A Compact Approximate Solution to the Friedel-Anderson Impurity Problem

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Abstract

An approximate groundstate of the Anderson-Friedel impurity problem is presented in a very compact form. It requires solely the optimization of two localized electron states and consists of four Slater states (Slater determinants). The resulting singlet ground state energy lies far below the Anderson mean field solution and agrees well with the numerical results by Gunnarsson and Schoenhammer, who used an extensive $1/N_f$-expansion for a spin $1/2$ impurity with double occupancy of the impurity level.

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1 Introduction

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 1930’s 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 don’t. 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 ten-fold degeneracy of a real d-impurity is simplified and reduced to a two-fold 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

$$H_{FA} = \sum_{\sigma} \{ \sum_{\nu=1}^{N} \varepsilon_{\nu} c_{\nu\sigma}^{\dagger} c_{\nu\sigma} + E_{dd} d_{\sigma}^{\dagger} d_{\sigma} + \sum_{\nu=1}^{N} V_{sd}(\nu)[d_{\sigma}^{\dagger} c_{\nu\sigma} + c_{\nu\sigma}^{\dagger} d_{\sigma}] \} + U n_{d+} n_{d-} \quad (1)$$

Here a finite s-band with $N$ states is used. The $c_{\nu\sigma}$ and the $d_{\sigma}^{\dagger}$ are the creation operators of the (free) s-electrons and the d-impurity. The $d_{\sigma}$-states are assumed to be orthogonal to the s-states $c_{\nu}^{\dagger}$.

Kondo [3] 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 non-magnetic state. To name a few of these methods: scaling [4], renormalization [5], [6], Fermi-liquid theory [7], [8], slave-bosons (see for example [9]), large-spin limit [10], [11], and the Bethe-ansatz [12], [13]. For a review see [14]. After decades of research exact solutions of the Kondo and Friedel-Anderson problems were derived [12], [15] representing a magnificent theoretical achievement.

The exact solution does not solve all questions. It uses a s-electron band with a constant density of states which extends from minus infinity to plus infinity (the cut-off is only performed at the end of the calculation). Furthermore it is such a complex solution that only a limited number of parameters can be calculated and many non-critical or non-divergent contributions are neglected. For the majority of practical problems one uses approximate solutions. One particularly popular method is the large-spin method which will be discussed below.

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While the single impurity problem is intensively studied and well understood the many-impurity problem and the periodic Anderson problem are still in a rather incomplete state [16]. Any simplified treatment of the single impurity may provide a new tool to improve the treatment of the latter.

In this paper I wish to introduce a new method to treat the Friedel-Anderson problem. This approach can be best explained by a discussion of the ground state of the Friedel Hamiltonian. This is done in chapter 2. In chapter 3 the singlet state of the Friedel-Anderson model is derived. In chapter 4 the results are discussed. In the appendix some details of the calculation are summarized.

2 The Friedel Resonance

The author’s method to treat the Friedel-Anderson problem can be best explained by a discussion of the ground state of the Friedel (resonance) Hamiltonian $H_{Fr}$. For an s-band with $N$ states and a $d$ resonance $H_{Fr}$ has the form:

$$H_{Fr} = \sum_{\nu=1}^{N} \varepsilon_{\nu} c_{\nu}^{\ast} c_{\nu} + E_{d} d^{\ast} d + \sum_{\nu=1}^{N} V_{sd}(\nu)[d^{\ast} c_{\nu} + c_{\nu}^{\ast} d]$$  (2)

Since $H_{Fr}$ is identical for spin up and down, I will ignore the spin at the moment.

As shown in ref. [17], [18] the exact ground state of $H_{Fr}$ with $n$ (spinless) electrons can be written in the form

$$\Psi_{Fr} = [A' a_{0}^{\ast} + B' d^{\ast}] \prod_{i=1}^{n-1} a_{i}^{\ast} \Phi_{0}$$  (3)

Here $\Phi_{0}$ is the vacuum state and $a_{0}^{\ast}$ is a localized state which is built from the states of the s-band

$$a_{0}^{\ast} = \sum_{\nu=1}^{N} \alpha_{\nu}^{0} c_{\nu}^{\ast}$$  (4)

The $a_{i}^{\ast}$ ($1 \leq i \leq N - 1$) together with $a_{0}^{\ast}$ represent a new basis. The $a_{i}^{\ast}$ are orthogonal to $a_{0}^{\ast}$ and to each other and their $(N - 1)$ sub-matrix of the s-band Hamiltonian $H_{0} = \sum \varepsilon_{\nu} n_{\nu}$ is diagonal. (The construction of the states

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\{a^*_0, a^*_i\} is discussed in appendix A. The states \(a^*_i\) are uniquely determined from the state \(a^*_0\). Their form is

\[ a^*_i = \sum_{\nu=1}^{N} \alpha^i_{\nu} c^*_\nu \] (5)

In this new basis the (spin independent) Friedel Hamiltonian can be written as

\[
H_{Fr} = \sum_{i=1}^{N-1} E(i) a^*_i a_i + E(0) a^*_0 a_0 + \sum_{i=1}^{N-1} V^a_{fr}(i) [a^*_0 a_i + a^*_i a_0] \\
+ E_d d^* d + V^a_{sd}(0) [d^* a_0 + a^*_0 d] + \sum_{i=1}^{N-1} V^a_{sd}(i) [d^* a_i + a^*_i d]
\] (6)

where

\[
E(i) = \sum_{\nu} \alpha^i_{\nu} \varepsilon_{\nu} \alpha^i_{\nu} \quad E(0) = \sum_{\nu} \alpha^0_{\nu} \varepsilon_{\nu} \alpha^0_{\nu} \\
V^a_{sd}(i) = \sum_{\nu} V^a_{sd}(\nu) \alpha^i_{\nu} \quad V^a_{fr}(i) = \sum_{\nu} \alpha^i_{\nu} \varepsilon_{\nu} \alpha^0_{\nu}
\] (7)

In the Hamiltonian (6) the first three terms represent the free electron Hamiltonian. The \(a^*_0\)-state represents an artificial Friedel resonance state (AFR state). It is interesting to note that the \(d^*\)-state and the localized \(a^*_0\)-state in (6) are on equal footing. The AFR state \(a^*_0\) is a sister state to the state \(d^*\).

The terms with the matrix elements \(V^a_{fr}(i)\) and \(V^a_{sd}(i)\) yields the hopping between \(a^*_i\) and \(d^*\) and \(a^*_i\) and \(a^*_0\). For the state \((A^*a^*_0 + B^*d^*)\) the individual hopping matrix elements cancel each other, making \(\Psi_{Fr}\) the ground-state.

Now I consider a conduction band and a \(d\) state with two spin components. Again I take the Friedel Hamiltonian as given by eq. (2). Then the ground state is given by the product of the spin up and down states of eq. (3). This exact ground state can be written as
\[ \Psi_{MS} = \left[ A_- a_{0-}^* + B_- d_-^* \right] \left[ A_+ a_{0+}^* + B_+ d_+^* \right] \prod_{\sigma,i=1}^{n-1} a_{\sigma\sigma}^* \Phi_0 \]

\[ = \left[ A a_{0-}^* a_{0+}^* + B d_-^* a_{0+}^* + C a_{0-}^* d_+^* + D d_-^* d_+^* \right] \prod_{\sigma,i=1}^{n-1} a_{\sigma\sigma}^* \Phi_0 \quad (8) \]

\[ = A \Psi_A + B \Psi_B + C \Psi_C + D \Psi_D \]

where

\[ A_A^2 + B_B^2 = 1 \quad , \quad A_A^2 + B_B^2 = 1 \]

\[ A = A_+ A_- \quad , \quad B = A_- B_+ \quad (9) \]

\[ C = A_+ B_- \quad , \quad D = B_+ B_- \]

Each of the four states \( \Psi_A, \Psi_B, \Psi_C \) and \( \Psi_D \) is normalized and they are all orthogonal to each other because they differ in the occupations of the \( d_+^* \) or \( d_-^* \)-state. In Fig.1 the four components \( \Psi_A, \Psi_B, \Psi_C \) and \( \Psi_D \) of the state \( \Psi_{MS} \) are graphically shown.

In the present case one has \( A_+ = A_- \) and \( B_+ = B_- \). With the right choice of \( a_0^* \) the above state is the exact ground state of the Friedel Hamiltonian.
Fig. 1: The four Slater states used in the present calculation. In each component either the $d^*$-state or the AFR state $a^*_0$ is occupied.

3 The Friedel-Anderson Model

In the presence of a Coulomb exchange interaction $U$ one can use the general form of the state $\Psi_{MS}$ as an approximate ground state. This state consists of four Slater states and possesses considerable flexibility. One may drop the condition $A_+ = A_-$ and $B_+ = B_-$ and use $A, B, C, D$ as free parameters fulfilling the condition

$$|A|^2 + |B|^2 + |C|^2 + |D|^2 = 1$$

and optimizes these coefficients. Far more important is the optimization of the states $a_{0+}$ and $a_{0-}$. With $a_{0+}$, $a_{0-}$ the full new bases $\{a_{i+}^*\}$, $\{a_{i-}^*\}$ are uniquely determined. Details of the numerical optimization are discussed in the appendix.
In the following calculations a half filled s-subband is used, i.e. the number of occupied states in each s-subband is $n = N/2$. The energy expectation value of the state $\Psi_{MS}$ is calculated. For zero Coulomb exchange energy $U$ the spin up and down bases are identical as are the coefficients $B$ and $C$. With increasing $U$ the spin up and down bases are shifted with respect to each other, the coefficients $B$ and $C$ differ and a magnetic moment develops. The size of this moment and a comparison with the mean field solution is discussed elsewhere [19].

### 3.1 The singlet state

The ground state of the Friedel-Anderson problem is a singlet state. From $\Psi_{MS}$ one can construct a mirror state by exchanging spin up and down. Combining the two states yields then a singlet state which I denote as $\Psi_{SS}$. It is given by the following expression

$$\Psi_{SS} = \Psi_{MS}(\uparrow\downarrow) \mp \Psi_{MS}(\downarrow\uparrow)$$

$$= [Aa_{0-\downarrow}^* a_{0+\uparrow}^* + Bd_{-\downarrow}^* d_{0+\uparrow}^* + Ca_{0-\downarrow}^* d_{+\uparrow}^* + Dd_{-\downarrow}^* d_{+\uparrow}^*] \prod_{i=1}^{n-1} a_{i+\uparrow}^* \prod_{i=1}^{n-1} a_{i-\downarrow}^* \Phi_0$$

$$\mp [Aa_{0-\uparrow}^* a_{0+\downarrow}^* + Bd_{-\uparrow}^* a_{0+\downarrow}^* + Ca_{0-\uparrow}^* d_{+\downarrow}^* + Dd_{-\uparrow}^* d_{+\downarrow}^*] \prod_{i=1}^{n-1} a_{i+\downarrow}^* \prod_{i=1}^{n-1} a_{i-\uparrow}^* \Phi_0$$

The sign $\mp$ is chosen so that one obtains a singlet state. This state is not normalized and the ”$B$” and ”$C$” components are not orthogonal to each other. This introduces some additional terms in the ground-state energy. Furthermore the matrix elements between the states $\Psi_{MS\uparrow}$ and $\Psi_{MS\downarrow}$ become determinants of single electron matrix elements. This is discussed in the appendix.

For the numerical calculation an s-band with $N$ electron states $c^*_\nu$ is used (in the following I denote single electron states by their creation operator). A logarithmic energy scale is used, as introduced by Wilson [3] in his Kondo paper. One uses a finer and finer energy scale when approaching the Fermi energy $\epsilon_F = 0$. A brief description of these electron states is given in the appendix.

The ground-state energy of the singlet state is shown in Fig.3 as a function of $U$ with $E_d = -U/2$ and compared with the mean field ground state energy. Its energy clearly lies below the energy of the mean field state.
4 Discussion

4.1 Comparison with the large $N_f$-expansion

A number of approximate solutions have been suggested in the literature in which a localized electron state forms a singlet state with the magnetic impurity, see for example [20], [21], [10]. They have been suggested for the Kondo problem and the Friedel-Anderson model. One particularly popular approximation is the large $N_f$ expansion (see for example [10], [11]). In the large $N_f$ expansion one assumes that the impurity has a large total angular momentum $J_f$ ($J_f$ because this method is often used for f-impurities). The ”spin” has then a degeneracy of $N_f = (2J_f + 1)$ of the total angular momentum states. In the limit of infinite $N_f$ (the large $N_f$ limit) this method yields an exact ground state. For smaller spin, in particular for spin 1/2, one generally performs an expansion in powers of $1/N_f$. 

Fig.2: A comparison between the ground-state energies of the Anderson’s mean field calculation and the singlet state $\Psi_{ss}$. 

\[ V_{sd}=0.25 \]
\[ E_d=U_{Coul}/2 \]
Gunnarsson and Schoenhammer (G&S) [22] applied the large $N_f$ method to a finite Coulomb interaction and spin $\frac{1}{2}$, including double occupancy of the impurity level. They calculated the ground-state energy in different approximations. G&S give their energy parameters in units of [eV]. I denote their parameters with the index ”GS”. These parameters are: half the bandwidth $B_{GS}$, the d-state energy $E_{d,GS}$, the Coulomb energy $U_{GS}$. For the s-d-hopping transition they use an elliptic form

$$[V(\varepsilon)]^2 g(\varepsilon) = \frac{2V_{GS}^2}{\pi B_{GS}^2} \sqrt{(B_{GS}^2 - \varepsilon^2)}$$

(10)

where $g(\varepsilon)$ is the density of states (per spin). All these parameters are energies or potentials. By dividing these energy parameter by $B_{GS}$ one obtains the appropriate parameters for the present calculation. When the numerical calculation is completed the resulting ground-state energy must be multiplied with $B_{GS}$ for a comparison with GS’s results.

Gunnarsson and Schoenhammer calculated in ref. [22] the ground-state energy (for $N_f = 2$) with the following parameters: $B_{GS} = 6$ eV, $U_{BS} = 5$ eV, $E_{d,BS} = -2.5$ eV. They performed two calculations, one for $V_{GS} = 1$ eV and another for $V_{GS} = 2$ eV. The results are shown in tables 1 and 2. The first column gives the electron states used in the calculation (for details see [22] and the appendix). The second column gives the calculated ground-state energies. In the third, fourth and fifth columns the symbols $f_0, f_1, f_2$ give the probabilities for a d-occupation of 0,1,2. The last column gives the power of the $(1/N_f)$-expansion. The last row gives the results of the present calculation for the singlet state. The values for $f_0, f_1, f_2$ agree perfectly. Also the ground-state energies are quite close with $E_{GS} = -0.245$ eV and $E_0 = -0.239$ eV of the present calculation.

For $V_{GS} = 2$ eV the ground-state energy of the present calculation lies even below the value of the $1/N_f$-expansion, as shown in table 2.

The state ”g” requires the variation of more than $15^6$, i.e. more than $10^7$ amplitudes. In the present calculation the singlet state requires the variation of $2N=60$ amplitudes. Keeping this in mind, the resulting ground state of the present calculation is rather compact.
Table 1: A comparison between the numerical results by Gunnarsson and Schoenhammer and the author for the case of $N_f = 2$. The parameters, given in the units used by GS, are $B_{GS} = 6$ eV, $E_{d,GS} = -2.5$ eV, $V_{GS} = 1.0$ eV, $U_{GS} = 5$ eV. The first column gives the states included in the large spin-method, the second column gives the groundstate energy. The third, fourth and fifth columns give the weight of zero, single and double occupation of the d-states. The sixth column gives the number of optimized parameters (amplitudes) in this calculation.

| states          | $E_0$ [eV] | $f_0$ | $f_1$ | $f_2$ | param.       |
|-----------------|-----------|------|------|------|--------------|
| $|0\rangle+a+b$ | -0.108    | 0.001| 0.974| 0.025| $(1/N_f)^0$  |
| $+c+d+e$        | -0.238    | 0.031| 0.938| 0.031| $(1/N_f)^1$  |
| $+f+g$          | -0.245    | 0.034| 0.931| 0.034| $(1/N_f)^2$  |
| singlet state   | -0.239    | 0.035| 0.931| 0.034|              |

Table 2: A comparison between the numerical results by Gunnarsson and Schoenhammer and the author for the case of $V_{GS} = 2eV$. Everything else is identical to table 1.

| states          | $E_0$ [eV] | $f_0$ | $f_1$ | $f_2$ | expans.      |
|-----------------|-----------|------|------|------|--------------|
| $|0\rangle+a+b$ | -0.628    | 0.141| 0.778| 0.081| $(1/N_f)^0$  |
| $+c+d+e$        | -1.126    | 0.140| 0.745| 0.115| $(1/N_f)^1$  |
| $+f+g$          | -1.217    | 0.137| 0.732| 0.132| $(1/N_f)^2$  |
| singlet state   | -1.234    | 0.140| 0.722| 0.138|              |
4.2 Properties of the Artificial Resonance State

The states $a^*_{0\pm}$ and $a^*_{0-}$ are of particular importance of the present treatment of the Friedel-Anderson impurity. They determine the rotation of the s-electron basis in Hilbert space and therefore the solution of the problem. We analyze the composition of $a^*_{0\pm}$ in terms of the original s-state energies $\varepsilon_{\nu}$. As discussed above, $a^*_{0\pm}$ is composed of the original s-basis $c^*_{\nu}$ with the amplitudes $a^0_{\nu\pm}$

$$a^*_{0\pm} = \sum_{\nu=1}^{N} a^0_{\nu\pm} c^*_{\nu\pm}$$

In Fig.3a,b the coefficients $a^0_{\nu-}$ and $a^0_{\nu+}$ of the states $a^*_{0+}$ and $a^*_{0-}$ are plotted for the parameters: $U_{\text{cou}} = 1$, $E_d = -0.5$, $|V_{sd}|^2 = 0.1$ and the number of s-states is $N = 32$. One recognizes that the amplitudes at large absolute energies is very different for spin up and down. They are almost mirror images.

Fig.3a,b: The coefficients $a^0_{\nu}$ for the AFR states $a^*_{0+}$ and $a^*_{0-}$. The Wilson spectrum is used (for the region on the left side of the arrow the numbers $\nu$ corresponds to an energy of $E_\nu = -1/2^\nu$). The energy of the s-electron $c^*_{\nu}$ is $(E_\nu + E_{\nu-1})/2$. On the right side of the arrow one has the corresponding positive energies.

For the analysis at small energies we plot the occupation density $|a^0_{\nu\pm}|^2 / (E_\nu + E_{\nu-1})$ as a function of $\nu$. In Fig.4a,b these densities are shown for $N = 32$ and
$N = 48$. In the latter case the energy interval next to the arrow (zero energy) is $1/2^8$ times smaller than for the left plot. Obviously the sub-division at the Fermi energy is not yet sufficiently small at the left plot for $N = 32$.

![Diagram](image)

**Fig. 4a,b:** The low energy occupation in the state $a_{0+}^*$ for different sub-division of the energy close to the Fermi energy. In a) the smallest sub-division is $\Delta = 2^{-16} \approx 1.5 \times 10^{-5}$ and in b) it is $\Delta = 2^{-24} \approx 6 \times 10^{-8}$. While in the left plot $\Delta$ is not yet small enough, one observes in the right plot the occupation of $a_{0+}^*$ has saturated.

While amplitudes and occupations for large energies were rather different for $a_{0+}^*$ and $a_{0-}^*$ the occupation at small energies is almost identical. This is shown in Fig. 5 where the occupations of $a_{0+}^*$ and $a_{0-}^*$ are plotted in the same figure. At energies close to the Fermi energy the occupation of $a_{0+}^*$ and $a_{0-}^*$ are essentially identical. On a linear energy scale at small energies the plots
in Fig.4b and Fig.5 are essentially identical.

Fig.5: The occupation of the spin up and down AFR states for \( N = 52 \). At small energies (close to the center arrow) the two are almost identical. (The difference between \( \Phi_{0^+} \) and \( \Phi_{0^-} \) is of the order of the width of the curve.)

The average occupation density of the states \( a_{0^+}^* \) and \( a_{0^-}^* \) is 1/2 since the band ranges from -1 to +1. Therefore a density of more than 100 is quite large.

The AFR states have weight at small and large energies. The weight at large energies is responsible for the large "perturbative" part of the ground-state energy. The weight at small energies is responsible for the anomalous behavior at low temperatures, the Kondo effect.

5 Conclusions

In this paper I suggest a very compact approximate ground state for the Friedel-Anderson impurity. Its center piece are two artificial resonance states
\( a_{0+}^*, a_{0-}^* \) for the spin up and down s-electrons. These are combined with the d-electrons for spin up and down \( d_{\pm}^*, d_{\pm}^* \) into two-electron states of total spin zero, i.e. \([Aa_{0-}^*a_{0+}^* + Bd_{-}^*d_{+}^* + Ca_{0-}^*d_{+}^* + Dd_{-}^*d_{+}^*]\). Then for each spin a new s-electron basis \( \{a_{i\pm}^*\} \) is built. These two bases are completely determined by the AFR states. Finally the \((n-1)\) lowest states of the two basis are occupied yielding the s-electron background \( \prod_{i=1,\sigma}^{n-1} a_{i\sigma}^* \Phi_0 \). The compositions of the AFR states \( a_{0+}^*, a_{0-}^* \) are calculated by numerical variation which rotates the s-electron bases in Hilbert space. This ansatz is exact for a spin degeneracy \( N_f \) of "1" and infinity.

The properties of the singlet state are investigated. Its ground-state energy and the occupations \( f_0, f_1, f_2 \) of the d-states are in good agreement with the extensive calculations by Gunnarsson and Schoenhammer using the large \( N_f \)-expansion. However, while in the large \( N_f \)-expansion one has to go to a large basis of states to obtain a good ground-state energy the present solution is extremely compact.

The spectral composition of the two AFR states is quite interesting. Their composition is quite different away from the Fermi energy. Close to the Fermi energy one finds a large peak in the occupation density which saturates only for very small energies. This low energy occupation is essentially identical for the spin up and down AFR state.

The structure presented here of the ground state allows a number of variations. Instead of using just two bases \( \{a_{0+}^*, a_{i+}^*\} \) and \( \{a_{0-}^*, a_{i-}^*\} \) one can use four or eight bases, for each of the \( \psi_X \ (X = A, B, C, D) \) a different one for spin up and down. These solutions improve the ground-state energy only slightly for the singlet state.

A detailed analysis of the present solution is planned. For example, the construction of the triplet state and the calculation of transport scattering by the impurity in this ground state are desirable. Above all, it is of interest whether an extension of the presented solution can contribute to the periodic Anderson impurity problem.
A Some Details about the Numerical Calculations

A.1 Wilson’s s-electron basis

Wilson [5] in his Kondo paper considers an s-band with energy values ranging from $-1$ to $1$. In the next step Wilson replaced the continuum of s-states by a discrete set of states. This is done on a logarithmic scale. The discrete energy values are $1, 1/\Lambda, 1/\Lambda^2$, etc and $-1, -1/\Lambda, -1/\Lambda^2$, etc where $\Lambda$ is a parameter larger than one. (In this paper $\Lambda = 2$ is chosen). These discrete $\xi_\nu$ points are used to define a sequence of intervals: the interval $\nu$ (for $\nu<\frac{N}{2}$) is $\xi_{\nu-1} = -1/2^{\nu-1} < \varepsilon < -1/2^\nu = \xi_\nu$ (there are equivalent intervals for positive $\xi$-values where $\nu$ is replace by $(N - \nu)$ but we discuss here only the negative energies). The new Wilson states $c^*_\nu$ are a superposition of all states in the energy interval $(\xi_{\nu-1}, \xi_\nu)$ and have an (averaged) energy $(\xi_\nu + \xi_{\nu-1})/2 = (\frac{-3}{2})1/2^\nu$, i.e. $-\frac{3}{4}, -\frac{3}{8}, -\frac{3}{16}, \ldots, -\frac{3}{22^{N/2}}, -\frac{1}{22^{N/2}}$. This spectrum continues symmetrically for positive energies.

The amplitude of the states at the origin are chosen to be $\phi_\nu(0) = (\xi_\nu - \xi_{\nu-1})/\sqrt{2} = 1/2^{\nu+1}$. A state which is homogeneously composed of all energies in the full band has than an amplitude of ”1”.

Therefore this choice of $s^*$-states yields a dependence of the s-d matrix element $V_{sd}(\nu)$ on the state $\nu$. The essential advantage of the Wilson basis is that it has an arbitrarily fine energy spacing at the Fermi energy.

A.2 Construction of the Basis $a^*_0$, $a^*_i$

For the construction of the state $a^*_0$ and the rest of basis $a^*_i$ one starts with the s-band electrons $\{c^*_\nu\}$ which consists of $N$ states (for example Wilson’s states). The $d^*$-state is ignored for the moment.

- In step (1) one forms an normalized state $a^*_0$ out of the s-states with:

$$a^*_0 = \sum_{\nu=1}^{N} \alpha^0_\nu c^*_\nu \quad (11)$$
The coefficients $\alpha^0_{\nu}$ can be at first arbitrary. One reasonable choice is $\alpha^0_{\nu} = 1/\sqrt{N}$

- In step (2) $(N-1)$ new basis states $a^*_i$ ($1 \leq i \leq N-1$) are formed which are normalized and orthogonal to each other and to $a^*_0$.

- In step (3) the s-band Hamiltonian $H_0$ is constructed in this new basis. One puts the state $a^*_0$ at the top so that its matrix elements are $H_{0i}$ and $H_{00}$.

- In step (4) the $(N-1)$-sub Hamiltonian which does not contain the state $a^*_0$ is diagonalized. The resulting Hamilton matrix for the s-band then has the form

$$H_0 = \begin{pmatrix} E(0) & V_{fr}(1) & V_{fr}(2) & \ldots & V_{fr}(N-1) \\ V_{fr}(1) & E(1) & 0 & \ldots & 0 \\ V_{fr}(2) & 0 & E(2) & \ldots & 0 \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ V_{fr}(N-1) & 0 & 0 & \ldots & E(N-1) \end{pmatrix}$$

The creation operators of the new basis are given by a new set of $\{a^*_i\}$, $(0 < i < N - 1)$. Again the $a^*_i$ can be expressed in term of the s-states; $a^*_i = \sum_{\nu=1}^{N} \alpha^0_{\nu} c^*_\nu$. After the state $a^*_0$ is constructed the other states $a^*_i$ are uniquely determined. The additional s-d hopping Hamiltonian can be expressed in the terms of new basis and one obtains the Friedel Hamiltonian as given in eq. (6). The state $\Psi_{SS}$ is formed and its energy expectation value is calculated.

- In the final step (5) the state $a^*_0$ is rotated in the $N$ dimensional Hilbert space until one reaches the absolute minimum of the energy expectation value. In the example of the Friedel resonance Hamiltonian this energy agrees numerically with an accuracy of $10^{-15}$ with the exact ground-state energy of the Friedel Hamiltonian [17].

### A.3 The effective s-d matrix element for the multi-electron states

The calculation of the energy expectation value requires the calculation of many-electron matrix elements in different bases. We sketch here an example.
We consider the more general case that we have two wave functions \( \Psi_A = a_0^* a_0^+ \prod_{i=1}^{n-1} a_i^* \Phi_0 \) and \( \Psi_B = b_0^* d_0^+ \prod_{i=1}^{n-1} b_i^* \Phi_0 \). Each is built from two different bases: \( \{a_0^+, a_i^+\} \), \( \{a_0^-, a_i^-\} \) and \( \{b_0^+, b_i^+\} \), \( \{b_0^-, b_i^-\} \) (only within this section the operators \( b_i^* \) \( b_i^* \) are used for the AFR states to distinguish the different basis systems). The energy expectation value contains for example a matrix element of the form \( \langle \Psi_B | H_{sd}^+ | \Psi_A \rangle \). Here the s-d Hamiltonian \( H_{sd}^+ \) can be expressed in any basis but for this matrix element the \( a_0^+ \) \( a_0^+ \) representation is the optimal one. For the above matrix element one needs only the hopping for spin up (+):

\[
H_{sd}^+ = \sum_{i=0}^{N-1} V_{sd}^{a+} (i) \left[d_i^+ a_i + a_i^* d_i^+ \right]
\]

(13)

The only term in \( H_{sd}^+ \) which yields a non-vanishing contribution to \( \langle V_{sd}^{AB} \rangle \)
is \( \langle \Psi_B | \sum_{i=0}^{N-1} V_{sd}^{a+} (i) d_i^+ a_i^+ | \Psi_A \rangle \).

This matrix element contains

(a) the multi-scalar product of the two \( n \) electron states for spin down

\( F^{AB} = \langle b_0^* \prod_{i=1}^{n-1} b_i^* \Phi_0 | a_0^* \prod_{i=1}^{n-1} a_i^* \Phi_0 \rangle \)

and

(b) the matrix element \( M_{sd}^{AB} = \langle d_i^+ \prod_{i=1}^{n-1} b_i^* \Phi_0 | \sum_{i=0}^{N-1} V_{sd}^{a+} (i) d_i^+ a_i^+ | a_0^* \prod_{i=1}^{n-1} a_i^* \Phi_0 \rangle \).

The multi-scalar product is a determinant of order \( n \) containing the single electron scalar products between all occupied states.

\[
F^{AB} = \begin{vmatrix}
\langle b_0^* | a_0^* \rangle & \langle b_0^* | a_1^- \rangle & \cdots & \langle b_0^* | a_{(n-1)}^- \rangle \\
\langle b_1^* | a_0^* \rangle & \langle b_1^* | a_1^- \rangle & \cdots & \langle b_1^* | a_{(n-1)}^- \rangle \\
\vdots & \vdots & \ddots & \vdots \\
\langle b_{(n-1)}^* | a_0^* \rangle & \langle b_{(n-1)}^* | a_1^- \rangle & \cdots & \langle b_{(n-1)}^* | a_{(n-1)}^- \rangle 
\end{vmatrix}
\]

(14)

When the two AFR states are identical then the underlying matrix becomes the unity matrix.
Part (b) yields

$$\langle M_{sd}^{AB} \rangle = \begin{vmatrix}
V_{sd}^{a+}(0) & V_{sd}^{a+}(1) & \cdots & V_{sd}^{a+}(n-1) \\
\langle b_1^{*+} | a_0^{*+} \rangle & \langle b_1^{*+} | a_1^{*+} \rangle & \cdots & \langle b_1^{*+} | a_{(n-1)}^{*+} \rangle \\
\cdots & \cdots & \cdots & \cdots \\
\langle b_{(n-1)+}^{*+} | a_0^{*+} \rangle & \langle b_{(n-1)+}^{*+} | a_1^{*+} \rangle & \cdots & \langle b_{(n-1)+}^{*+} | a_{(n-1)}^{*+} \rangle
\end{vmatrix} \quad (15)$$

### A.4 Details of the comparison with Gunnarsson and Schoenhammer’s numerical evaluation

Gunnarsson and Schoenhammer (GS) \[22\] applied the large \(N_f\) method to finite Coulomb interaction and spin 1/2. They calculated the ground-state energy in different approximations. Since it is interesting to compare their results with the present calculation I sketch briefly the different states they considered. The corresponding graphical sketch of these states can be found in figure 1 of ref. \[22\]. These states are collected in table ???. The first column gives GS’s code for the state, the second column shows in which power of the \(1/N_f\) expansion the state occurs, the third column gives the occupation of the d-level in the considered state, the fourth column the number of holes and electrons (above the Fermi energy) in the s-band, and finally the fifth column gives the number of amplitudes (parameters) which one has to optimize in the numerical evaluation (again \(N\) is the number of band states in the numerical evaluation). As an example the state "d" is part of the \((1/N_f)^1\) expansion, it has, for example, the \(d_{\uparrow}^{+}\)-state occupied, the s-band has one hole in the \(s_{\uparrow}\)-band, another electron-hole pair is either in the \(s_{\uparrow}\)- or \(s_{\downarrow}\)-band. The total multiplicity of the state "d" is therefore \(2 \times (N/2) \times 2 \times (N/2)^2\). The prefactor \(2^2\) is replaced by "\(\alpha\)" in column 5 (\(\alpha \geq 1\)).
| name of state | power of expans. | occup. of d-states | s-band | no of param. |
|---------------|-----------------|-------------------|---------|-------------|
| $|0\rangle$    | $(1/N_f)^0$     | empty d-states    | half occupied band for spin $\uparrow$ and $\downarrow$ | 0 |
| a             | $(1/N_f)^0$     | 1 $d\uparrow$ or $d\downarrow$ | one $\uparrow$- or $\downarrow$-hole in $|0\rangle$ | $N/2$ |
| b             | $(1/N_f)^0$     | 2 d-states        | $\uparrow$-hole and $\downarrow$-hole in $|0\rangle$ | $\alpha (N/2)^2$ |
| c             | $(1/N_f)^1$     | empty d-states    | one $\uparrow$- or $\downarrow$ electron-hole pair in $|0\rangle$ | $\alpha (N/2)^4$ |
| d             | $(1/N_f)^1$     | 1 $d\uparrow$ or $d\downarrow$ | two holes in $|0\rangle$ and one electron | $\alpha (N/2)^3$ |
| e             | $(1/N_f)^1$     | 2 d-states        | three holes in $|0\rangle$ and one electron | $\alpha (N/2)^5$ |
| f             | $(1/N_f)^2$     | empty d-states    | two $\uparrow$- or $\downarrow$ electron-hole pairs in $|0\rangle$ | $\alpha (N/2)^4$ |
| g             | $(1/N_f)^2$     | 1 $d\uparrow$ or $d\downarrow$ | three holes in $|0\rangle$ and two electrons | $\alpha (N/2)^6$ |
| h             | $(1/N_f)^2$     | 2 d-states        | four holes in $|0\rangle$ and two electrons | $\alpha (N/2)^6$ |

Table 3: Gunnarsson and Schoenhammer states

G&S use a (different) exponential energy mesh of the form $\varepsilon_i = \pm [\alpha - \exp (x_i)]$. They use the value $\alpha = 0.2$, and $x_i$ lies in the range $(\ln (\alpha), \ln (\alpha + B_{GS})) = (-1.609, 1.824)$. This means $x_i$ takes the values $x_i = \ln (\alpha) + i/N \ast [\ln (\alpha + B_{GS}) - \ln (\alpha)]$. G&S used for $N$ the values 9, 19, 29 and extrapolated to $N \rightarrow \infty$. For this comparison I use the corresponding energy mesh and extrapolation. The only difference is that in my calculation the $\varepsilon_i$ yield the energy frame and the energy states lie in the center between two $\varepsilon_i$ whereas G&S used the $\varepsilon_i$ as their energy states. After the extrapolation towards $N \rightarrow \infty$ this difference should be negligible.

The energy dependent s-d-matrix element $V(\varepsilon)$ adds a complication in the numerical evaluation. It varies strongly with energy. I average $[V(\varepsilon)]^2$ over each energy range.
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