Functional-Integral Approaches to the Anderson Model: A Comparison of Results in Limiting Cases

R. F. Hassing*† and D. M. Esterling*
Department of Physics, Indiana University, Bloomington, Indiana 47401
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Functional-integral approaches to the Anderson model are checked and compared in simple limiting cases. We examine eight approximation schemes and no single scheme is found to perform correctly in all of the ten limiting cases. The two most sophisticated schemes we have investigated are those of Keiter and Hamann, respectively. The former suffers from deficiencies inherent in the 1-field functional-integral formalism (as described by Keiter), the latter from difficulties related to the extremal approximation to the y field.

I. INTRODUCTION

During the last three years the method of functional integration has been extensively applied to the calculation of the partition function and magnetic susceptibility of the Anderson model.[1] The crucial term in the Hamiltonian is the two-body interaction

$$Un_\uparrow n_\downarrow \tag{1.1}$$

describing the repulsion between electrons on the d site, where $n_\sigma = d_\sigma^\dagger d_\sigma$ is the number operator for the d level. The functional-integral (FI) transformation can be applied, however, only to cases in which the perturbation is of the form

$$\sum_r \alpha_r O_r^2 \ , \tag{1.2}$$

where O_r is a quantum mechanical operator. Accordingly, (1.1) must be appropriately transformed. Since there are many ways of casting (1.1) in the form (1.2), there are correspondingly many FI schemes. Principal among them are the "1-field" formalism, corresponding to

$$Un_\uparrow n_\downarrow = \tfrac{1}{2} U(n_\uparrow + n_\downarrow) - \tfrac{1}{2} U(n_\uparrow - n_\downarrow)^2 \tag{1.3}$$

(the first term on the right-hand side is then absorbed in the unperturbed Hamiltonian), which has been investigated by Schrieffer, Evenson, and Wang[2,3] and by Keiter,[4] and the "2-field" formalism, corresponding to

$$Un_\uparrow n_\downarrow = \tfrac{1}{4} U(n_\uparrow + n_\downarrow)^2 - \tfrac{1}{4} U(n_\uparrow - n_\downarrow)^2 \ , \tag{1.4}$$

which has been employed by Hamann.[5] Within each of these formalisms, moreover, one must make approximations. As a result, there has arisen a somewhat bewildering series of FI schemes: 1-field static, 2-field static, 2-field static with extremal approximation to the y field, 1- and 2-field random-phase approximation (RPA) and RPA′, not to mention quartic′, Hamann's hopping function, and Keiter's particle-hole ladder sum. For the intrepid, 3-field and 4-field formalisms are also possible. As is fairly well known, not all of the schemes perform equally well in limiting cases, and to date, none has provided an adequate theory of the Kondo regime $U/\Gamma \gg 1$, where Γ is the d-level width.

In order to clarify the situation for those following the literature, we have looked at the most important of these schemes in various simple limiting cases in which the answer is known from less sophisticated (usually perturbation-theoretic) methods. Each of the FI schemes claims to be exact in certain limiting cases. (We include mean-field theory as a "limiting case" even though it does not refer to a limiting value of U/Γ.) Our summary aims to compare the schemes and make clear in what sense a given FI scheme is "correct" in the limit of weak and strong coupling, $U/\Gamma \ll 1$ and $U/\Gamma \gg 1$, respectively. We shall see that no single FI scheme gives the correct result in all of the limit cases. In addition, by investigating the behavior for vanishing Γ we gain insight into the validity of various schemes for finite Γ. Our results are displayed in Table I. The following is a discussion of the indicated schemes and limits. For the sake of brevity we have not described in detail the eight FI schemes listed on the vertical axis, but have merely indicated the features which distinguish each from the others (Sec. II). The reader is referred to the original works for a more comprehensive description of the schemes. In Sec. III we explain what is meant by each of the limits listed on the horizontal axis of the table and analyze the behavior of the various FI schemes.

II. FI SCHEMES

The FI method effectively transforms a two-body interaction into a one-body interaction with time-dependent external fields which are to be averaged over with Gaussian weight.[2,4,5] Specifically, one begins with the partition function

$$Z = \mathrm{Tr} e^{-\beta(H_0 + H_1)} \ , \tag{2.1}$$

where in the present case

$$H_0=\sum_{k\sigma}\epsilon_{k\sigma}c^\dagger_{k\sigma}c_{k\sigma}+\sum_{k\sigma}(V_{kd}c^\dagger_{k\sigma}d_\sigma+\text{H.c.})+\sum_\sigma\epsilon_d d^\dagger_\sigma d_\sigma \ . \tag{2.2}$$

Energies are measured from the Fermi surface and H_1 is given by (1.3) or (1.4). The width of the d level is $\Gamma=\pi|V_{kd}|^2N_0$, where N_0 is the density of band states at the Fermi surface. Under the FI transformation, (2.1) becomes [choosing (1.3) for H_1, as done in Refs. 2–4]

$$Z=\int D\xi e^{-\|\xi\|^2}Z[\xi] \ , \tag{2.3}$$

in which $\xi(\tau)$ is any real continuous function on $[0,1]$, $\int D\xi$ indicates functional integration over all ξ's, $\|\xi\|^2=\pi\int_0^1 d\tau\,\xi(\tau)^2$, and

$$Z[\xi]=Z_0\times\langle T\exp\{(2\pi\beta U)^{1/2}\int_0^1 d\tau\,\xi(\tau)[n_\uparrow(\tau)-n_\downarrow(\tau)]\}\rangle_0 . \tag{2.4}$$

The measure $D\xi$ is represented in terms of the Fourier coefficients of $\xi(\tau)$, Z_0 is the partition function for $H_0+\frac{1}{2}U(n_\uparrow+n_\downarrow)$. Using nonequilibrium-Green's-function techniques,[2] one finds that

$$Z[\xi]=Z_0\exp\left(\sum_{n\sigma}e^{i\omega_n 0^+}\{\ln(1-\underline{K}^\sigma[\xi])\}_{nn}\right) , \tag{2.5}$$

in which $\underline{K}^\sigma$ is a matrix in discrete frequency variables:

$$(\underline{K}^\sigma[\xi])_{nn'}=-(2\pi\beta U)^{1/2}\sigma\xi_{n-n'}G^0_\sigma(n') \ . \tag{2.6}$$

In (2.6), $\sigma=+1\,(-1)$ for up (down) spin and $\xi_{n-n'}$ is the $n-n'$ Fourier coefficient of $\xi(\tau)$. $G^0_\sigma(n')$ is the d-level Green's function for $H_0+\frac{1}{2}U(n_\uparrow+n_\downarrow)$ given by

$$G^0_\sigma(n)=[i\omega_n-\beta(\epsilon_d+\tfrac{1}{2}U)-S_\sigma(n)]^{-1} \ , \tag{2.7}$$

where

$$S_\sigma(n)=\beta^2\sum_k|V_{kd}|^2(i\omega_n-\beta\epsilon_k)^{-1}$$

and $i\omega_n=i(2n+1)\pi$. Equations (2.3) and (2.5) are the basic equations of the 1-field formalism. Using (1.4) for H_1 leads to the 2-field formalism in which

$$Z=\int DX\int DY\,e^{-\|X\|^2-\|Y\|^2}Z[XY] \ , \tag{2.8}$$

with

$$Z[XY]=Z_0\exp\left(\sum_n e^{i\omega_n 0^+}\{\ln(1-\underline{K}^\sigma[XY])\}_{nn}\right) \tag{2.9}$$

and

$$(\underline{K}^\sigma[XY])_{nn'}=-\frac{(\pi\beta U)^{1/2}(\sigma x_{n-n'}+iy_{n-n'})}{i\omega_{n'}-\beta\epsilon_d-S_\sigma(n')} \ . \tag{2.10}$$

In the 2-field formalism the coupling constant for the "time"-dependent problem is $(\pi\beta U)^{1/2}$ as opposed to $(2\pi\beta U)^{1/2}$ in the 1-field formalism, and the d-level energy is not shifted by $\frac{1}{2}U$. It should be noted that (1.3) introduces interactions between d electrons of equal spin. This leads to technical difficulties as discussed by Keiter.[4] The 2-field

TABLE I. Performance of functional-integral schemes in limiting cases.

Schemes		Limits 1: $T>0$ lim $\Gamma\to 0$	2: $T\to 0$ lim $\Gamma\to 0$	3: $\Gamma\to 0$ lim $T\to 0$	4: $O(\Gamma/U)$	5: $O(\Gamma^2/U^2)$	6: $O(U/\Gamma)$	7: HF	8: $T>0$ lim $U\to 0$	9: $T\to 0$ lim $U\to 0$	10: $U\to 0$ lim $T\to 0$
1. 1-field static (Refs. 2 and 3)	1-field	yes	yes	yes	no	no	no	no	yes	yes	yes
2. 1-field RPA′ (Refs. 2 and 3)	1-field	yes	yes	yes	no	no	yes	no	yes	yes	yes
3. Amit–Bender (Ref. 9)	1-field	yes	yes	yes	no	no	no	no	yes	yes	yes
4. Keiter (Ref. 4)	1-field	yes	yes	yes	yes	yes	yes	no	yes	yes	yes
5. 2-field static	1-field	yes	yes	⋯	yes	no	yes	yes	yes	yes	yes
6. 2-field static, extremal[a] y_0	2-field	no	yes if $-\frac{3}{4}U<\epsilon_d<-\frac{U}{4}$	yes if $-\frac{3}{4}U<\epsilon_d<-\frac{U}{4}$	yes	no	yes	yes	yes	yes	yes
7. 2-field RPA′	2-field	yes	yes	⋯	yes	no	yes	no	yes	yes	yes
8. Hamann (Ref. 5)	2-field	no	yes if $-\frac{3}{4}U<\epsilon_d<-\frac{U}{4}$	yes if $-\frac{3}{4}U<\epsilon_d<-\frac{U}{4}$	⋯	⋯	⋯	yes	yes	yes	yes
		Z	GS energy, $\Gamma=0$			χ_{dc}			Z	GS energy, $U=0$	

[a] Extremal approximation to the y_0 integration: $y_0=i(\beta U/4\pi)^{1/2}$.

scheme based on (1.4) does not introduce interactions between electrons of equal spin, and therefore avoids the extensive "renormalization" procedure required in Keiter's calculation.[6] As we shall see, however, neither formalism is free from defects. Note that, given (2.5), (2.3) assumes the form

$$Z = Z_0 \int D\xi e^{-\beta F[\xi]} \tag{2.11}$$

and similarly for the 2-field formalism, Eq. (2.8).

Given the basic equations of the 1- and 2-field formalisms, the various FI schemes may be regarded as approximations to the exponent in (2.5) and/or (2.9). Hence all the schemes lead to a Z of the general form (2.11), in which each scheme produces a particular approximate F. For example, expanding $\ln(1-\underline{K})$ to second-order results in the RPA. This approximation is only good for $U/\Gamma \ll 1$ and introduces mathematical (nonphysical) divergences for $U/\Gamma \approx 1$. It is not, therefore, of much use for arbitrary U/Γ. The simplest useful scheme is the static approximation in which the range of functional integration in (2.3) [or (2.8)] is restricted to "time"-independent constants ξ_0 (or x_0, y_0). In other words, one sets $\xi_{n-n'} = \delta_{nn'}\xi_0$ in (2.6) [and similarly in (2.10)]. There results

$$Z_{\rm st} = Z_{\rm band}\int_{-\infty}^{\infty} d\xi_0 e^{-\beta F_{\rm st}(\xi_0)} \tag{2.12}$$

and a similar expression in variables x_0, y_0 for the 2-field formalism. Note that we have included the contribution from the last two terms on the right-hand side of (2.2) in $e^{-\beta F_{\rm st}}$. The forms of $F_{\rm st}$ may be obtained from Refs. 2, 4, and 5. These are the schemes listed in rows 1 and 5 of Table I. The ξ_0 (or x_0, y_0) integral(s) cannot be performed exactly for arbitrary values of U/Γ and our calculations rely on expansions of $F_{\rm st}$ appropriate to limiting values of U/Γ. The static approximation is of use, even though (2.12) cannot in general be evaluated, because $F_{\rm st}$ can be plotted for all values of U/Γ. For example, in the 1-field scheme the result is particularly simple: As a function of ξ_0, $F_{\rm st}$ has a single minimum at the origin for $U/\Gamma \ll 1$, and goes smoothly to a function with two minima, corresponding to up and down localized moments for $U/\Gamma \gg 1$.[2] The static approximation thus provides a qualitative insight into the transition from a Pauli susceptibility to a local moment regime.

Given the free-energy functionals $F_{\rm st}(\xi_0)$ and $F_{\rm st}(x_0, y_0)$ in the 1-field and 2-field formalisms, respectively, the extremal values of ξ_0 and x_0, y_0 can be determined from the equations

$$\frac{dF_{\rm st}}{d\xi_0}(\bar{\xi}_0) = 0 \ , \tag{2.13}$$

$$\frac{\partial F_{\rm st}}{\partial x_0}(\bar{x}_0\bar{y}_0) = \frac{\partial F_{\rm st}}{\partial y_0}(\bar{x}_0\bar{y}_0) = 0 \ . \tag{2.14}$$

[It is known that, in general, the extremal functions $\bar{\xi}(\tau)$ and $\bar{x}(\tau)$, $\bar{y}(\tau)$, which minimize (2.5) and (2.9), respectively, are "time" independent.[5,7]] Within the 2-field static approximation a further ("lower level") approximation results by simply setting $y_0 = \bar{y}_0$ as given by (2.14), and deleting the y_0 integration. This is the scheme listed in row 6 in the table. Justification for the extremal approximation to the y_0 integral (but not the x_0 integral) is based on the fact that the y field couples to the d-level charge density, $n_\uparrow + n_\downarrow$, which, it is argued,[5] undergoes negligible thermodynamic fluctuations (owing to a large energy cost) in comparison to the spin, $n_\uparrow - n_\downarrow$, to which is coupled the x field. This scheme, however, is attended by peculiarities, as Bari[8] has recently noted and as we shall discuss in Sec. III. For the moment let us note that setting $y_0 = i(\beta U/4\pi)^{1/2}$ (valid if $-U < \epsilon_d < 0$ for $\Gamma \to 0$) leads to an incorrect partition function as $\Gamma \to 0$, and, in general, to the wrong ground-state energy as $\Gamma \to 0$ (taking $\lim_{T\to 0}$ either before or after $\lim_{\Gamma\to 0}$). Note also that $y_0 = -i(\beta U/4\pi)^{1/2}$ appears in Hamann's paper[5] corresponding to a coupling constant $-(\pi\beta U)^{1/2}$ in (2.10). The difference in sign is unimportant.

The RPA′ scheme in rows 2 and 7 of the table results upon setting

$$\underline{K}^\sigma = \underline{K}_0^\sigma + \underline{K}_1^\sigma \tag{2.15}$$

in (2.5) or (2.9), where $\underline{K}_0^\sigma$ in the diagonal part of $\underline{K}^\sigma$ (leading to the static approximation), writing

$$\ln(1-\underline{K}^\sigma) = \ln(1-\underline{K}_0^\sigma) + \ln[1-(1-\underline{K}_0^\sigma)^{-1}\underline{K}_1^\sigma] \tag{2.16}$$

and expanding the second term to second order. (Expanding to fourth order gives the quartic′ as discussed in Ref. 3. We have not included it since it offers no advantage in the physically interesting regime $U/\Gamma \gg 1$.) There results

$$Z_{\rm RPA'} = Z_{\rm band}\int_{-\infty}^{\infty} d\xi_0 \times \exp\left(-\beta F_{\rm st} - \sum_{\nu>0}\ln[1-2\beta U\Phi_\nu(\xi_0)]\right) \ , \tag{2.17}$$

in which $\Phi_\nu(\xi_0)$ is a polarization bubble, as described in Refs. 2 and 4.

At this point we note an interesting feature of the static approximation: If $\xi(\tau)$ is restricted to a τ-independent constant, (2.4) may be written

$$Z(\xi_0) = \mathrm{Tr}\exp\{-\beta[H_0 - (2\pi U/\beta)^{1/2}(n_\uparrow - n_\downarrow)\xi_0]\} \ . \tag{2.18}$$

In general, however, the explicit "time" dependence of $\xi(\tau)$ requires the presence of the T operator in (2.4). Thus only in the static approximation do we have $Z = \int d\xi_0 e^{-\pi\xi_0^2} Z(\xi_0)$, in which $Z(\xi_0)$ is a "true" partition function in the sense

that it can be written $\mathrm{Tr}e^{-\beta H}$. This fact may well be of no importance and has been so treated, yet to our knowledge no one has investigated this by examining the connection between the finite frequency variables ξ_ν and the noncommutativity of H_1 and H_0. For if $[H_1, H_0]=0$ the "time"-ordering operator in (2.4) is unimportant and the static approximation becomes exact.

The scheme of Amit and Bender,[9] row 3 of the table, may be most easily understood in contrast to the RPA′: Instead of expanding the second term of (2.16) to second order in all the variables ξ_ν [Fourier coefficients of $\xi(\tau)$], it was treated to all orders in the two variables ξ_1 and ξ_{-1}. The partition function was then given as an integral over variables ξ_0, ξ_1, ξ_{-1}. While this scheme offers no advantage over RPA′ from the viewpoint of simple limit cases, it sheds light on the form of the functional $F[\xi]$, which was the main intent of the paper. Its chief drawback lies in the fact that all variables ξ_ν for $\nu \leq \beta\Gamma/2\pi$ are believed to be important[3,9] and therefore, as $T \to 0$, one must worry about ξ_ν for many values of the frequency index ν not only $0, \pm 1$.

The remaining two schemes in the table are those of Keiter[4] and Hamann,[5] listed in rows 4 and 8. They represent more advanced (higher level) approximations than the other schemes, and are aimed at the problems encountered in the Kondo regime ($\Gamma \ll U$). Keiter used the 1-field formalism, comparing the FI method with standard diagrammatic perturbation theory. In this way he demonstrated the complications resulting from artificially introduced interactions between electrons of equal spin, endemic to the 1-field formalism and of importance when $U/\Gamma \gg 1$. Following a renormalization procedure (valid for $U/\Gamma \gg 1$) designed to overcome this difficulty, a particular subset of diagrams (the particle-hole ladder series) was summed and inserted in the FI expression for the partition function. It was shown that the resulting dc susceptibility contained a Kondo-like logarithmic divergence in $O(\Gamma^2/U^2)$. We note that Keiter's calculation can be more easily done within the 2-field formalism since the renormalization procedure mentioned previously is circumvented; there are interactions between electrons of opposite spin only.

Hamann's scheme uses the 2-field formalism with extremal approximation to the y_0 integration. An approximation to the exponent of (2.9) is made based on the physical idea that certain functions $x(\tau)$—the "hopping paths" describing spin flips on the d level—provide the dominant contribution to the partition function for $U/\Gamma \gg 1$ and low temperatures. Using the technique of Nozières and De-Dominicis (ND)[10] Hamann obtained a partition function identical to that derived by Yuval and Anderson[11] for the Kondo Hamiltonian (also based on ND [10]). No explicit calculation of the susceptibility was given, although results from the Yuval–Anderson theory were cited.[12] We note that as T decreases below the Kondo temperature the number of hops (measured by T_K/T)[13] and thus the amplitude of the high-frequency components of the field $x(\tau)$ (each hop being of duration $\tau \approx 1/U$) become increasingly large. (The contribution from the nonhorizontal portions of the paths is contained in the "transient" term T.) The ND approximation, however, is an asymptotic approximation, correctly describing only the large "time" response, $\tau \gg 1/U$, of the d level to the random field $x(\tau)$. The validity of the ND approximation in describing the d-level response therefore comes in question[14]: Does the approximate Green's function adequately describe the response of the d level to the hopping paths for $T \ll T_K$? Hamann has presented arguments in support of the ND approximation, notably that the resulting partition function is insensitive to the high-frequency details of the paths. Schotte and Schotte,[15] based on numerical calculations of the Yuval–Anderson s-d model,[11] have asserted the adequacy of the asymptotic time approximation. A discussion of Refs. 11, 12, and 15 is beyond the scope of this paper, since they involve the scaling approach to the s-d model. The issue, however, has to our knowledge not been definitively resolved. In any event, leaving aside the question of the transient term and the ND approximation, the use of the extremal approximation for the y field leads to difficulties (Sec. III) and is, in our view, an unsound basis for higher approximations.

It is worthwhile noting that the Keiter and Hamann schemes proceed from fundamentally different points of view: Keiter's method is formalistic, relying on a diagrammatic calculation, while Hamann's is intuitive, relying on physical insights about the nature of paths in function space. Schrieffer has also investigated this approach (the "time-domain approach"[3]) although apparently without conclusive results.[16] At present no connection between the two has been established. It would be of interest to see whether or not the diagrammatic series and the hopping paths are in any way related.

In Sec. III we explain the ten limiting cases listed along the top of Table I and discuss the behavior of the FI schemes in greater detail.

III. LIMITS

In this section we explain the limits and discuss the performance of the schemes in each case. Where "$T \to 0$" is written, it refers to the thermodynamic potential; that is, we are then talking about a ground-state (GS) energy, $\lim_{T\to 0}(-k_B T$

$\times \ln Z$). Furthermore, for $U=0$ or $\Gamma=0$ the partition function for the Anderson model can be calculated exactly, hence one can speak of an "exact" $U=0$ or $\Gamma=0$ partition function (and/or GS energy). We discuss the simplest cases first, those in which $U/\Gamma \ll 1$.

Table I, columns 8–10. $T>0$, $\lim_{T\to 0}$; $\lim_{T\to 0} \lim_{U\to 0}$; $\lim_{U\to 0} \lim_{T\to 0}$; these refer to the cases in which U is set equal to zero—with T nonzero (column 8); before T is set equal to zero (column 9); and after T is set equal to zero (column 10). For $U=0$, the Anderson model becomes a simple one-body problem. All the FI schemes reproduce the exact $U=0$ partition function (and susceptibility). In particular, the order of limits $T\to 0$, $U\to 0$, is unimportant. Note lastly that a "yes" in column 8 guarantees a "yes" in column 9. A "yes" in column 9, however, need not imply a "yes" in column 8, for a GS energy may be right even though the partition function is wrong. The $U=0$ cases are somewhat trivial and have been included for completeness. (The $\Gamma=0$ cases are not so trivial.)

Table I, column 6. $O(U/\Gamma)$; columns 4–6 refer to the (weak-field) dc susceptibility of the d level calculated to low orders in U/Γ or Γ/U as indicated. The exact dc susceptibility to first order in U/Γ can be obtained using standard techniques and is given by

$$\chi^{O(U/\Gamma)} = 2\mu_B^2 A_d(0)[1 + UA_d(0)] \ , \tag{3.1}$$

in which $A_d(0)$ denotes the d-level spectral form or "state density" evaluated at the Fermi surface. In the "symmetric" case, $\epsilon_d = -\frac{1}{2}U$, $A_d(0) = 1/\pi\Gamma$.

Within the FI approach, the d-level susceptibility is given by

$$\chi = \begin{cases} \dfrac{\mu_B^2}{U}\,(2\pi\langle \xi_0^2\rangle_{\rm FI} - 1) & \text{(1 field)} \\ \dfrac{2\mu_B^2}{U}\,(2\pi\langle x_0^2\rangle_{\rm FI} - 1) & \text{(2 field)} \end{cases} \ , \tag{3.2}$$

where

$$\langle \xi_0^2\rangle_{\rm FI} = \frac{\int D\xi\ \xi_0^2 e^{(-\beta F[\xi])}}{\int D\xi\ e^{(-\beta F[\xi])}} \tag{3.3}$$

and similarly for the 2-field formalism. Each FI approximation scheme for $U/\Gamma \ll 1$ leads to an expression for F which is minimized in ξ_0 at $\xi_0 = 0$ (or $x_0 = 0$ for fixed y_0). Expanding F in ξ_0 (or x_0) to second order leads to a simple Gaussian integral for $\langle \xi_0^2\rangle_{\rm FI}$ (or $\langle x_0^2\rangle_{\rm FI}$). The resulting expression for x can be compared with (3.1) above. For example the 1-field static approximation yields

$$\chi = 2\mu_B^2 A_d(0)[1 + 2UA_d(0)] \ . \tag{3.4}$$

The coefficient of U is incorrect by a factor of 2,[2–4] hence a "no" appears in row 1, column 6 of the table. All the remaining schemes give the correct result.

Table I, column 7. Hartree–Fock (HF); here we are concerned with the relation between the FI method and the mean-field theory of the Anderson model.[1] Applying a mean-field or "Hartree–Fock" approximation to the interaction term $Un_\uparrow n_\downarrow$ leads to a self-consistent equation for the d-level occupation:

$$\langle n_\sigma\rangle = \frac{1}{2} - \frac{1}{\pi}\tan^{-1}\left(\frac{\epsilon_d + U\langle n_{-\sigma}\rangle}{\Gamma}\right) \ . \tag{3.5}$$

Column 7 then answers the following question: Can Eqs. (2.13) and (2.14) for the extremal values $\bar{\xi}_0$ and $\bar{x}_0, \bar{y}_0$ be made identical to (3.5) for all $\bar{Y}/\Gamma$ by appropriately relating $\langle n_\sigma\rangle$ to $\bar{\xi}_0$ or $\bar{x}_0$, y_0? All 1-field schemes fail: In the static approximation, (2.13) can be transformed to (3.5) but with a factor of $2/\pi$ instead of $1/\pi$. The RPA′ scheme is valid only for $U<\pi\Gamma$ and gives a free-energy functional divergent for $2U=\pi\Gamma$. Keiter's scheme (aimed at the local-moment regime) involves an expression for Z which is valid only for $\Gamma/U \ll 1$ and which therefore corrects the deficiencies of the 1-field scheme only in that region. (Using Keiter's approach within the 2-field formalism produces a "yes" in this column.)

The 2-field schemes are consistent with mean-field theory, with the exception of the 2-field RPA′ which, similar to the 1-field RPA′, leads to a logarithmically divergent free-energy functional for $U=\pi\Gamma$. Specifically, the mean-field quantities $\langle N\rangle = \langle n_\uparrow\rangle + \langle n_\downarrow\rangle$ and $\langle \sigma_z\rangle = \langle n_\uparrow\rangle - \langle n_\downarrow\rangle$ are related to the extremal values $\bar{x}_0$ and $\bar{y}_0$ according to

$$\bar{x}_0 = \left(\frac{\beta U}{4\pi}\right)^{1/2}\langle \sigma_z\rangle, \quad \bar{y}_0 = i\left(\frac{\beta U}{4\pi}\right)^{1/2}\langle N\rangle \ . \tag{3.6}$$

Equations (3.6) will be important for the discussion of the extremal approximation of row 6 of the table.

Columns 6–10 (in particular columns 6 and 7) check the behavior of the FI schemes for small U/Γ (recall that mean-field theory is valid for small U/Γ). We now turn to their behavior for large U/Γ.

Table I, column 1. $T>0$, $\lim_{\Gamma\to 0}$; one sets $\Gamma=0$ in the expression for Z obtained in each FI scheme and compares the result with the exact $\Gamma=0$ partition function. All schemes reproduce the exact result except the 2-field static scheme with extremal approximation to the y_0 integral, row 6 in the table (as noted by Schrieffer and Wang[17] and by Bari[8]) and, therefore, Hamann's method (row 8 of the table), which incorporates it. Since the extremal approximation to the y_0 integral neglects charge fluctuations on the d level, and since charge fluctuations are strictly nonvanishing for $T>0$, it is not surprising that the scheme of row 6 pro-

duces the wrong $\Gamma = 0$ partition function. The difficulty, however, goes deeper than this as can be seen from the following. For $\Gamma = 0$, the partition function in the 2-field static approximation is easily shown to be[4]

$$Z_{\rm st}^{\Gamma=0} = Z_{\rm band}\int_{-\infty}^{\infty} dx_0 \int_{-\infty}^{\infty} dy_0 \times \exp\left(-\pi(x_0^2+y_0^2) + \sum_\sigma \ln(1+e^{-\beta E_\sigma(x_0 y_0)})\right) , \tag{3.7}$$

where

$$\beta E_\sigma(x_0 y_0) = \beta\epsilon_d - \alpha(\sigma x_0 + i y_0), \quad \alpha = (\pi\beta U)^{1/2} . \tag{3.8}$$

That is,

$$Z_{\rm st}^{\Gamma=0} = Z_{\rm band}\int_{-\infty}^{\infty} dx_0 \int_{-\infty}^{\infty} dy_0\, e^{-\pi(x_0^2+y_0^2)} \times (1 + e^{-\beta 2\epsilon_d + 2\alpha i y_0} + e^{-\beta\epsilon_d + \alpha x_0 + \alpha i y_0} + e^{-\beta\epsilon_d - \alpha x_0 + \alpha i y_0}) , \tag{3.9}$$

$$Z_{\rm st}^{\Gamma=0} = Z_{\rm band}(1 + 2e^{-\beta\epsilon_d} + e^{-\beta(2\epsilon_d + U)}) . \tag{3.10}$$

Note that $Z_{\rm st}^{\Gamma=0}/Z_{\rm band}$ is of the form $\sum_r e^{-\beta E_r}$, where $E_r = 0, \epsilon_d, \epsilon_d, 2\epsilon_d + U$, corresponding to states $|r\rangle = |0,0_\downarrow\rangle, |1,0_\downarrow\rangle, |0,1_\downarrow\rangle, |1,1_\downarrow\rangle$. The extremal equations (2.14) become [$F_{\rm st}(x_0 y_0)$ = exponent of (3.7)]

$$\sigma\bar{x}_0 - i\bar{y}_0 = (\beta U/\pi)^{1/2} f[\epsilon_d - (\pi U/\beta)^{1/2}(\sigma\bar{x}_0 + i\bar{y}_0)] \tag{3.11}$$

or, using (3.6),

$$\langle n_\sigma\rangle = f(\epsilon_d + U\langle n_{-\sigma}\rangle) . \tag{3.12}$$

f is the Fermi function. We thus recover the mean-field-theory result[1] for $\Gamma = 0$. For $T \to 0$ the Fermi function approaches a step function and the solutions of (3.11) and (3.12) are

$$\begin{array}{llll}
\langle n_\uparrow\rangle = 1, & \langle n_\downarrow\rangle = 0, & \bar{x}_0 = (\beta U/4\pi)^{1/2}, & \bar{y}_0 = i(\beta U/4\pi)^{1/2}, \\
\langle n_\uparrow\rangle = 0, & \langle n_\downarrow\rangle = 1, & \bar{x}_0 = -(\beta U/4\pi)^{1/2}, & \bar{y}_0 = i(\beta U/4\pi)^{1/2}, \\
\langle n_\uparrow\rangle = \langle n_\downarrow\rangle, & & \bar{x}_0 = 0, & \bar{y}_0 = i(\beta U/4\pi)^{1/2} 2\langle n_\sigma\rangle, \\
\langle n_\uparrow\rangle = \langle n_\downarrow\rangle = 0, & & \bar{x}_0 = 0, & \bar{y}_0 = 0, \\
\langle n_\uparrow\rangle = \langle n_\downarrow\rangle = 1, & & \bar{x}_0 = 0, & \bar{y}_0 = i(\beta U/\pi)^{1/2},
\end{array}
\begin{array}{l}
\left.\begin{array}{l}\\\\\\\end{array}\right\} -U < \epsilon_d < 0 \\
\epsilon_d > 0 \\
\epsilon_d + U < 0 .
\end{array} \tag{3.13}$$

The various values of $\bar{y}_0$ correspond to the d-level occupations $\langle N\rangle$, which for $\Gamma = 0$ and $T \to 0$ can only be 0, 1, 2 (recall Γ is the energy broadening of the d level). In particular, $\bar{y}_0 = i(\beta U/4\pi)^{1/2}$ means $\langle N\rangle = 1$. Setting $y_0 = i(\beta U/4\pi)^{1/2}$ in (3.9) and deleting the y_0 integration yields

$$Z^{\Gamma=0}_{{\rm st},y_0\ {\rm ext}} = Z_{\rm band} e^{\beta U/4}\int_{-\infty}^{\infty} dx_0\, e^{-\pi x_0^2} \times (1 + e^{-\beta(2\epsilon_d + U)} + e^{-\beta(\epsilon_d + U/2) - \alpha x_0} + e^{-\beta(\epsilon_d + U/2) + \alpha x_0}) \tag{3.14}$$

$$= Z_{\rm band}(e^{\beta U/4} + 2e^{-\beta\epsilon_d} + e^{-\beta(2\epsilon_d + 3U/4)}). \tag{3.15}$$

As in (3.10), the partition function (3.15) is that for a 4-state system (the d orbital) but with energies $-\frac{1}{4}U$, ϵ_d, ϵ_d, $2\epsilon_d + \frac{3}{4}U$; the states with $\langle N\rangle = 0, 2$ are thus assigned the wrong energies, $-\frac{1}{4}U$, $2\epsilon_d + \frac{3}{4}U$, respectively. Accordingly, the ground-state energy is

$$E_{\rm GS}^{\Gamma=0} = E_{\rm band}^0 + \begin{cases} -\frac{1}{4}U, & -\frac{1}{4}U < \epsilon_d < 0 \\ \epsilon_d, & -\frac{3}{4}U < \epsilon_d < -\frac{1}{4}U \\ 2\epsilon_d + \frac{3}{4}U, & -U < \epsilon_d < -\frac{3}{4}U \end{cases} . \tag{3.16}$$

In order to obtain the correct partition function and ground-state energy for $\Gamma = 0$ using an extremal approximation to the y_0 integration, one must use different values of $\bar{y}_0$ in the four terms of (3.9), appropriate to the occupation of the four states to which the terms respectively correspond. Furthermore, since a nonzero Γ merely broadens the atomic levels, this difficulty persists for finite but small Γ/U. However, the use of separate $\bar{y}_0$'s for each term in Z is then impossible since Z is no longer a sum of four terms. Before discussing this case (column 3 of the table), we describe the ground-state-energy limit of column 2.

Table I, column 2. $\lim_{T\to 0}\lim_{\Gamma\to 0}(-k_B T \ln Z)$; a "yes" in column 1 clearly implies a "yes" in column 2, hence only schemes 6 and 8 are of interest, because a "no" in column 1 could still be followed by a "yes" in column 2. As shown above, however, the schemes employing the extremal approximation [$\bar{y}_0 = i(\beta U/4\pi)^{1/2}$] to the y_0 integration yield the correct $\Gamma = 0$ ground-state energy $E_{\rm band}^0 + \epsilon_d$ (for $-U < \epsilon_d < 0$) only if $-\frac{3}{4}U < \epsilon_d < -\frac{1}{4}U$.

Table I, column 3. $\lim_{\Gamma\to 0}\lim_{T\to 0}(-k_B T \ln Z)$; the limit of column 2 cannot be taken if we require $k_B T < \Gamma$. For example, the explicit form of $F_{\rm st}(\xi_0)$ shown in Refs. 2 and 4 was derived for the case $\beta\Gamma \gg 1$. We therefore consider the reverse order of limits: first $T \to 0$, then $\Gamma \to 0$.

Our procedure in this case was to begin with the forms of $F_{\rm st}(\xi_0)$ and $F_{\rm st}(x_0 y_0)$ appropriate to $\beta\Gamma \gg 1$, expand to $O(\Gamma/U)$ about the minima for $\Gamma/U \ll 1$, take $\lim_{T\to 0}(-k_B T \ln Z)$, and then set $\Gamma = 0$. This is essentially a steepest descent evaluation of Z and after the limits $T \to 0$, $\Gamma \to 0$ are taken, the resulting

ground-state energy is simply the minimal value of F_{st}. For example, if $\beta\Gamma \gg 1$ the form of the 2-field static-free-energy function(al) is

$$\beta F_{st}(x_0 y_0) = \pi(x_0^2 + y_0^2) + \beta\epsilon_d - \alpha i y_0 + \frac{1}{\pi}\sum_\sigma \left\{ \frac{\beta\Gamma}{2} \ln\left[1 + \left(\frac{E_\sigma}{\Gamma}\right)^2\right] - \beta E_\sigma \tan^{-1}\frac{E_\sigma}{\Gamma} \right\}, \tag{3.17}$$

where E_σ is given by (3.8). For $-U < \epsilon_d < 0$ and $\Gamma \ll U$ the extremal Eqs. (2.14) [identical with (3.5), using (3.6)], give a minimum at $\bar{y}_0 = i(\beta U/4\pi)^{1/2}$, $\bar{x}_0 = \pm(\beta U/4\pi)^{1/2}$. From (3.17) we find, for $\Gamma \to 0$,

$$\beta F_{st}\left[\pm\left(\frac{\beta U}{4\pi}\right)^{1/2}, i\left(\frac{\beta U}{4\pi}\right)^{1/2}\right] = \beta\epsilon_d + O\left(\frac{\Gamma}{U}\right) \tag{3.18}$$

as desired. However, an additional calculation shows

$$\beta F_{st}\left[0, i\left(\frac{\beta U}{4\pi}\right)^{1/2}\right] = \begin{cases} -\beta U/4\pi + O(\Gamma/U), & -\frac{1}{2}U < \epsilon_d < 0 \\ \beta(2\epsilon_d + \frac{3}{4}U) + O(\Gamma/U), & -U < \epsilon_d < -\frac{1}{2}U . \end{cases} \tag{3.19}$$

Thus for $-\frac{1}{4}U < \epsilon_d < 0$ or $-U < \epsilon_d < -\frac{3}{4}U$, the absolute minimum of $\beta F_{st}[x_0, i(\beta U/4\pi)^{1/2}]$ occurs at $x_0 = 0$ with value $-\frac{1}{4}\beta U$ or $\beta(2\epsilon_d + \frac{3}{4}U)$, respectively, not $\beta\epsilon_d$. The extremal approximation to the y_0 integral (row 6 and row 8, which incorporates it), therefore, receives a "yes if $-\frac{3}{4}U < \epsilon_d < -\frac{1}{4}U$" in column 3, as in column 2; the order of the $\Gamma \to 0$, $T \to 0$ limits does not matter. The 1-field schemes present no problem: The expansion of $\beta F_{st}(\xi_0)$ about the extremal points for $\Gamma/U \ll 1$ leads to

$$\beta F_{st}(\bar{\xi}_0) = \beta\epsilon_d + O(\Gamma/U) .$$

Hence there appears a "yes" in rows 1–4. Row 5, the 2-field static scheme, and row 7, which incorporates it, were left blank since our method of calculating the limit of column 3 is equivalent to an extremal approximation; a true calculation of $\lim_{\Gamma\to 0}\lim_{T\to 0}(-k_B T \ln Z)$ requires an exact evaluation of $\int dx_0\, dy_0\, e^{-\beta F_{st}(x_0 y_0)}$ using (3.17) for βF_{st}, followed by the indicated limits. This we have been unable to do, and have therefore made no entry in column 3, rows 5 and 7.

Table I, column 4. $O(\Gamma/U)$ (dc susceptibility): to $O(\Gamma/U)$ the dc susceptibility of the Anderson model[18] is

$$\chi = \frac{\mu_B^2}{k_B T}\left(1 - \frac{8\Gamma}{\pi U}\right). \tag{3.20}$$

The 1-field formalism of rows 1 and 2 yield $(\mu_B^2/k_B T)(1 - 4\Gamma/\pi U)$, incorrect by the characteristic factor of 2. Keiter[4] has shown that this failure is due to the inability of the static and RPA′ approximations to sum diagrams with interactions between electrons of equal spin which are artificially introduced by (1.3). Keiter's renormalization procedure involved summing these diagrams such that the correct susceptibility is recovered.

Since the 2-field formalism does not introduce interaction between electrons of equal spin, the correct dc susceptibility is recovered to $O(\Gamma/U)$[19] by all the FI schemes based upon it.

Table I, column 5. $O(\Gamma^2/U^2)$ (dc susceptibility): the Schrieffer–Wolff transformation connects the Kondo Hamiltonian and Anderson Hamiltonian for $\Gamma/U \ll 1$ according to $J = 8\Gamma/\pi U$. Logarithmic divergences should, therefore, appear in the coefficient of the Γ^2/U^2 term in the dc susceptibility of the Anderson model. (Ultimately one hopes to see a treatment of the Anderson model for $\Gamma/U \ll 1$ in which these divergences are removed.) Keiter's scheme is the only one to reproduce this behavior.

No calculation of the susceptibility was presented in Hamann's paper. His partition function is identical to that of Ref. 11 which in turn is equivalent to the partition function of certain classical one-dimensional systems (charged rods and Ising model with logarithmic and inverse-square interactions, respectively) and has been studied by Anderson, Yuval, and Hamann.[12] Computer calculations of the static susceptibility have been made by Schotte and Schotte,[15] who found Curie–Weiss behavior at high temperatures and a finite susceptibility at $T = 0$. A closed analytic expression for the susceptibility was not given.

IV. CONCLUSION

The FI method as applied to the Anderson model remains enigmatic. It offers itself in general as the method most capable of treating the Anderson model for all values of U/Γ within a single approximation. In particular, one hopes for a good description of both the Kondo regime ($U/\Gamma \gg 1$) and the intermediate coupling case ($U/\Gamma \approx 1$). Presently, neither case has been adequately treated. We think it not unfair to require that prior to a successful attack on these problems, the simpler cases listed in Table I be correctly described. The two most sophisticated schemes are those of Keiter and Hamann. As we have seen, none of the schemes gets a "yes" across all columns. Keiter's scheme comes closest but is in general not consistent with mean-field theory. This difficulty can be removed by applying his technique within the 2-field formalism. The calculation is straightforward and leads to the same result for the dc susceptibility while avoiding the "renormalization" procedure required for the 1-field formalism. It is doubtful, however, that his diagrammatic-FI approach can be extended to the intermediate cou-

pling case, for it is generally agreed that for $U \approx \Gamma$ no particular subset of diagrams is dominant. Furthermore, having obtained a Kondo-like logarithmic divergence, it is not clear how to renormalize such that a well-behaved local moment susceptibility, consistent with experiment, results.

Hamann's scheme, less formalistic and perhaps on firmer ground than Keiter's in terms of physical insight, suffers from the two difficulties discussed in Sec. III; the extremal approximation to the y field does not appear to be as innocuous as previously thought, and the ND approximation may be only marginally adequate for the calculation of the d-state Green's function for the "time"-dependent problem.

The 2-field formalism without extremal approximation thus appears to us to be the best framework for more powerful schemes. Furthermore, the limitations of the ND approximation can perhaps be overcome or shown to be unimportant. Although one can hope for a new breakthrough, for the present we must conclude that the FI method as applied to the Anderson model has proven more exotic than effective.

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Electron Distribution around a Magnetic Impurity in a Nonmagnetic Host*

P. Jena and D. J. W. Geldart
Department of Physics, Dalhousie University, Halifax, Nova Scotia, Canada
(Received 19 June 1972)

The spatial dependence of the electron density polarization per spin $\delta n^{\sigma}(r)$, produced by a magnetic ion in a nonmagnetic host, has been calculated in terms of the Friedel–Anderson model. The numerical results are found to be rather insensitive to variations of the model parameters describing the virtual bound state provided self-consistency is maintained. Our numerical results differ considerably, even in sign, from the well-known asymptotic form at first-nearest-neighbor distances and the asymptotic form is not adequate until $r \gtrsim 10 k_F^{-1}$. An interpolation formula, incorporating lowest-order preasymptotic corrections, has also been given.

I. INTRODUCTION

It is well known that Mössbauer and nuclear-magnetic-resonance experiments probe local electronic spin and charge polarization at selected nuclear sites in alloys. The results of such experiments yield very sensitive tests of current theories of the electronic structure of alloys. For a brief review, we refer to the articles of Daniel and Friedel[1] and Blandin.[2] In almost all theoretical work to date, two assumptions have been made. First, the magnetic impurity ions are considered