three factors in the integrand may vary on quite different energy scales. If the weaker of either

$$|\tau| \gg 1/\epsilon_d \tag{3.3}$$

or

$$|\tau| \gg 1/\Delta \tag{3.4}$$

is satisfied, the Lorentzian may be regarded as slowly varying compared to the exponential and removed from the integral. On the other hand, if

$$\tau \ll \beta , \tag{3.5}$$

the Fermi function may be regarded as a step compared to the exponential. For this "asymptotic" range of τ,

$$G_d^0(\tau) \sim \frac{-\Delta}{\epsilon_d^2 + \Delta^2} \int_0^\infty \frac{d\epsilon}{\pi} e^{-\epsilon\tau} = -\frac{\Delta}{\epsilon_d^2 + \Delta^2} \frac{1}{\tau} . \tag{3.6}$$

Since we intend to calculate integrals involving G_d^0 using the asymptotic form, we must specify

how to treat the $\tau = 0$ singularity. This can be determined by requiring that integrals produce the correct result when G_d^0 is multiplied by a slowly varying function.[12] If the function is constant over a range $-\alpha < \tau < \alpha$, where α is large compared to the appropriate cutoff (3.3) or (3.4), then the integral using the exact form is

$$\int_{-\alpha}^{\alpha} d\tau\, G_d^0(\tau) = -\epsilon_d/(\epsilon_d^2 + \Delta^2) \,. \tag{3.7}$$

This result does not require that $\tau \ll \beta$. The asymptotic function will simulate the exact function and reproduce (3.7) if we set

$$G_d^0(\tau) \approx \frac{-\Delta}{\epsilon_d^2 + \Delta^2}\left(\frac{P}{\pi\tau} + \frac{\epsilon_d}{\Delta}\,\delta(\tau)\right) . \tag{3.8}$$

We shall also need the exact zero-time limit,

$$G_d^0(0^-) = \int_{-\infty}^{\infty} \frac{d\epsilon}{\pi}\,\frac{\Delta}{(\epsilon - \epsilon_d)^2 + \Delta^2}\, f(\epsilon)$$

$$= \tfrac{1}{2} - (1/\pi)\tan^{-1}(\epsilon_d/\Delta) \,, \tag{3.9}$$

where we have assumed $1/\beta \ll \epsilon_d$ or Δ.

The actual H_0 that we wish to use after incorporating the average value of the density field has a net $\epsilon_d = 0$. The general expressions (3.8) and (3.9) will, however, be necessary at later stages of the calculation.

B. Solution of Integral Equation

If we substitute our version of the ND approximation, (3.8) in (2.26), we obtain

$$G_d(\tau, \tau') = -\frac{P}{\pi\Delta(\tau - \tau')} - \frac{P}{\pi}\int_0^{\beta} \frac{d\tau''}{\tau - \tau''}\,\xi(\tau'')\, G_d(\tau'', \tau') \,, \tag{3.10}$$

where we have dropped the spin index and coupling constant temporarily and introduced the dimensionless form of the instantaneous d-state potential

$$\xi(\tau) = v(\tau)/\Delta \,. \tag{3.11}$$

The variable τ' is strictly a parameter in (3.10), which is already in a standard form treated by Muskhelishivili.[24] Making the following identifications, we may substitute directly in his formulas:

$$\psi = G_d(\tau, \tau') \,, \tag{3.12}$$

$$A = 1 \,, \tag{3.13}$$

$$B = i\xi(\tau) \,, \tag{3.14}$$

$$g(\tau) = P/\Delta\pi(\tau - \tau') \,. \tag{3.15}$$

From his (107.7), (79.2), and (79.6) we find that the related homogeneous Hilbert problem

$$\frac{X^+(\tau)}{X^-(\tau)} = \frac{1 - i\xi(\tau)}{1 + i\xi(\tau)} \tag{3.16}$$

has the solution

$$X(z) = \exp\frac{1}{2\pi i}\int_0^{\beta} \frac{d\tau}{\tau - z}\ln\frac{1 - i\xi(\tau)}{1 + i\xi(\tau)} \,, \tag{3.17}$$

where z is the complex continuation of τ and the superscripts $\pm$ denote the limit as the real axis is approached from above or below. Since we will assume $\xi(0) = \xi(\beta) = 0$ later in this analysis, (3.17) is the unique solution that is bounded at infinity.[13]

It is instructive to rewrite (3.17) as

$$X(z) = \exp\frac{1}{\pi}\int_0^{\beta} \frac{d\tau\,\eta(\tau)}{\tau - z} \,, \tag{3.18}$$

where $\eta = -\tan^{-1}\xi$, identified from (2.11) as the change in Fermi-surface phase shift which would be produced by a constant potential equal to the instantaneous potential. This "instantaneous phase shift" occurs continually in the remainder of the paper.

Substituting in Muskhelishivili's (108.9) and using our (3.15) to simplify the expression yields the solution of the related inhomogeneous Hilbert problem:

$$\Psi(z) = \frac{P}{4\pi^2 i\,\Delta X(z)}\int_0^{\beta} d\tau\,\frac{X^+(\tau) - X^-(\tau)}{(\tau - z)(\tau - \tau')} \,. \tag{3.19}$$

The Green's function is then found from his (108.2) to be

$$G_d(\tau, \tau') = [\Psi^+(\tau) - \Psi^-(\tau)]/i\xi(\tau) \,. \tag{3.20}$$

The preceding has been straightforward, but reducing the formal solution to usable expressions requires some work. First we note that the real-axis limits in (3.20) must be taken carefully because of the double singularity in (3.19). By use of the well-known Plemelj formula

$$1/(\tau \pm i\epsilon) = P/\tau \mp i\pi\delta(\tau) \,, \tag{3.21}$$

one can derive the needed expression,

$$\frac{1}{(\tau'' - \tau \pm i\epsilon)}\,\frac{P}{(\tau'' - \tau')} = \frac{P}{\tau' - \tau}\left(\frac{P}{\tau'' - \tau'} - \frac{P}{\tau'' - \tau} \pm i\pi\delta(\tau'' - \tau)\right) + \pi^2\delta(\tau' - \tau)\delta(\tau'' - \tau) \,, \tag{3.22}$$

where the limit $\epsilon \to 0$ is to be taken *after* the limit defining the principal value on the left. It is then straightforward algebra to combine (3.16), (3.19), (3.20), and (3.22) and show

$$G_d(\tau, \tau') = -\frac{1}{\Delta}\,\frac{1}{1 + \xi^2(\tau)} \times\left(\frac{P}{\pi(\tau - \tau')} + \Delta\xi(\tau)\delta(\tau - \tau')\right)$$

$$-\frac{1}{2\pi^2\Delta\xi(\tau)}\left(\frac{1}{X^+(\tau)}-\frac{1}{X^-(\tau)}\right)\frac{\varphi(\tau)-\varphi(\tau')}{\tau-\tau'}\,, \tag{3.23}$$

where

$$\varphi(\tau)=\frac{P}{2}\int_0^\beta d\tau''\,\frac{X^+(\tau'')-X^-(\tau'')}{\tau''-\tau}\,. \tag{3.24}$$

The terms which are singular as $\tau-\tau'$ goes to zero have been grouped in the first large parentheses in (3.23). They can be immediately identified from (3.8) as the approximate G_d^0 evaluated with ϵ_d/Δ replaced by the instantaneous potential $\xi(\tau)$. We will call this the adiabatic part of G_d, implying that it follows the fluctuating field adiabatically. The remaining "transient" term is finite at $\tau=\tau'$. This term appears singular at $\xi=0$, but it is in fact regular at such points as may be shown using (3.16).

The integral φ defined in (3.24) is easily evaluated. Since $X(z)$ is by construction an analytic function except for a branch cut from 0 to β,

$$X(z)=1+\frac{1}{2\pi i}\int_0^\beta d\tau''\,\frac{X^+(\tau'')-X^-(\tau'')}{\tau''-z}\,, \tag{3.25}$$

where the constant 1 has been added to give the correct limit as $z\to\infty$. Thus,

$$\varphi(\tau)=\tfrac{1}{2}\pi i\left[X^+(\tau)+X^-(\tau)-2\right]\,. \tag{3.26}$$

Using these results, G_d can be more simply rewritten as

$$G_d(\tau,\tau')=G_d^0[\tau,\tau';\xi(\tau)]+\frac{1}{4\pi i\Delta\xi(\tau)}\left(\frac{1}{X^+(\tau)}-\frac{1}{X^-(\tau)}\right)\times\left(\frac{X^+(\tau)+X^-(\tau)-X^+(\tau')-X^-(\tau')}{\tau-\tau'}\right)\,. \tag{3.27}$$

C. Linked-Cluster Sum

Our next step must be to evaluate (2.27) using the calculated Green's function. A difficulty is immediately apparent, since the first term in (3.27) diverges when we take the limit $\tau'\to\tau^+$ required in (2.27). Its resolution is obvious. Our integral equation has done the best it can to make this term look like G_d^0 for $\epsilon_d=v(\tau)$. To get the correct equal-time limit, which our equation cannot give us, we should use the exact G_d^0 to "continue" our expression. Therefore, we will use the previously calculated limit (3.9). A similar divergence occurs in the ND solution of the x-ray problem where it is identified as a shift of the absorption threshold.[12] Substituting (3.9) in (2.29) the coupling-constant integral is elementary, and we obtain the contribution of the adiabatic part of G_d to the exponent of Z_σ,

$$A_\sigma=-\frac{\Delta}{\pi}\int_0^\beta d\tau\,\xi_\sigma(\tau)\left(\frac{\pi}{2}-\tan^{-1}\xi_\sigma(\tau)+\frac{1}{2\xi_\sigma(\tau)}\ln\left[1+\xi_\sigma^2(\tau)\right]\right)\,. \tag{3.28}$$

The transient term is well defined in the equal-time limit. To express it most simply, let us define $X(\tau)$ with no superscript as

$$X(\tau)=\exp\frac{P}{\pi}\int_0^\beta\frac{d\tau'\,\eta(\tau')}{\tau'-\tau}\,. \tag{3.29}$$

Then,

$$X^\pm(\tau)=e^{\pm i\eta(\tau)}X(\tau)\,. \tag{3.30}$$

The transient part of G_d now gives the limit

$$G_d^{\mathrm{tr}}(\tau,\tau^+)=\frac{-1}{\pi\Delta\xi(\tau)}\,\frac{\sin\eta(\tau)}{X(\tau)}\,\frac{d}{d\tau}\left[\cos\eta(\tau)X(\tau)\right]\,, \tag{3.31}$$

$$G_d^{\mathrm{tr}}(\tau,\tau^+)=\frac{1}{\pi\Delta\xi}\left(\sin^2\eta\,\frac{d\eta}{d\tau}-\sin\eta\cos\eta\,\frac{d}{d\tau}\ln X\right), \tag{3.32}$$

where the argument τ is to be understood in (3.32).

Substituting the first term of (3.32) in (2.27), we are led to the integral

$$\int_0^\beta d\tau\sin^2\eta\,\frac{d\eta}{d\tau}=\left(\frac{\eta}{2}-\frac{\sin2\eta}{4}\right)_{\eta(0)}^{\eta(\beta)}\,. \tag{3.33}$$

As we will see in the Appendix, we must have $\eta(0)=\eta(\beta)$, so this term is zero.

The other term gives the entire transient contribution to the exponent of Z_σ,

$$B_\sigma=\frac{1}{\pi^2}\int_0^1\frac{dg}{g}\int_0^\beta d\tau\,\sin\eta(\tau)\cos\eta(\tau)\,\frac{d}{d\tau}\times P\int_0^\beta d\tau'\,\frac{\eta(\tau')}{\tau'-\tau}\,. \tag{3.34}$$

To carry out the coupling-constant integration, the τ derivative is first taken inside the τ' integral. It is allowed to act on τ' instead of τ, and then switched to act on $\eta(\tau')$ through integration by parts. The assumption $\eta(0)=\eta(\beta)=0$ is made to drop the end contributions. (This requirement is removed in the Appendix.) This yields

$$B_\sigma=-\frac{2P}{\pi^2}\int_0^\beta\frac{d\tau\,d\tau'}{\tau-\tau'}\int_0^1\frac{dg}{g}\sin2\eta(\tau)\,\frac{d\eta(\tau')}{d\tau'}\,. \tag{3.35}$$

The definition of $\eta(\tau)$ in the presence of the coupling constant is

$$\eta(\tau)=-\tan^{-1}g\xi(\tau)\,. \tag{3.36}$$

If this is substituted in (3.35), the coupling-constant integral becomes

$$\int_0^1 dg\,\frac{g\xi(\tau)}{\left[1+g^2\xi^2(\tau)\right]\left[1+g^2\xi^2(\tau')\right]}\,\frac{d\xi(\tau')}{d\tau'}\,, \tag{3.37}$$

which is elementary. We find

$$B_\sigma = -\frac{P}{2\pi^2}\int_0^\beta \frac{d\tau\, d\tau'}{\tau-\tau'}\,\xi(\tau)\frac{d\xi(\tau')}{d\tau'} \times \frac{1}{\xi^2(\tau)-\xi^2(\tau')}\ln\frac{1+\xi^2(\tau)}{1+\xi^2(\tau')} \quad . \tag{3.38}$$

This completes our program of evaluating the partition function as a path integral

$$Z = Z_0 \int \delta\xi\, Z(\xi) \quad . \tag{3.39}$$

We can collect terms from (3.28) and (3.38), and combine the results for both spin systems noting that $\xi_+(\tau) = -\xi_-(\tau)$. The "partition functional" may be written

$$Z(\xi) = \exp\{-\int_0^\beta d\tau\,[V(\xi)+T(\xi)]\} \quad . \tag{3.40}$$

$V(\xi)$ includes the original Gaussian weighting factor and depends only on the instantaneous value of ξ:

$$V = (\Delta^2/U)\xi^2 - (2\Delta/\pi)[\xi\tan^{-1}\xi - \tfrac{1}{2}\ln(1+\xi^2)] \quad . \tag{3.41}$$

Although we have not carried it through the calculation, it is easy to show that an external magnetic field H_0 simply adds to (3.41) the term

$$V' = (2\Delta/U)\mu_B H_0 \xi \quad . \tag{3.42}$$

The transient term is a nonlocal operator on ξ:

$$T = \frac{P}{\pi^2}\int_0^\beta d\tau'\,\frac{1}{\tau-\tau'}\,\xi(\tau)\frac{d\xi(\tau')}{d\tau'} \times \frac{1}{\xi^2(\tau)-\xi^2(\tau')}\ln\frac{1+\xi^2(\tau)}{1+\xi^2(\tau')} \quad . \tag{3.43}$$

(This term inadvertently appeared with a minus sign in Ref. 1.) The result of the Appendix shows that when ξ has important very low-frequency components (of order $1/\beta$), the replacement

$$\frac{1}{\tau-\tau'} \to \frac{\pi}{\beta}\cot\left(\frac{\pi(\tau-\tau')}{\beta}\right) \tag{3.44}$$

should be made in (3.43). This is really quite a simple result, since we had no reason at the outset to believe that the functional would only depend on ξ at two times rather than arbitrarily many times.

Briefly, the approximations leading to (3.39)–(3.43) are the following: (i) the ND approximation, which has been discussed at length; (ii) the use of the exact G_d^0 to continue the adiabatic part of our calculated G_d to its limit; (iii) neglect of the coupling of density fluctuations. If we included these, ξ would be complex. The entire analysis would still be valid, since we never make use of the reality of ξ. [Paths that wound around either branch point of $\tan^{-1}\xi$ would cause uniqueness difficulties in the solution of the integral equation. However, these are excluded by the requirement $\xi(0) = \xi(\beta)$ if we recognize that equality includes being on the same Riemann surface.] Since the density fluctuations have frequencies which lie predominantly beyond the limit of validity of ND, we do not believe it would be physically meaningful to include them.

IV. EVALUATION OF FUNCTIONAL

A. Simple Approximations

There are no known systematic methods to evaluate functional integrals. Our approach will be to attempt to select the most important paths and relate the sum of our functional over these paths to previously studied problems. $Z(\xi)/Z$ can be regarded as the probability of a path, and $-(1/\beta)\ln Z(\xi)$ as an energy associated with that path. It may be conceptually helpful to think of $\xi(\tau)$ as the coordinate of a particle; then the two terms V and T in the path-energy functional can be thought of, respectively, as the potential and kinetic energy of the particle.

The function V is shown in Fig. 3 for several values of U. For $U/\pi\Delta < 1$, it has a single minimum at the origin, while for $U/\pi\Delta > 1$, it develops a pair of minima symmetrically located about the origin, and the origin becomes a maximum.

It appears that the T functional must be positive definite. Each term in the trace defining $Z(\xi)$, (2.24), is the amplitude for finding the electron gas in its initial state after it has been subjected to the potential ξ. It is clear that a fluctuating potential will scatter more amplitude out of the initial state than a τ-independent potential of the same average value. Hence T must favor straight paths. We shall prove that this is so for all the types of paths which we study in detail.

The most probable path is thus τ independent and at the minimum of V, the position of which is

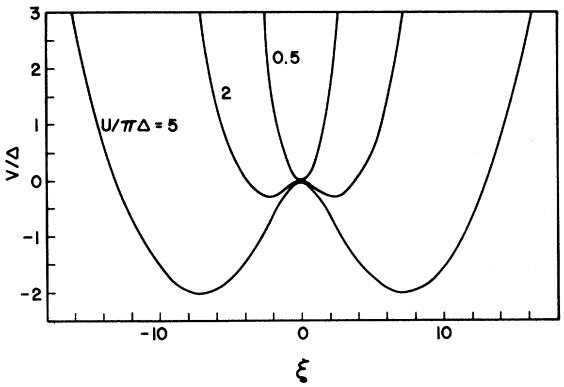

FIG. 3. The function $V(\xi)$, (3.41), for $U/\pi\Delta = 0.5$, 2, and 5.

determined by differentiating (3.41):

$$\xi_0 = (U/\pi\Delta)\tan^{-1}\xi_0 \,. \tag{4.1}$$

This is just Anderson's Hartree-Fock equation for the self-consistent potential.[2] For large U, the solution is

$$\xi_0 = U/2\Delta - 2/\pi + O(\Delta/U) \,. \tag{4.2}$$

The extremal approximation for the partition function is

$$Z = 2Z_0 e^{-\beta V(\xi_0)} \cosh[(2\Delta\xi_0/U)\beta\mu_B H_0] \,, \tag{4.3}$$

where we have included both minima and the magnetic field term (3.42). This clearly leads to a Curie law, with the correct moment in the large U limit. We can identify $\xi = +\xi_0$ as a spin-up configuration and $\xi = -\xi_0$ as spin-down.

For $U/\pi\Delta < 1$, $\xi_0 = 0$. In this case, we shall examine the first corrections to the extremal approximation. Since the energy of a path rises rapidly away from the minimum of V, only small values of ξ should be important. If we expand the functional and keep only the leading terms, we obtain

$$Z(\xi) = \exp\left[-\int_0^\beta d\tau \left(\frac{\Delta^2}{U} - \frac{\Delta}{\pi}\right)\xi^2(\tau) - \frac{P}{\pi^2}\int_0^\beta d\tau\, d\tau' \frac{1}{\tau-\tau'}\xi(\tau)\frac{d\xi(\tau')}{d\tau'}\right] . \tag{4.4}$$

With this simplified functional, it is, in fact, possible to integrate over all paths. To do so, we first express ξ in a Fourier series,

$$\xi(\tau) = \sum_n a_n e^{i\omega_n\tau} \,, \tag{4.5}$$

where $\omega_n = 2\pi n/\beta$, so that the requirement $\xi(0) = \xi(\beta)$ is satisfied, and $a_{-n} = a_n^*$, so that ξ is real. The nonlocal kernel in (4.4) can be expressed as a Fourier integral,

$$P/\tau = (i/2)\int_{-\infty}^{\infty} d\omega\, \mathrm{sgn}(\omega)\, e^{-i\omega\tau} \,. \tag{4.6}$$

We shall approximate this Fourier integral by a Fourier series,

$$P/\tau \approx (i/2)(2\pi/\beta)\sum_n \mathrm{sgn}(\omega_n)\, e^{-i\omega_n\tau} \,, \tag{4.7}$$

which is, in fact, the more exact expression (3.44). Substituting (4.5) and (4.7) in (4.4) yields

$$Z(\xi) = \exp\{-\beta\textstyle\sum_n |a_n|^2[(\Delta^2/U) - (\Delta/\pi) + |\omega_n|/\pi]\} \,. \tag{4.8}$$

This is just a Gaussian in each Fourier coefficient, so we can carry out the functional integral. To ensure that the Jacobian for the new variables of integration is chosen correctly, we note that the first term in the square bracket in (4.8) came from the original Gaussian weighting factor, and that the integral with this term alone should be unity, so

$$\int \delta\xi\, Z(\xi) = \int \left(\frac{\pi U}{\beta\Delta^2}\right)^{1/2} da_0 \left[\prod_{n>0}\left(\frac{\pi U}{2\beta\Delta^2}\right) d^2 a_n\right] Z(\xi) \,. \tag{4.9}$$

This integral factors into a product, and we obtain for the correction to the free energy

$$\Delta\Omega = (1/2\beta)\textstyle\sum_n \ln[1 - (U/\pi\Delta) + (U/\pi\Delta^2)|\omega_n|] \,. \tag{4.10}$$

The sum in (4.10) must be restricted because the ND approximation is not valid for high-frequency fluctuations. Since the effective ϵ_d entering G_d^0 is zero in the symmetric case, condition (3.4) should apply. This suggests the cutoff $|\omega_n| < \Delta$.

The result (4.10) is most important in its role as a check on our procedure to this point. We are expanding the exponent in $Z(\xi)$ to second order in ξ. If we go back to (2.27), this could be expressed as an electron loop with two external-potential vertices in the linked-cluster diagram sum. The corresponding unlinked diagrams would have an arbitrary number of loops, but each with just two vertices. If the functional integral is performed on this expansion, the discussion in Sec. II A indicates that we connect "external" vertices by interaction ion lines in all possible ways. But all possible ways in this case only produce chains of bubble diagrams (Fig. 4). The free-energy contribution of these diagrams is easily evaluated by conventional means, and is

$$\Delta\Omega = (1/2\beta)\textstyle\sum_n \{\ln[1 - U\chi_0(\omega_n)] + \ln[1 + U\chi_0(\omega_n)]\} \,. \tag{4.11}$$

The single bubble χ_0 is for $\omega > 0$:

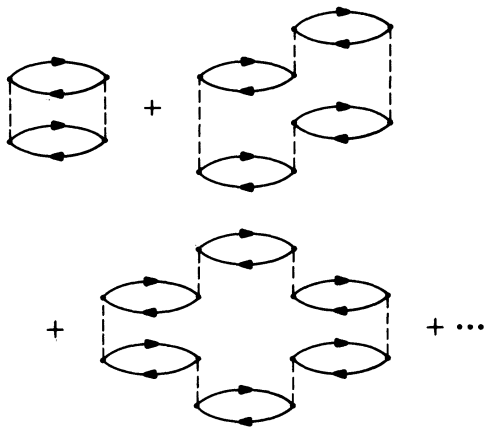

FIG. 4. Bubble diagram sum in a conventional diagrammatic formulation of the Anderson model. The solid lines are G_d^0 Green's functions and the dotted lines are the interaction U.

$$\chi_0(\omega)=\frac{\Delta}{\pi\omega(\omega+2\Delta)}\ln\left(1+\frac{\omega(\omega+2\Delta)}{\Delta^2(1+\xi_0^2)}\right), \qquad (4.12)$$

where we have made provision for a nonzero Hartree-Fock (HF) field ξ_0. The first term in (4.11) comes from the triplet part of the bubble sum, and the second term from the singlet part. Comparing (4.10) with the exact expression shows that only the triplet (spin-fluctuation) part occurs, and that $\chi_0(\omega)$ is replaced by the first two terms in its expansion about zero frequency. The cutoff $|\omega_n|<\Delta$ is also correct in the sense of being a best approximation to (4.12). Therefore, in this small-fluctuation limit, we have a precise check on the ND approximation.

It is also possible to calculate the free-energy contribution from small fluctuations about the polarized HF solution. In this case, more care must be exercised in expanding the T term. We can verify that the functional reproduces the correct ξ_0 dependence of the first two terms in the low-frequency expansion of $\chi_0(\omega)$. When $\xi_0\gg 1$, however, the cutoff $|\omega|<\Delta$ does not properly represent χ_0. A cutoff $|\omega|<\Delta\xi_0$ would be a better approximation although the linear frequency dependence is only accurate for $|\omega|<\Delta$. From Sec. III A we see that if a nonzero Hartree-Fock potential had been included in H_0, we would have predicted $|\omega|<\Delta\xi_0$ as the cutoff from (3.4). The order of doing the calculation should not matter, so we infer that the larger cutoff is the better one, even though it is not a strict consequence of the way we actually did the calculations.

The identification of the bubble-diagram sum as the small-fluctuation expansion of our functional raises another question. It is well known that ladder diagrams, corresponding to transverse spin fluctuations, make a free-energy contribution equal to twice the expression obtained from the longitudinal spin fluctuations. It is clear from the diagram analogy that the ladder sums are related to terms in all powers of ξ in the functional, and will not separate out in any simple fashion. We believe that the resolution of this apparent paradox lies in the fact that neither ladders nor bubbles are especially important in this problem. When the mean-square fluctuation amplitude is really small, the bubble sum is equal to its lowest term, which also happens to be a ladder. When $U/\pi\Delta$ is close to 1 so that the bubble sum is large, the fluctuations are large and the expansion of the functional is invalid. In this case higher terms corresponding to all types of diagrammatic topologies will come in together.

Ladder and bubble sums have been selected in other studies of the magnetic-impurity problem because they are the simplest structures that can give a susceptibility which tends to diverge. If, however, one takes a double-peaked spectral density for the d-state Green's function of the type predicted by equation-of-motion studies,[25] $\chi_0\sim 1/2U$, and the bubble and ladder sum are not even close to being singular. This is independent evidence that other diagrammatic topologies are important. In the perturbation treatments of the x-ray problem, where the electron-gas phase-space considerations are similar to this problem, ladder structures play no special role.[10,11] None of these arguments apply to uniform systems where the phase-space considerations are very different and where a susceptibility divergence associated with a ferromagnetic transition can occur.[8]

B. Hopping Paths

The case of most interest is that of large U/Δ, where there are two wells in the potential V corresponding to the polarized Hartree-Fock solutions. If there were only a single minimum, we could work on fluctuations about it to whatever order we liked, and that would be that. Here, however, a totally different possibility arises. A path can hop back and forth between $+\xi_0$ and $-\xi_0$ an arbitrary number of times and still have a potential energy equal to that of the Hartree-Fock solution. Such paths will have a larger "kinetic" energy T than the extremal paths. Since the cutoff requirements of our theory exclude functions which pass over the potential hump instantaneously, there will be a small extra V contribution as well. Such a path is illustrated in Fig. 5. The extra energy of many of these paths may be sufficiently small that their lessened probability is more than compensated by their large number, and they make an important contribution to the partition function.

There are no other paths which appear to be as important. One could refine the basic hopping paths by considering fluctuations about each mini-

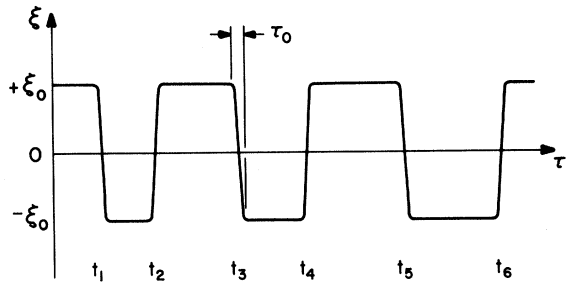

FIG. 5. Typical "hopping" path. $\pm\xi_0$ are the positions of the minima of $V(\xi)$, and the positions t_i of the hops are arbitrary, except for the obvious requirement $t_{i+1}-t_i>\tau_0$.

mum, but any radically different path will become less and less probable as U/Δ becomes larger. Therefore, we will evaluate our functional for such paths, and consider that they form the "adequate set" of paths we hoped to select.

To evaluate the T term for a hopping path, we substitute (3.43) in (3.40) and integrate by parts on τ:

$$-\int_0^\beta d\tau\, T=\frac{1}{\pi^2}\int_0^\beta d\tau\, d\tau'\ln|\tau-\tau'|\frac{d\xi(\tau')}{d\tau'}\ \frac{d}{d\tau}\times\left(\frac{\xi(\tau)}{\xi^2(\tau)-\xi^2(\tau')}\ \ln\frac{1+\xi^2(\tau)}{1+\xi^2(\tau')}\right). \qquad (4.13)$$

We have assumed $\xi(0)=\xi(\beta)=0$ again, although the weaker condition $\xi(0)=\xi(\beta)$ would suffice if the kernel of the Appendix were used. Now we define hopping paths such that the derivative of ξ is strictly zero unless $t_i<\tau<t_i+\tau_0$. Then (4.13) only has contributions when both τ and τ' are inside hops, and we will write the integral as

$$-\int_0^\beta d\tau\, T=\sum_{i\neq j}\int_{t_i}^{t_i+\tau_0}d\tau\int_{t_j}^{t_j+\tau_0}d\tau'\,F(\tau,\tau')+\sum_i\int_{t_i}^{t_i+\tau_0}d\tau\,d\tau'\,F(\tau,\tau'), \qquad (4.14)$$

where F is the integrand in (4.13). We will assume that the mean spacing between hops is much greater that τ_0. Then the ln comes out of the integral when $i\neq j$, and we may write the long-range term

$$L_{ij}=\frac{1}{\pi^2}(\ln|t_i-t_j|)\int_{t_i}^{t_i+\tau_0}d\tau\int_{t_j}^{t_j+\tau_0}d\tau'\,\frac{d\xi(\tau')}{d\tau'}\times\frac{d}{d\tau}\frac{\xi(\tau)}{\xi^2(\tau)-\xi^2(\tau')}\ln\frac{1+\xi^2(\tau)}{1+\xi^2(\tau')}\ . \qquad (4.15)$$

The τ integrand is a derivative, so this integral is trivial. The τ' integral is converted to an integral over $d\xi(\tau')\equiv d\xi'$ by the presence of the derivative. Therefore,

$$L_{ij}=(-1)^{i+j}(2/\pi^2)(\ln|t_i-t_j|)\times\int_{-\xi_0}^{\xi_0}d\xi'\,\frac{\xi_0}{\xi_0^2-\xi'^2}\ln\frac{1+\xi_0^2}{1+\xi'^2}\ . \qquad (4.16)$$

The $(-1)^{i+j}$ occurs because the sense of each successive hop is reversed. The easiest way we have found to do this integral employs a trick. We transform to a normalized variable and differentiate with respect to ξ_0:

$$\frac{dI(\xi_0)}{d\xi_0}=\frac{2\xi_0^2}{1+\xi_0^2}\int_{-1}^{1}dx\,\frac{1}{1+\xi_0^2x^2}=4\frac{\tan^{-1}\xi_0}{1+\xi_0^2}=2\frac{d}{d\xi_0}(\tan^{-1}\xi_0)^2\ . \qquad (4.17)$$

Since $I(0)=0$,

$$L_{ij}(-1)^{i+j}[2(\tan^{-1}\xi_0)/\pi]^2\ln|t_i-t_j|\ . \qquad (4.18)$$

Correction terms are of order $\tau_0/(t_i-t_j)$. The coefficient in (4.18) is just the square of the change of Fermi-surface phase shift when the hop takes place. An analogous quantity enters the exponent of the deep-hole propagator in the ND theory.[12]

The short-range term is somewhat more difficult to evaluate. First, we integrate by parts on τ and obtain

$$S_{i1}=\frac{1}{\pi^2}\int_{t_i}^{t_i+\tau_0}d\tau'\ln|(t_i+\tau_0-\tau')(t_i-\tau')|\times\frac{d\xi(\tau')}{d\tau'}\ \frac{\xi_0}{\xi_0^2-\xi^2(\tau')}\ln\frac{1+\xi_0^2}{1+\xi^2(\tau')}\ , \qquad (4.19)$$

$$S_{i2}=-\frac{1}{\pi^2}\int_{t_i}^{t_i+\tau_0}d\tau\,d\tau'\,\frac{P}{\tau-\tau'}\,\frac{d\xi(\tau')}{d\tau'}\times\frac{\xi(\tau)}{\xi^2(\tau)-\xi^2(\tau')}\ln\frac{1+\xi^2(\tau)}{1+\xi^2(\tau')}\ . \qquad (4.20)$$

We cannot proceed without making some assumption about the form of ξ within the hop. The simplest choice is a linear variation:

$$\xi(\tau)=-\xi_0+2\xi_0(\tau-t_i)/\tau_0\ , \qquad (4.21)$$

where we have assumed a $-$ to $+$ hop. Substituting, we separate S_{i1} into

$$S_{i1a}=\frac{2}{\pi^2}\ln\left(\frac{\tau_0}{2}\right)\int_{-\xi_0}^{\xi_0}d\xi'\,\frac{\xi_0}{\xi_0^2-\xi'^2}\ln\frac{1+\xi_0^2}{1+\xi'^2} \qquad (4.22)$$

and

$$S_{i1b}=\frac{1}{\pi^2}\int_{-1}^{1}dx\,\frac{\ln(1-x^2)}{1-x^2}\ln\frac{1/\xi_0^2+1}{1/\xi_0^2+x^2}\ . \qquad (4.23)$$

The integral in the first term is the same as that in (4.16). The effect of (4.22), therefore, will be to replace $\ln|t_i-t_j|$ by $\ln|(t_i-t_j)/\tau_0|$ in (4.18). [The cancellation in the double sum caused by $(-1)^{i+j}$ is just such as to leave one factor of $\ln\tau_0$ over for each hop.]

The second integral (4.23) cannot be expressed in known functions and has no convenient expansion. In the large ξ_0 limit,

$$S_{i1b}=-\frac{1}{\pi^2}\int_{-1}^{1}dx\,\frac{\ln x^2\ln(1-x^2)}{1-x^2}\ . \qquad (4.24)$$

The integrand is regular at $x=0$ and has integrable logarithmic singularities at $x=\pm1$, so it is a finite constant which we estimate numerically to be $-(4/\pi^2)[(1.20)]$.

To evaluate the last contribution [(4.20)], we substitute the linear hopping form (4.21), τ_0 cancels out, and we obtain

$$S_{i2}=-\frac{P}{\pi^2}\int_{-\xi_0}^{\xi_0}d\xi\,d\xi'\,\frac{\xi}{(\xi-\xi')(\xi^2-\xi'^2)}\ln\frac{1+\xi^2}{1+\xi'^2}\,. \tag{4.25}$$

This may be simplified by interchanging ξ and ξ' and taking half the sum. The resulting integral in normalized variables is

$$S_{i2}(\xi_0)=-\frac{1}{2\pi^2}\int_{-1}^{1}dx\,dx'\frac{1}{x^2-x'^2}\ln\frac{1/\xi_0^2+x^2}{1/\xi_0^2+x'^2}\,. \tag{4.26}$$

To evaluate this integral, we differentiate with respect to ξ_0:

$$\frac{dS_{i2}}{d\xi_0}=-\frac{1}{\pi^2\xi_0^3}\left(\int_{-1}^{1}dx\frac{1}{(1/\xi_0^2+x^2)}\right)^2$$
$$=-\frac{4}{\pi^2\xi_0}(\tan^{-1}\xi_0)^2\,. \tag{4.27}$$

Since $S_{i2}(0)=0$,

$$S_{i2}(\xi_0)=-(4/\pi^2)\int_0^{\xi_0}d\xi\,(\tan^{-1}\xi)^2/\xi\,. \tag{4.28}$$

This integral has an obvious logarithmic divergence at large ξ_0. Integrating by parts and expanding, we find

$$S_{i2}\to-\ln\xi_0-4/(\pi\xi_0)+2/(\pi\xi_0)^2+\cdots$$
$$+(8/\pi^2)\int_0^\infty d\xi(\ln\xi)(\tan^{-1}\xi)/(1+\xi^2)\,, \tag{4.29}$$

where the integral is a constant which we estimate numerically to be $+0.852$.

The integral of the V term requires the assumption of a hopping shape, and is completely straightforward for linear hops. The leading term at large U is

$$\int_0^\beta d\tau\,V=\tfrac{1}{6}n\tau_0U\,, \tag{4.30}$$

where n is the number of hops and we have neglected the constant Hartree-Fock contribution.

We have not yet determined τ_0. It clearly can be varied to minimize the energy of the path:

$$E(\tau_0)=n(\tfrac{1}{6}\tau_0U-\ln\tau_0)\,, \tag{4.31}$$

where we have also taken the large U limit of the coefficient of $\ln\tau_0$. This leads to

$$\tau_0=6/U\,, \tag{4.32}$$

so the contribution of the V term is of order unity per hop and, in fact, independent of path shape.

The value we have found for τ_0 is at the limit of validity for the ND approximation, even taking the smaller of the cutoffs discussed in Sec. IV A. This should lead us to question the various contributions to the path energy found from within the hops. In each case, however, we have evidence that the leading terms are independent of detailed assumptions of the path shape, and therefore of the absolute accuracy of the ND form. The $\ln\tau_0$ factor (4.22) is necessary to give the long-range term (4.18) the correct dimensionality. The $\ln\xi_0$ term (4.29) is independent of τ_0 and comes from an integral in which the equal-time singularity of the ND kernel is canceled. Finally, the potential contribution (4.30) is initially shape and τ_0 dependent, but this dependence is canceled by our variational choice of τ_0. We believe that the inaccuracies are all contained in numerical terms which are negligible compared to $n\ln\xi_0$ in the large U limit.

To evaluate the contribution to the partition function from all hopping paths, we must sum over all possible even numbers of hops and integrate over the positions of each hop. The number of distinguishable positions is of order β/τ_0 and two hops cannot approach closer than τ_0. Our result for the partition function is

$$Z=\sum_{n=0}^{\infty}\xi_0^{-2n}\int_0^\beta\frac{dt_{2n}}{\tau_0}\int_0^{t_{2n}-\tau_0}\frac{dt_{2n-1}}{\tau_0}\cdots\int_0^{t_2-\tau_0}\frac{dt_1}{\tau_0}$$
$$\times\exp\left[\left(\frac{2\tan^{-1}\xi_0}{\pi}\right)^2\sum_{i\neq j}(-1)^{i+j}\ln\left|\frac{t_i-t_j}{\tau_0}\right|\right]. \tag{4.33}$$

The result of using the more exact kernel (3.44) in T would be the replacement

$$\ln\left|\frac{t_i-t_j}{\tau_0}\right|\to\ln\left|\frac{\beta}{\pi\tau_0}\sin\left(\frac{\pi(t_i-t_j)}{\beta}\right)\right|\,. \tag{4.34}$$

A new study of the ground-state energy of the s-d exchange model was recently published by Anderson and Yuval.[16] Their procedure is to write a perturbation expansion in the transverse (spin-flip) parts of the exchange interaction, use the ND asymptotic form for the conduction-electron Green's function, and include the longitudinal part of the exchange to all orders in each term of the expansion within the ND approximation. Their expression (for the exponential of β times the ground-state energy) is identical to (4.33) in form. The correspondence of the various parameters is

$$[2(\tan^{-1}\xi_0)/\pi]^2\to1-J_zN(0)\,, \tag{4.35}$$
$$\xi_0^{-2n}\to(J_\pm\tau_0)^{2n}\,. \tag{4.36}$$

The Schrieffer-Wolff transformation gives the relation

$$JN(0)\longleftrightarrow8\Delta/\pi U \tag{4.37}$$

in our symmetric case.[26] Since $\xi_0=U/2\Delta$ in the large U limit, (4.35) agrees with (4.37). Anderson and Yuval's τ_0 is an arbitrary cutoff parameter which they set equal to $1/\epsilon_F$ [or $N(0)$], the only

high-energy cutoff in their model.[16] The fact that our $\tau_0 = 6/U$ is not a serious discrepancy, since the Anderson model has an additional "natural" cutoff and since U is generally considered to be of order ϵ_F. Each theory, in fact, has just a single dimension-setting energy and a single dimensionless ratio (for $J_\pm = J_z$). Equation (4.36) fails to correspond to (4.37) only by a numerical factor, whose determination is outside the range of validity of both theories.

This comparison leads to the important conclusion that within theories which treat all Fermi-surface anomalies correctly, the s-d exchange model and the Anderson model behave identically. Furthermore, the relation between parameters which was derived only to lowest order[26] persists in these asymptotically exact theories. It is clear that the correspondence breaks down when the fluctuations about our hopping paths become so large as to destroy their identity. Such cases of weakly magnetic impurities are thus not properly described by the s-d exchange model with a large J.

The hopping-path partition function (4.28) has been analyzed in an approximation good for small $JN(0)$.[17] It is found to undergo a "phase transition" as a function of its parameters. For $J_z < 0$ (corresponding to ferromagnetic exchange in our present notation) and $|J_\pm| < |J_z|$, the average

$$\langle \xi(\tau)\xi(\tau') \rangle \equiv Z^{-1} \int \delta\xi \, \xi(\tau)\xi(\tau') Z(\xi) \tag{4.38}$$

approaches a finite limit for large $\tau - \tau'$. For $|J_\pm| > |J_z|$ or $J_z > 0$, this correlation function falls to zero for $\tau - \tau' > \tau_K$, where

$$\tau_K = \tau_0 e^{1/JN(0)} \tag{4.39}$$

is the inverse of the Kondo energy. Of course the Anderson model can only correspond to the s-d exchange model with antiferromagnetic coupling. However, it can come arbitrarily close to the phase-transition line.

In the initial presentation of this work, τ_0 was taken to be $1/\Delta$ and the V term in the functional was stated to be responsible for a characteristic energy of the order of the Kondo energy, with the T term contributing numerical factors.[1] Ramakrishnan points out that one would not obtain a temperature-dependent free energy if this were so.[27] As our present analysis shows, it is, in fact, not so. After the V term dictates hopping paths, the T term dominates the behavior of the fluctuations, and the V term's only additional role is fixing τ_0.

V. TRANSPORT PROPERTIES

The susceptibility and specific heat may be found directly from the partition function. The scattering of conduction electrons from the impurity must be found from their t matrix, which is in turn proportional to the d-state Green's function.

It is obvious that the complete d-state Green's function should be given by the path average of G_d for particular paths:

$$G_d(\tau - \tau') = Z^{-1} \int \delta\xi \, G_d(\tau, \tau'; \xi) Z(\xi) \, . \tag{5.1}$$

This is easily proved by starting with the interaction representation form of the Green's function[20] and applying the Hubbard transformation to the S matrix.

To find the total scattering cross section, we need the imaginary part in the zero-frequency limit of

$$G_d(i\omega) = \int_{-\infty}^{\infty} d\tau \, e^{i\omega\tau} G_d(\tau) \, . \tag{5.2}$$

Suppose

$$\Delta G_d(\tau) \xrightarrow[\tau \to \infty]{} \frac{-\varphi}{\pi\tau} \, . \tag{5.3}$$

Then (5.2) does not exist, strictly speaking, at $\omega = 0$, but displays the well-known discontinuity of $G_d(z)$ across the real-z axis. The scattering rate, in unitarity-limit units, is given by

$$-\Delta \mathrm{Im} G_d(i0^+) = \varphi \, . \tag{5.4}$$

This argument was carried out in the zero-temperature limit, but presumably can be generalized in parallel with the theory of the Appendix.

The Green's function for a particular path is given in (3.27), and both the "adiabatic" and "transient" terms contribute to the coefficient of $1/(\tau - \tau')$. We find

$$\pi\Delta(\tau - \tau') G_d(\tau - \tau') = -\langle [X(\tau')/X(\tau)] \cos\eta(\tau) \cos\eta(\tau') \rangle \, , \tag{5.5}$$

where $\langle\,\rangle$ denotes the path average weighted by $Z(\xi)$ as in (5.1), $\eta(\tau)$ is the instantaneous Fermi-surface phase shift, and $X(\tau)$ is the functional defined in (3.29).

For hopping paths, it is adequate to treat η as equal to its values in the minima, $\pm\eta_0$; then,

$$\varphi = \cos^2\eta_0 \lim_{\tau - \tau' \to \infty} \langle X(\tau')/X(\tau) \rangle \, . \tag{5.6}$$

Written out, this expression is like the partition function (4.33) with external sources at τ and τ' "interacting" with each hop via $\ln|(\tau - t_i)/(\tau' - t_i)|$. This expression is far too difficult to evaluate in detail, even by the approximate methods used on Z.[16] However, we can estimate (5.6) by quite a simple argument. $X(\tau)$ is a functional of $\xi(\tau)$, and

$\xi(\tau)$ and $\xi(\tau')$ are found to be uncorrelated for $\tau-\tau'\gg\tau_K$, [(4.38)]. Therefore, we might expect $X(\tau)$ and $X(\tau')$ to be similarly uncorrelated, so

$$\langle X(\tau)/X(\tau')\rangle \xrightarrow[\tau-\tau'\to\infty]{} \langle X(\tau)\rangle\langle 1/X(\tau')\rangle \ . \qquad (5.7)$$

For hopping paths, it is easily shown that

$$X(\tau)=\left|\prod_j \frac{t_{2j+1}-\tau}{t_{2j}-\tau}\right|^{2\eta_0/\pi} , \qquad (5.8)$$

where t_j are the positions of the hops and τ is outside each hop. We can evaluate the average of the single X if we assume strictly periodic hopping, $t_{i+1}=t_i+\frac{1}{2}\pi\tau_c$. Then

$$X(\tau)=\left|\tan[(\tau/\tau_c)+\theta]\right|^{2\eta_0/\pi} , \qquad (5.9)$$

and the average over all phases θ (and hopping periods τ_c, which is trivial since the θ-averaged result is independent of τ_c) is[28]

$$\begin{aligned}\langle X(\tau)\rangle &= \langle 1/X(\tau)\rangle \\ &= (2/\pi)\int_0^{\pi/2} d\theta\,(\tan\theta)^{2\eta_0/\pi} \\ &= \sec\eta_0 \ . \end{aligned} \qquad (5.10)$$

Substituting in (5.7) and (5.6) yields $\varphi=1$, which corresponds to unitarity-limit scattering. This result has been obtained in a number of approximations for both the s-d exchange[29] and Anderson[8] models, although these calculations do not agree on the manner in which this zero-temperature limit is approached. The present crude argument should only be taken as a demonstration that this result is plausible in terms of the path integral theory.

It is possible to push this approach a bit further and consider periodic hopping functions which spend more time at $+\xi_0$ than $-\xi_0$. Such functions might be representative paths in an external field which induced a net magnetization. The average in this case is

$$\langle X(\tau)\rangle=\frac{1}{\pi}\int_{-\pi/2}^{\pi/2} d\theta\left|\frac{\sin(\theta-\psi)}{\cos\theta}\right|^{2\eta_0/\pi} . \qquad (5.11)$$

This may be reduced to a known integral by treating $\sin(\theta-\psi)/\cos\theta$ as the independent variable,[30] and

$$\langle X(\tau)\rangle=\frac{\cos(2\psi\eta_0/\pi)}{\cos\eta_0} \ . \qquad (5.12)$$

This yields for the scattering

$$\varphi=\cos^2(\eta_0 M/M_0) , \qquad (5.13)$$

where M/M_0 is the fractional magnetization compared to the Hartree-Fock state. For $M/M_0=1$, this reduces to the resistivity that could be obtained directly from the Hartree-Fock approximation. An expression similar to (5.13) was recently derived by Ishii for the ground state of the s-d exchange model.[31]

Finally, we can argue about what happens above the Kondo temperature. In this case, $\beta<\tau_K$, so the size of the classical system represented by the partition function is small compared to the range of correlations in the corresponding infinite system. We expect that the system is then "effectively ordered," so that $\xi(\tau)$ and $\xi(\tau')$ are strongly correlated for all possible $\tau-\tau'$. The same argument should hold for $X(\tau)$ and $X(\tau')$, so

$$\langle X(\tau)/X(\tau')\rangle\approx 1 , \qquad (5.14)$$

and the resistivity assumes its Hartree-Fock value.

VI. DISCUSSION

A. Obtaining Path Integral

The first decision made in this calculation was to use the particular diagonal quadratic form (2.20) of the interaction Hamiltonian to generate the Stratonovich-Hubbard transformation. It was pointed out that only for this particular choice did the most probable τ-independent path correspond to the best variational choice of one-electron potentials in the untransformed problem (the Hartree-Fock approximation). The importance of this is clear from the result, since the hopping paths are at the most probable magnitude almost all the time. Another choice, such as (2.29), would have produced a formally similar result, but with the most probable path giving twice the Hartree-Fock d-state potential. This would indicate that straight sections of the hopping paths had no physical meaning, and that large and presumably high-frequency fluctuations were important and would have to be dealt with appropriately before hops were even considered.[21] "Appropriately" would certainly be beyond the ability of the ND approximation.

The next choice was to use the ND approximation.[12] This is a purely mathematical approximation, replacing the kernel in the integral equation (2.26) by a function to which it is equal only for sufficiently large time differences. The approximate kernel is singular and makes the solution too sensitive to rapid fluctuations in $v(\tau)$, which the discontinuous but bounded exact kernel would smear over. The approximation is thus self-checking; we need only verify that we have adequately restricted the choice of paths. The insensitivity of our key result (4.33) to high-frequency details of the hopping paths has been discussed. The previous work on the spin-fluctuation picture of dilute alloys discussed in Sec. I provided independent justification for favoring slowly fluctuating paths.

The decision to neglect contributions to the partition function from electron charge-density fluctuations on the d site followed the ND choice from physical (although not mathematical) necessity. To estimate the effect of these fluctuations, we could assume that they adiabatically follow the slowly fluctuating magnetic potential. Then the density fluctuation contribution to the random-phase-approximation expression (4.11), which is a function of ξ, would be added to $V(\xi)$. This has been found to lower the hump of V somewhat, but its height remains of order U, and only the numerical factor in τ_0 is changed.

B. Using Path Integral

Having obtained the explicit path functional [(3.40)–(3.43)] what can be done with it? The precise value of the Anderson model's free energy is of rather limited interest. Of real interest is the nature of the dominant paths, their change from high to low temperatures, and how this affects thermodynamic and transport properties. We identified a set of low-energy paths by inspection. This step could be turned into a classification of paths rather than the selection of a small set, since all paths can be obtained by adding fluctuations to the hopping paths. In the large U/Δ limit, the neglected contributions to the free energy from all the paths in a class should not vary appreciably from class to class. This follows because the dominantly small-amplitude fluctuations about each minimum are the same in either minimum, and should not be sensitive to the number or position of hops. The restricted "hopping" partition function (4.28) is therefore a model for the complete expression which omits only a temperature-independent contribution to the free energy.

Since this hopping model is identical to the Anderson-Yuval partition function for the s-d exchange model,[16] the question of which hopping paths are most important has the same answer in each case. We have found that the average hopping path has the following description[17]: Most hops are close to one of their neighbors. A row of such paired hops leads to a predominantly spin-up or spin-down region of the path. The pairs only interact weakly with distant pairs or isolated hops. The occasional isolated hops separate (by definition) dominantly spin-up from dominantly spin-down regions. The size of these regions is, on the average, the inverse Kondo temperature.[17] We thus expect T_K/T isolated hops, so that the average path is ordered (predominantly in one minimum or the other) at high T, and disordered at low T. The correlation function (4.38) is believed to fall off for $\tau \gg 1/T_K$ as τ^{-2}, which is the same as the spin correlation function on an impurity with no Coulomb interaction. Therefore, the thermodynamic properties of dilute alloys should not be singular at zero temperature and should approach their limits as simple powers of T.

Another interpretation can be given to the hopping partition function which is useful for discussion and perhaps for calculation. If one substitutes a hopping path in (3.43), integrates by parts on τ, and introduces a discrete mesh with spacing τ_0 to approximate the τ and τ' integrals, the result is[17]

$$Z = \sum_c \exp\{ -\tau_0 \mu_B H \sum_i S_i + \ln\xi_0 \sum_i S_i S_{i+1} + [(\tan^{-1}\xi_0)/\pi]^2 \sum_{i \neq j} S_i S_j/(i-j)^2 \} . \qquad (6.1)$$

The indices i and j run from 1 to β/τ_0, $S_i = \pm 1$, and the outside sum is over all configurations of the S_i. This is just a one-dimensional Ising model. Unfortunately, for $(i-j)^{-\alpha}$ exchange interactions in one dimension, it is only for $\alpha = 2$ that a rigorous proof of the existence of a phase transition has not been found.[32] Thouless has proved that if such a transition exists, the magnetization cannot go continuously to zero,[33] which agrees with the approximate results on the other form of the partition function.[17]

One simple thing that can be done with the Ising model is to set up a variational principle for the free energy based on an approximate Hamiltonian. This has been carried out using a nearest-neighbor interaction model and choosing the interaction strength to minimize the free energy. The spin correlation function is found to have a range $\exp[2b/(4a-1)]$, where b is the coefficient to the nearest-neighbor term in (6.1) and a is the coefficient of the long-range term. While this is not the correct Kondo-energy expression, it is not bad for such a crude treatment.

The hopping-path formulation suggests an interesting interpretation of local-moment formation. Suppose we could only calculate the "adiabatic" part of the path energy V, which gives the Hartree-Fock local moment criterion. Suppose further that we know the maximum-fluctuation frequency to be of order U. This would lead to a noninteracting Ising model, with only the first term in (6.1). The susceptibility in this approximation is $\chi \sim \mu_B^2/U$, and is temperature independent. Therefore, the basic Hartree-Fock approximation is insufficient to predict local-moment behavior, as experimentally defined, without more detailed information about the dynamic response of the electron gas.

Next, suppose we add the short-range dynamic contribution (that from within each hop), which is represented by the second term in (6.1). This leads to $\chi \sim \mu_B^2 U/\Delta$, independent of temperature

until $T > \Delta^2/U$. Once again, this is far from local-moment behavior.

We must not only add the long-range term, but adjust its coefficient so that the model is close to a phase transition to obtain $\chi \sim \mu_B^2/T_K$ and a Curie law for $T > T_K$. The dominant role played by the long-range term provides further justification for the use of the ND approximation.

Performing detailed calculations of the β dependence of the partition function remains a difficult task. The theory developed in Ref. 17 can, in principle, be used for this. It was conceived primarily as a means for understanding the low-temperature behavior, however, and may not be the best way to deal with finite β effects. Since the qualitative features of the behavior of the classical model are understood, it should be possible to complete this task with a confidence in one's approximation procedure which has heretofore been lacking.

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APPENDIX

In deriving the ND approximation, Sec. III A, the stipulation $|\tau| \ll \beta$ was made, so that the Fermi function in (3.2) could be treated as a step function. This is a good approximation for $T \ll T_K$, since the correlation range of the fluctuations is of order $1/T_K$.[17] It is possible to relax this restriction and carry through the same calculations, although it requires rederiving Muskhelishvili's theory[13] for singular integral equations with a modified kernel.[34] Since the derivations here parallel those of Sec. III, only the new mathematical operations will be discussed, and occasional references to equations in the main text will indicate where more complete discussion may be found.

From (3.2), for $\tau_0 \ll \tau < \beta$,

$$G_d^0(\tau) = -\frac{\Delta}{\epsilon_d^2+\Delta^2}\int_{-\infty}^{\infty}\frac{d\epsilon}{\pi}\frac{e^{\epsilon(\beta-\tau)}}{e^{\beta\epsilon}+1} \ . \tag{A1}$$

The contour may be deformed into the upper-half ϵ plane, and the contribution from the semicircle at ∞ vanishes. Each pole on the imaginary axis contributes, so

$$G_d^0(\tau) = \frac{2i\Delta/\beta}{\epsilon_d^2+\Delta^2}\sum_{n=0}^{\infty}\exp\left(\frac{(2n+1)(\beta-\tau)\pi i}{\beta}\right). \tag{A2}$$

$$G_d^0(\tau) = \frac{-\Delta}{(\epsilon_d^2+\Delta^2)}\ \frac{1}{\beta\sin(\pi\tau/\beta)} \ . \tag{A3}$$

The δ-function part of G_d^0 is the same, so

$$G_d^0(\tau) \approx \frac{-\Delta}{\epsilon_d^2+\Delta^2}\left(\frac{P}{\beta\sin(\pi\tau/\beta)} + \frac{\epsilon_d}{\Delta}\,\delta(\tau)\right). \tag{A4}$$

This clearly reduces to (3.8) for $\tau \ll \beta$.

We will need to use two types of sectionally holomorphic functions which are periodic generalizations of the Cauchy integral used by Muskhelishvili.[13] Suppose $\rho(\tau)$ is analytic in a strip $\pm i\eta$ about the real axis from 0 to β, where $\eta \to 0^+$. Define

$$\Phi(z) = (\pi/\beta)\int_0^\beta \csc[\pi(\tau-z)/\beta]\,\rho(\tau)\,d\tau \ , \tag{A5}$$

$$\Psi(z) = (\pi/\beta)\int_0^\beta \cot[\pi(\tau-z)/\beta]\,\rho(\tau)\,d\tau \ . \tag{A6}$$

It is obvious that Φ and Ψ are analytic functions of z except for a cut on the real axis. In addition,

$$\Phi(z+\beta) = -\Phi(z) \ , \tag{A7}$$

$$\Psi(z+\beta) = \Psi(z) \ . \tag{A8}$$

Now for $0 < \tau' < \beta$ and $\delta < \eta$,

$$\Phi(\tau'+i\delta) - \Phi(\tau'-i\delta) = \frac{\pi}{\beta}\oint d\tau\ \csc\left(\frac{\pi(\tau-\tau')}{\beta}\right)\rho(\tau)\,d\tau \ , \tag{A9}$$

where the contour encircles the real τ axis from 0 to β counterclockwise, and lies completely within the region of analyticity of ρ. The only singularity within the contour is that of csc, the contour can be shrunk to an infinitesimal circle about it, and

$$\Phi(\tau'+i\delta) - \Phi(\tau'-i\delta) = 2\pi i\rho(\tau') \ . \tag{A10}$$

Note that this implies $\rho(\beta) = -\rho(0)$. Otherwise, ρ would change discontinuously in the vicinity of 0 or β, contradicting our analyticity assumption. Similarly, we can prove

$$\Psi^+(\tau') - \Psi^-(\tau') = 2\pi i\rho(\tau') \ , \tag{A11}$$

where the + and − superscripts mean the same as the limits in (A10), and $\rho(\beta) = \rho(0)$.

For full generality, we shall keep a nonzero average d-state potential $\Delta\xi_0$ in our G_d^0. We will assume only that the path is periodic, $\xi(\beta) = \xi(0)$, since the stronger assumption $\xi(\beta) = \xi(0) = 0$ will not be needed. The integral equation (3.10) becomes

$$[1+\xi_0^2+\xi_0\xi(\tau)]\,G_d(\tau,\tau') = (1+\xi_0^2)\,G_d^0(\tau,\tau') + \frac{1}{\beta}P\int_0^\beta d\tau''\csc\left(\frac{\pi(\tau''-\tau)}{\beta}\right)\xi(\tau'')\,G_d(\tau'',\tau') \ . \tag{A12}$$

Paralleling (3.12)–(3.15),

$$\psi(\tau) = G_d(\tau,\tau') \ , \tag{A13}$$

$$A(\tau) = 1+\xi_0^2+\xi_0\xi(\tau) \ , \tag{A14}$$

$$B(\tau) = i\xi(\tau) \ , \tag{A15}$$

$$g(\tau) = (1+\xi_0^2)\, G_d^0(\tau - \tau') \ . \tag{A16}$$

Then (A12) may be rewritten in Muskhelishvili's standard form,

$$A(\tau)\psi(\tau) - \frac{1}{\pi i} P\int \frac{\pi}{\beta} \csc\left(\frac{\pi(\tau'' - \tau)}{\beta}\right) B(\tau'')\psi(\tau'')d\tau'' \ . \tag{A17}$$

Define

$$\Phi(z) = \frac{1}{2\pi i}\int_0^\beta \frac{\pi}{\beta} \csc\left(\frac{\pi(\tau'' - z)}{\beta}\right) B(\tau'')\psi(\tau'')\, d\tau'' , \tag{A18}$$

then (A17) may be written

$$A\psi = \Phi^+ + \Phi^- + g \ , \tag{A19}$$

where all arguments are understood to be τ. From (A10),

$$B\psi = \Phi^+ - \Phi^- \ . \tag{A20}$$

We can eliminate ψ from (A19) and (A20), and find

$$(A-B)\Phi^+ - (A+B)\Phi^- = Bg \ . \tag{A21}$$

Now suppose we introduce a function $X(z)$ which is analytic except for a real-axis cut, and satisfies

$$X(z+\beta) = X(z) \tag{A22}$$

and

$$X^+/X^- = (A-B)/(A+B) \ . \tag{A23}$$

Substituting in (A21),

$$X^+\Phi^+ - X^-\Phi^- = X^-Bg/(A+B) \ . \tag{A24}$$

Now $X(z)\Phi(z)$ is analytic by construction except for a real-axis cut, and satisfies

$$X(z+\beta)\Phi(z+\beta) = -X(z)\Phi(z) \ . \tag{A25}$$

We verify from (A10) that a particular function satisfying (A24) and (A25) is

$$X(z)\Phi(z) = \frac{1}{2\pi i}\int_0^\beta \frac{\pi}{\beta} \csc\left(\frac{\pi(t-z)}{\beta}\right) \frac{X^-(t)\, B(t)\, g(t)}{A(t)+B(t)}\, dt \ . \tag{A26}$$

The most general solution is (A26) plus a polynomial in $\sin \pi z/\beta$ and $\cos \pi z/\beta$. We reject these additions because Φ, in general, does not have any shorter periods than β.

We find a solution to the homogeneous equation (A23) by taking its logarithm

$$\ln X^+ - \ln X^- = \ln[(A-B)/(A+B)] \ . \tag{A27}$$

Now $\ln X(z)$ is an analytic function except for the real-axis branch cut, and has the periodicity of X, (A22). We verify from (A11) that a particular solution of (A27) is

$$X(z) = \exp\frac{1}{2\pi i}\int_0^\beta \left(\frac{\pi}{\beta}\right) \operatorname{ctn}\left(\frac{\pi(t-z)}{\beta}\right) \ln\frac{A-B}{A+B}\, dt \ . \tag{A28}$$

More general solutions are rejected for the same reason as above. Substituting A and B, (A28) may be simplified and written in the form of (3.18),

$$X(z) = \exp\left(\frac{1}{\beta}\right)\int_0^\beta dt \ \operatorname{ctn}\left(\frac{\pi(t-z)}{\beta}\right)[\eta(t) - \eta_0] \ , \tag{A29}$$

where

$$\eta(t) = -\tan^{-1}[\xi(t) + \xi_0] \tag{A30}$$

and

$$\eta_0 = -\tan^{-1}\xi_0 \ . \tag{A31}$$

We will find ψ from (A20). The $\pm$ limits of (A26) require us to consider the product of two singular functions, csc and g. In analogy to (3.22) we can write, after a good deal of algebra,

$$\begin{aligned}
&\frac{\pi}{\Delta\beta} \csc\left(\frac{\pi(t-\tau \mp i\epsilon)}{\beta}\right) g(t) \\
&= \frac{1}{2\pi}\left[\frac{P\pi}{\beta} \sec\left(\frac{\pi(2t-\tau-\tau')}{2\beta}\right) \csc\left(\frac{\pi(\tau'-\tau)}{2\beta}\right)\right] \\
&\times\left[\frac{P\pi}{\beta} \csc\left(\frac{\pi(t-\tau)}{\beta}\right) - \frac{P\pi}{\beta} \csc\left(\frac{\pi(t-\tau')}{\beta}\right)\right] \\
&+ \pi[\pm i\delta(t-\tau) - \xi_0\delta(t-\tau')] \\
&\times\left[\frac{P\pi}{\beta} \csc\left(\frac{\pi(\tau'-\tau)}{\beta}\right) \pm i\pi\delta(\tau'-\tau)\right] \ .
\end{aligned} \tag{A32}$$

In deriving this result, we have restricted τ and τ' to the interval $(0, \beta)$ so that $\cos[\pi(\tau-\tau')/2\beta]$, which occurs in an intermediate step, can never go through zero. Substitution of (A32) and (A26) in (A20) yields after straightforward algebraic manipulations

$$\begin{aligned}
\Delta G_d(\tau, \tau') = &-\{[\xi(\tau)+\xi_0]^2 + 1\}^{-1} \\
&\times\left[\frac{P}{\beta} \csc\left(\frac{\pi(\tau-\tau')}{\beta}\right) + \Delta[\xi(\tau)+\xi_0]\delta(\tau-\tau')\right] \\
&+ [1/2\pi\xi(\tau)][1/X^+(\tau) - 1/X^-(\tau)] \\
&\times\left[\xi_0[C(\tau') - C(\tau)]\frac{P\pi}{\beta} \csc\left(\frac{\pi(\tau'-\tau)}{\beta}\right)\right. \\
&\left. - \int_0^\beta dt\, C(t)\, S_p(t, \tau, \tau')\right] ,
\end{aligned} \tag{A33}$$

where S_p is the first term on the right in (A32), containing principal value parts only, and

$$C(t) = -\tfrac{1}{2}[X^+(t) - X^-(t)] \ . \tag{A34}$$

Equation (A33) may be compared to (3.23). The first term is just G_d^0 in the instantaneous potential $\xi(\tau)+\xi_0$, and we will not discuss it further. The second term in (A33) is regular at $\tau=\tau'$, and corresponds to the "transient" term introduced previously. Unfortunately, it cannot be simplified by analogy with the steps leading from (3.21) to (3.25) because $S_p(t,\tau,\tau')$ is not fully separable as is its counterpart in (3.22).

Now we will calculate the contribution of the transient part to the linked-cluster expression (2.27). To evaluate the equal-time limit, we use l'Hopital's rule and find

$$I\equiv-\int_0^\beta d\tau\, v(\tau)\, G_d(\tau,\tau^+)$$

$$=-\frac{1}{2\pi^2}\int_0^\beta d\tau\left(\frac{1}{X^+(\tau)}-\frac{1}{X^-(\tau)}\right)\int dt\,\frac{(P\pi/\beta)^2C(t)}{\sin^2[\pi(t-\tau)/\beta]}$$

$$-\frac{\xi_0}{2\pi}\int_0^\beta d\tau\left(\frac{1}{X^+(\tau)}-\frac{1}{X^-(\tau)}\right)\frac{dC(\tau)}{d\tau}\,. \qquad \text{(A35)}$$

In the first term in (A35) we integrate by parts on t. The end contributions vanish because of the periodicity of all the functions and this term becomes

$$-\frac{1}{2\pi^2}\int_0^\beta d\tau\left(\frac{1}{X^+(\tau)}-\frac{1}{X^-(\tau)}\right)$$

$$\int_0^\beta dt\;\frac{P\pi}{\beta}\,\mathrm{ctn}\left(\frac{\pi(t-\tau)}{\beta}\right)\frac{dC(t)}{dt}\,. \qquad \text{(A36)}$$

The order of the t and τ integrations may be interchanged, since the principal value defines the positions of the singularities. Since $X(z)$ is analytic except for a real-axis cut and has no zeros in the finite z plane, the same is true of the function $1/X(z)$. Considering its periodicity, we can use (A6) and (A11) to write

$$\int_0^\beta d\tau\,\frac{P\pi}{\beta}\,\mathrm{ctn}\left(\frac{\pi(t-\tau)}{\beta}\right)\left(\frac{1}{X^+(\tau)}-\frac{1}{X^-(\tau)}\right)$$

$$=-\pi i\left(\frac{1}{X^+(t)}+\frac{1}{X^-(t)}\right). \qquad \text{(A37)}$$

Changing τ to t in the second integral in (A35) allows these terms to be combined:

$$I=-\frac{1}{2\pi i}\int_0^\beta dt\left(\frac{1+i\xi_0}{X^+(t)}+\frac{1-i\xi_0}{X^-(t)}\right)\frac{dC(t)}{dt}\,. \qquad \text{(A38)}$$

Using X without superscript to represent the principal value part in the exponent, this can be simplified to

$$I=\pi^{-1}\sec\eta_0\int_0^\beta dt\,X^{-1}(t)\cos\eta(t)\frac{d}{dt}\left[X(t)\sin(\eta(t)-\eta_0)\right]. \qquad \text{(A39)}$$

The term

$$\int_0^\beta dt\cos\eta(t)\frac{d}{dt}\sin[\eta(t)-\eta_0] \qquad \text{(A40)}$$

is zero because $\eta(\beta)=\eta(0)$ and the integrand depends on t only through η, which is the effective variable of integration.

The other term is

$$I=+\left(\frac{\sec\eta_0}{\pi^2}\right)\int_0^\beta dt\,dt'\cos\eta(t)\sin[\eta(t)-\eta_0]$$

$$\times\frac{d\eta(t')}{dt'}\,\frac{P\pi}{\beta}\,\mathrm{ctn}\left(\frac{\pi(t'-t)}{\beta}\right), \qquad \text{(A41)}$$

where we have taken the t derivative through the t' integral as in (3.32) to (3.33), but made use only of the periodicity of $\xi(t)$ to drop the end contributions.

For $\xi_0=0$, this is the same as (3.35) with

$$\frac{1}{(\tau-\tau')}\to\frac{\pi}{\beta}\,\mathrm{ctn}\left(\frac{\pi(\tau-\tau')}{\beta}\right). \qquad \text{(A42)}$$

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Thermal Shift of a Mössbauer Gamma Ray at a Magnetic Phase Transition

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The thermal shift of the ^{57}Fe Mössbauer γ ray in rhombohedral FeF_3 gives a weak indication of a magnetization-dependent Debye temperature. A small isomer-shift discontinuity exists at the transition to cubic structure at high temperature.

Effects of magnetic phase transitions on the Mössbauer effect thermal shift in insulators have recently received both theoretical[1] and experimental attention.[2] We have examined this effect in the compound FeF_3 and find a small magnetization-dependent change in the Debye temperature below the Curie point. This result is in accord with theoretical estimates[1] but differs from experimental results in another similar system.[2]

The thermal shift δE_T arises through the second-order relativistic Doppler effect from the thermal motion of atoms in a solid. It is related to the kinetic energy of atoms, and therefore to the lattice heat capacity[3] and internal energy per atom, U, by the equation

$$\delta E_T/E = -U/2Mc^2, \tag{1}$$

where E is the energy of the γ ray and c the velocity of light. The internal energy should include the zero-point energy U_0 in addition to the usual expression. In the Debye approximation, the zero-point energy is

$$U_0 = \tfrac{9}{8}k\Theta, \tag{2}$$

where Θ is the Debye temperature. The temperature-dependent term is