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Critical analysis of the mean-field approximation for the calculation of the magnetic moment in the Friedel-Anderson impurity model

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It is shown that the calculation of the magnetic moment of a Friedel-Anderson impurity in mean-field theory is unreliable. A class of approximate solutions, which contains the mean-field solution as an element, is expressed in rotated Hilbert space and optimized. The optimal state has considerably lower energy than the mean-field solution and requires almost twice the Coulomb exchange U to become magnetic. Since most moment calculations of magnetic impurities, for example the spin-density-functional theory, use the mean-field approximation the resulting magnetic moments have to be critically reexamined.

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The properties of magnetic impurities in a metal is one of the most intensively studied problems in solid state physics. Although some of the experimental anomalies were already discovered in the 1930s, it is still a subject of great interest. The work of Friedel[1] and Anderson[2] laid the foundation to understand why some transition metal impurities form a magnetic local moment, while others do not. They considered a host with an s band in which a transition metal atom is dissolved. The s electrons can hop onto the d impurity via the hopping matrix element V_{sd}. The tenfold degeneracy of a real d impurity is simplified and reduced to a twofold degeneracy for spin up and spin down. If both states are occupied they repel each other due to the Coulomb exchange energy. This yields the Friedel-Anderson Hamiltonian

$$H_{FA} = \sum_{\sigma} \left\{ \sum_{\nu=1}^{N} \varepsilon_\nu c_{\nu\sigma}^{*} c_{\nu\sigma} + E_d d_\sigma^{*} d_\sigma + \sum_{\nu=1}^{N} V_{sd}(\nu)[d_\sigma^{*} c_{\nu\sigma} + c_{\nu\sigma}^{*} d_\sigma] \right\} + U n_{d+} n_{d-}. \tag{1}$$

Here a finite s band with N states is used. The $c_{\nu\sigma}^{*}$ and the d_σ^{*} are the creation operators of the (free) s electrons and the d impurity. The d_σ^{*} states are assumed to be orthogonal to the s states c_ν^{*} (in the following I denote single electron states by their creation operator).

In the limit of $V_{sd}=0$ and $E_d < \varepsilon_F, E_d + U > \epsilon_F$ the d impurity is magnetic. Anderson concluded that the magnetic moment survives for small but finite V_{sd} and derived the criteria for a magnetic state and the size of the moment in a mean-field approximation. He found a magnetic state if the product of $U g_d > 1$ where g_d is the additional density of states of the d resonance.

Kondo[3] brought a new twist into the magnetic impurity problem when he showed that multiple scattering of conduction electrons by a magnetic impurity yields a divergent contribution to the resistance in perturbation theory. In the following three decades a large number of sophisticated methods were applied to better understand and solve the Kondo and Friedel-Anderson model, and it was shown that at zero temperature a Friedel-Anderson impurity is in a nonmagnetic singlet state. However, above the Kondo temperature the impurity shows a magnetic moment, and there is great interest in the size of this moment.

There is a large body of research in which the magnetic moment of impurities is calculated.[4–8] Generally spin-density-functional theory (SDFT) is used for this task. Within this theory the electronic structure of the host and the impurity is calculated from first principles without any adjustable parameters. In particular the strength of the Coulomb and exchange interaction are obtained from first principles. However, in the final step the mean-field method is applied to obtain the local magnetic moment. Although this is a zero-temperature calculation (where the impurity should be in the Kondo singlet state) it is generally argued that such a calculation yields the magnetic moment above the Kondo temperature (which, at lower temperatures, is hidden in the singlet state).

In this Brief Report I will show that the mean-field result for the magnetic moment of impurities is not reliable. By rewriting the mean-field solution in a rotated basis and optimizing the solution I obtain solutions which are much lower in energy, require a much larger critical U for the formation of a moment, and yield smaller moments. And this despite the fact that the improved solution has the same structure (in the rotated basis) as the mean-field solution. Since there is a large body of spin-density-functional theory calculations for magnetic impurities, a reevaluation of this method might be required.

I start with Anderson's (potentially) magnetic state which he obtained as a mean-field solution. Anderson replaced the Hamiltonian H_{FA} by

$$H_{mf} = H_{F+} + H_{F-} - U\langle n_{d+}\rangle\langle n_{d-}\rangle, \tag{2}$$

$$H_{F\sigma} = \Sigma_\nu \varepsilon_\nu c_{\nu\sigma}^{*} c_{\nu\sigma} + \sum_{\nu=1}^{N} V_{sd}(\nu)[d_\sigma^{*} c_{\nu\sigma} + c_{\nu\sigma}^{*} d_\sigma] + E_{d,\sigma} d_\sigma^{*} d_\sigma, \tag{3}$$

where $\langle n_{d+}\rangle$ and $\langle n_{d-}\rangle$ are the average occupation numbers of the states d_+^{*} and d_-^{*} and $E_{d,\sigma} = (E_d + U\langle n_{d,-\sigma}\rangle)$. The solution of the mean-field method requires the diagonalization of two

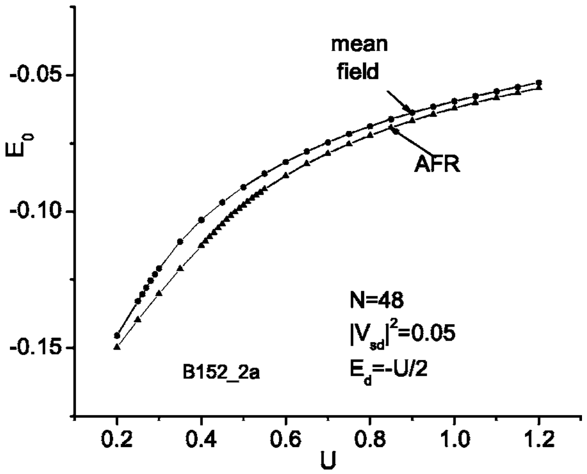

FIG. 1. A comparison between the ground-state energies of the mean-field calculation and the AFR method (see text below).

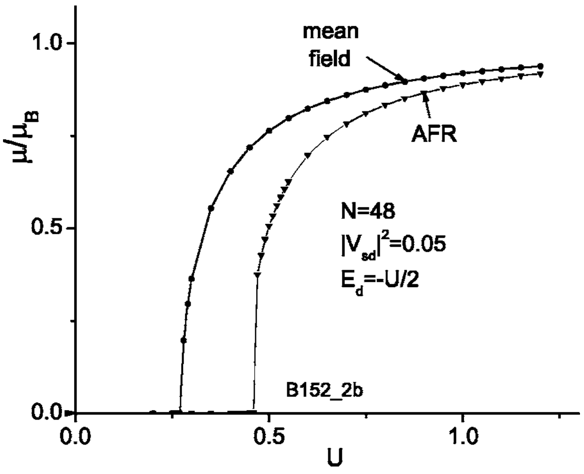

FIG. 2. The magnetic moment as a function of the Coulomb energy U, using the mean-field solution and the AFR method of the present calculation.

Friedel resonance Hamiltonians $H_{F\sigma}$ with self-consistent values for $\langle n_{d+}\rangle$ and $\langle n_{d-}\rangle$. This straightforward numerical calculation yields the mean-field ground state energy E_{mf} and the magnetic moment μ_{mf}. The energy of the bare magnetic state $E_{b.m.}$ is subtracted from E_{mf}, where

$$E_{b.m.} = 2\sum_{\nu=1}^{n} \varepsilon_\nu + E_d - \varepsilon_n \tag{4}$$

is the ground state energy for $V_{sd}=0$ and $E_d<\varepsilon_F, E_d+U>\varepsilon_F$.

For the numerical calculation an s band with a constant density of states is used, ranging from -1 to $+1$. This band is divided into $N=48$ equal cells. Each s subband is half filled, i.e., the number of occupied states in each spin subband is $n=N/2$. In Fig. 1 the numerical results for $E_{mf}-E_{b.m.}$ are plotted for $|V_{sd}|^2=0.05$. The Coulomb repulsion U is varied between 0.2 and 1.2. Together with the Coulomb repulsion the d^*-state energy E_d is varied so that E_d and (E_d+U) lie symmetrically about the Fermi energy, i.e., $E_d=-\frac{1}{2}U$.

In the mean-field calculation the impurity is nonmagnetic for $U<U_{cr}\approx 0.275$. For $U>U_{cr}$ the spin up and down subbands split. The resulting magnetic moments are plotted in Fig. 2 (curve with circles).

Since the mean-field solution is the product of two n-electron states of the two Friedel Hamiltonians F_{F+} and H_{F-} we consider these solutions of the Friedel Hamiltonian (3) in some detail. As shown in Refs. 9 and 10 the exact ground state of H_F with n (spinless) electrons can be written in the form

$$\Psi_F = [A' a_0^* + B' d^*]\prod_{i=1}^{n-1} a_i^* \Phi_0. \tag{5}$$

Here Φ_0 is the vacuum state and a_0^* is a sister state to d^* which is built from the states of the s band

$$a_0^* = \sum_{\nu=1}^{N} \alpha_\nu^0 c_\nu^*. \tag{6}$$

Reference 10 shows how to calculate the coefficients α_ν^0 from the parameters of the Hamiltonian H_F and the occupation number n. The a_i^* are orthogonal to a_0^* and to each other and their $(N-1)$ submatrix of the s band Hamiltonian $H_0=\Sigma\varepsilon_\nu n_\nu$ is diagonal [see Eq. (8)]. The states a_i^* are uniquely determined from the state a_0^*. Their form is

$$a_i^* = \sum_{\nu=1}^{N} \alpha_\nu^i c_\nu^*. \tag{7}$$

The a_i^* $(1\leq i\leq N-1)$ together with a_0^* represent an alternative basis.

In this alternative basis the free electron Hamiltonian $H_0=\Sigma_{\nu=1}^{N}\varepsilon_\nu c_\nu^* c_\nu$ takes the form

$$H_0 = \sum_{i=1}^{N-1} E(i) a_i^* a_i + E(0) a_0^* a_0 + \sum_{i=1}^{N-1} V_{fr}^a(i)[a_0^* a_i + a_i^* a_0]. \tag{8}$$

In the Hamiltonian (8) the a_0^*-state represents an artificial resonance state. I will call it in honor of Friedel an artificial Friedel resonance state (AFR state). It is a sister state to the state d^*.

The full (spin independent) Friedel Hamiltonian can be written as

$$\begin{aligned} H_F = {} & \sum_{i=1}^{N-1} E(i) a_i^* a_i + E(0) a_0^* a_0 + E_d d^* d + V_{sd}^a(0)[d^* a_0 + a_0^* d] \\ & + \sum_{i=1}^{N-1} V_{sd}^a(i)[d^* a_i + a_i^* d] + \sum_{i=1}^{N-1} V_{fr}^a(i)[a_0^* a_i + a_i^* a_0], \end{aligned} \tag{9}$$

where

$$E(i) = \sum_\nu \alpha_\nu^i \varepsilon_\nu \alpha_\nu^i,$$

$$E(0) = \sum_{\nu} \alpha_{\nu}^{0} \varepsilon_{\nu} \alpha_{\nu}^{0},$$

$$V_{sd}^{a}(i) = \sum_{\nu} V_{sd}(\nu) \alpha_{\nu}^{i},$$

$$V_{fr}^{a}(i) = \sum_{\nu} \alpha_{\nu}^{i} \varepsilon_{\nu} \alpha_{\nu}^{0}. \tag{10}$$

In the Hamiltonian (9) the d^* state and the localized a_0^* state are on equal footing. The second line in Eq. (9) yields the hopping between a_i^* and d^* (first term) and a_i^* and a_0^* (second term). For the state $(A' a_0^* + B' d^*)$ the individual hopping matrix elements cancel each other, making Ψ_{Fr} the ground state.

In the next step the mean-field solution is rewritten in the AFR form of the Friedel ground state. Since the Hamiltonian consists of a Friedel Hamiltonian for each spin the mean-field state is the product of two states of the form of Eq. (5). Therefore this mean-field state (the exact solution of the mean-field Hamiltonian) can be written as

$$\begin{aligned}\Psi_0 &= [A_- a_{0-}^* + B_- d_-^*][A_+ a_{0+}^* + B_+ d_+^*] \prod_{\sigma,i=1}^{n-1} a_{i\sigma}^* \Phi_0 \\ &= [A a_{0-}^* a_{0+}^* + B d_-^* a_{0+}^* + C a_{0-}^* d_+^* + D d_-^* d_+^*] \prod_{\sigma,i=1}^{n-1} a_{i\sigma}^* \Phi_0 \\ &= A \Psi_A + B \Psi_B + C \Psi_C + D \Psi_D,\end{aligned} \tag{11}$$

where

$$A_+^2 + B_+^2 = 1, \quad A_-^2 + B_-^2 = 1,$$

$$A = A_+ A_-, \quad B = A_+ B_-,$$

$$C = A_- B_+, \quad D = B_+ B_-. \tag{12}$$

Each of the four states Ψ_A, Ψ_B, Ψ_C, and Ψ_D is normalized, and they are all orthogonal to each other. In the magnetic solution one has $A_+ \neq A_-$ and $B_+ \neq B_-$. Also the two rotated bases $\{a_{0+}^*, a_{i+}^*\}$ and $\{a_{0-}^*, a_{i-}^*\}$ are different in the magnetic state.

So far the many electron state in Eq. (5) is identical to the mean-field solution. This state consists of an electron background $\Pi_{\sigma,i=1}^{n-1} a_{i\sigma}^* \Phi_0$ multiplied with the sum of four two-electron states, consisting of the combinations $[a_{0-}^* a_{0+}^*, d_-^* a_{0+}^*, a_{0-}^* d_+^*, d_-^* d_+^*]$ which have $S_z = 0$. The mean-field wave function opens an interesting playing field for variation to find the optimal state. One can optimize the coefficients A, B, C, and D while dropping the individual normalization conditions (12) and replacing them by

$$A^2 + B^2 + C^2 + D^2 = 1. \tag{13}$$

Far more important one can optimize the states a_{0+} and a_{0-}.

For this purpose the Hamiltonian H_{FA} is expressed in the bases $\{a_{0+}^*, a_{i+}^*\}$ and $\{a_{0-}^*, a_{i-}^*\}$. One obtains for the expectation value of the ground-state energy E_0

$$\begin{aligned}E_0 = {} & A^2[E_-(0) + E_+(0)] + B^2[E_-(0) + E_d] + C^2[E_+(0) + E_d] \\ & + D^2[2E_d + U] + 2(AB + CD)V_{sd}^-(0) + 2(AC \\ & + BD)V_{sd}^+(0) + \sum_{\sigma,i=1}^{n-1} E_\sigma(i).\end{aligned} \tag{14}$$

For a given set of states $\{a_{0\pm}^*, a_{i\pm}^*\}$ the energy E_0 in Eq. (14) depends on the coefficients A, B, C, and D. One obtains the lowest energy by varying E_0 with respect to these coefficients. This yields a 4×4 matrix for the coefficients vector (A, B, C, D). The lowest eigenvalue gives the energy expectation value, and its eigenvector gives the coefficients. The resulting state I denote as the magnetic state Ψ_{AFR} and the solution as the AFR solution.

The central part of the numerical calculation is the variation of the states a_{0+}^* and a_{0-}^* until the absolute minimum of the energy is reached.

As in the mean-field theory the numerical calculation itself determines whether the lowest state possesses a magnetic moment or not. If the solution is magnetic then a_{0+}^* and a_{0-}^* approach different states and the coefficients B and C have different values. The resulting magnetic moment is defined as the difference in the occupation of the d_+^* and d_-^* states, i.e., $\mu = B^2 - C^2$.

In Fig. 1 the energy expectation value E_0 of the optimal magnetic state Ψ_{AFR} is plotted as the curve with the triangles (again the same energy $E_{b.m.}$ has been subtracted). The new ground-state energy lies considerably below the mean-field energy.

In Fig. 2 the resulting magnetic moments that one obtains with the mean-field approximation and with the new method are plotted. One recognizes that the new solution suppresses the magnetic moment up to a considerably larger value of $U_{cr} \approx 0.46$. This is almost twice the value of the mean-field theory.

How do we have to interpret the fact that the AFR solution suppresses the magnetic moment up to a much larger critical Coulomb exchange interaction? Since this state has a lower energy expectation value, does this mean that its magnetic moment is more reliable? The author prefers a somewhat different interpretation. The Friedel-Anderson impurity does not like a broken symmetry. The mean-field approach does not give the multielectron state any wiggling room. Only the values for $E_{d,\sigma}$ can be altered with increasing U. The AFR solution on the other hand possesses a lot more flexibility since the AFR states can adjust. Therefore the symmetric multielectron state survives to a considerably larger Coulomb exchange interaction. It might be that neither state yields the right magnetic moment for the impurity. The present calculation raises serious questions about the mean-field approach. This might also apply to the spin-density-functional theory (SDFT) for magnetic impurities. This theory is a very complex theory and it is difficult to judge from the outside all the intricacies. It should yield the correct charge and spin densities for the correct functional. But in the final step the majority of SDFT calculations use a two-spin-fluid model where each electron fluid adjusts in the (mean) field of the other.

To conclude, in this paper an approximate solution for the

Friedel-Anderson impurity is expressed in a rotated Hilbert space $\{a_{0\pm}^{*}, a_{i\pm}^{*}\}$. Its center piece are two artificial resonance states a_{0+}^{*}, a_{0-}^{*} for the spin up and down *s* electrons. They determine uniquely the remaining bases $\{a_{i+}^{*}\}, \{a_{i-}^{*}\}$. The AFR states are combined with the *d*-electrons for spin up and down d_{+}^{*}, d_{-}^{*} into two-electron states of total $S_z=0$, i.e., $[Aa_{0-}^{*}a_{0+}^{*}+Bd_{-}^{*}a_{0+}^{*}+Ca_{0-}^{*}d_{+}^{*}+Dd_{-}^{*}d_{+}^{*}]$. Then the $(n-1)$ lowest states of the two $(N-1)$ bases $\{a_{i\pm}^{*}\}$ are occupied yielding the *s*-electron background $\Pi_{i=1,\sigma}^{n-1}a_{i\sigma}^{*}\Phi_0$. The compositions of the AFR states a_{0+}^{*}, a_{0-}^{*} are calculated by numerical variation which rotates the *s*-electron bases in Hilbert space.

The energy of the resulting state lies clearly below the mean-field solution. The critical value of the Coulomb exchange energy U_{cr} for the formation of a magnetic moment is almost twice as large as in the mean-field solution. Since in many calculations of the magnetic moment of impurities the mean-field approximation is used one has to reevaluate the resulting moments. This may also apply to the impurity calculations which use the spin-density-functional theory because in the majority of these calculations the mean-field theory is used in the final analysis.

Since the ground state of the Friedel-Anderson impurity is a singlet state one might suspect that the structure of the new solution with the lower energy and smaller magnetic moment is somewhat closer to the singlet state than the mean-field solution. This is not the case. Both the mean-field and the present solution are in a symmetric state for small U; both show a similar asymmetry between spin up and down in the magnetic state. The mean-field solution belongs to the same class of wave functions as presented here [which are given by the general form of Eq. (11)].

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