

# A new many-body solution of the Friedel resonance problem

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**Abstract.** It is numerically shown that the groundstate of the Friedel problem (consisting of a conduction band and a d-resonance), occupied with  $(n+1)$  electrons, can be written as  $\Psi = (Aa_0^* + Bd^*) \prod_{\nu=1}^n a_\nu^* \Phi_0$ , where  $a_0^*$  represents a localized conduction electron state,  $d^*$  is the Friedel resonance state and  $\prod_{\nu=1}^n a_\nu^* \Phi_0$  is a Slater determinant of  $n$  single electron states  $a_i^*$ , ( $\Phi_0$  is the vacuum state). The  $a_i^*$  together with  $a_0^*$  are part of a full orthonormalized basis of the conduction band.

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The Friedel resonance [1] is a classical problem in solid state physics. It describes a band of free electrons which interact with a resonance state, for example a  $d^*$  state. The Hamiltonian has the form:

$$H_0 = \sum_i \varepsilon_i c_i^* c_i + E_d + \sum_i V_{sd}(i) [d^* c_i + c_i^* d] \quad (1)$$

where the  $c_i^*$ ,  $c_i$  represent the creation and annihilation operators of s-like band electrons,  $d^*$  represent the d-resonance state. In the following I denote the states by their creation operators.  $V_{sd}(i)$  is the hopping matrix element between the  $d^*$  state and the band-electrons. If the s-d interaction is  $\delta$ -like then  $V_{sd}(i)$  is given by a constant  $V_{sd}$  times the amplitude of the free electron state  $c_i^*$  at the position of the  $d^*$  state. Later we will use Wilson's distribution of electron states [2] whose amplitude depends on the state  $c_i^*$ . Therefore the s-d-matrix-element may depend on  $c_i^*$ .

The Hamiltonian is a single particle Hamiltonian which can be diagonalized. The eigenstates have the energy  $E_j$  which fulfill the relation

$$E_j - E_d = \sum_i \frac{V_{sd}(i)^2}{E_j - \varepsilon_i} \quad (2)$$

The new creation operators  $b_j^*$  of the eigenfunctions  $\chi_j = b_j^* \Phi_0$  have the form

$$b_j^* = \sum_i \beta_{ji} c_i^* + \beta_j d^* \quad (3)$$

where  $\beta_j = [1 + \sum_i \frac{V_{sd}(i)^2}{(E_j - \varepsilon_i)^2}]^{-1/2}$  and  $\beta_{ji} = \frac{V_{sd}(i)}{E_j - \varepsilon_i} \beta_j$ .

If we have  $(n+1)$  electrons in the energy band of  $N$  states then the  $(n+1)$ -electron groundstate has the form

$$\Psi = \prod_{j=1}^{n+1} b_j^* \Phi_0 \quad (4)$$

where  $\Phi_0$  is the vacuum state. Using (3) and executing the multiplication one finds that this wave function can be written as

$$\Psi = A \Psi_{n+1} + B d^* \Psi_n \quad (5)$$

The function  $\Psi_n$  consists of  $\binom{N}{n}$  Slater determinants and  $\Psi_{n+1}$  contains  $\binom{N}{n+1}$  Slater determinants. It appears rather hopeless that these states can be expressed in simple terms. However, the author observed numerically that  $\Psi_n$  can be written as a single Slater determinant

$$\Psi_n = \prod_{i=1}^n a_i^* \Phi_0 \quad (6)$$

where the  $a_i^*$  are new creation operators for a basis of single electron states. The  $\Psi_{n+1}$  can be written as  $\Psi_n = a_0^* \prod_{i=1}^n a_i^* \Phi_0$  where  $a_0^*$  represents a localized free electron state. The total  $(n+1)$  electron state has then the form

$$\Psi = [Aa_0^* + Bd^*] \prod_{i=1}^n a_i^* \Phi_0 \quad (7)$$

Now I describe the construction of the state  $a_0^*$  and the rest of basis  $a_i^*$ . We start with a free electron band consisting of  $N$  states, which are represented by the creation operators  $c_i^*$ . We ignore the  $d^*$ -state for a short while.

In step (1) we form out of the free electron states a normalized state  $a_0^*$  (which is at first arbitrary) with:

$$a_0^* = \sum_{\nu=1}^N a_\nu^0 c_\nu^* \quad (8)$$

In step (2) we form  $(N-1)$  new basis states which are normalized and orthogonal to each other and to  $a_0^*$ .

In step (3) we construct the free electron Hamiltonian in this new basis. We put the state  $a_0^*$  at the top so that its matrix-elements are  $H_{0i}$  and  $H_{i0}$ .

In step (4) we diagonalize the (N-1) sub Hamiltonian which does not contain the state  $a_0^*$ . The creation operators of the new basis  $a_i^*$  can be expressed in term of the free electron states;  $a_i^* = \sum_{\nu=1}^N \alpha_{\nu}^i c_{\nu}^*$ . Then the free electron Hamiltonian takes the form

$$H_0 = \sum_{i=1}^{N-1} E(i) a_i^* a_i + E(0) a_0^* a_0 + \sum_{i=1}^{N-1} V_{fr}(i) [a_0^* a_i + a_i^* a_0] \quad (9)$$

where  $V_{fr}(i) = \sum_{\nu} \alpha_{\nu}^i \varepsilon_i \alpha_{\nu}^0$ ,  $E(i) = \sum_{\nu} \alpha_{\nu}^i \varepsilon_i \alpha_{\nu}^i$  and  $E(0) = \sum_{\nu} \alpha_{\nu}^0 \varepsilon_i \alpha_{\nu}^0$ .

I like to call this process ‘‘Friedel Reverse’’ and the state  $a_0^*$  the ‘‘artificial Friedel’’ state because we generated an (artificial) Friedel Hamiltonian out of our free electron Hamiltonian. It should be emphasized that the state  $a_0^*$  determines uniquely the rest of the new basis, i.e., the states  $a_i^*$ . (If some of the energies  $E(i)$  are degenerated then there is a trivial ambiguity in the basis states  $a_i^*$ .)

The total Hamiltonian takes now the form

$$H_0 = \sum_i E(i) a_i^* a_i + E(0) a_0^* a_0 + E_d d^* d + V'_{sd}(0) [d^* a_0 + a_0^* d] + \sum_i V_{fr}(i) [a_0^* a_i + a_i^* a_0] + \sum_i V'_{sd}(i) [d^* a_i + a_i^* d] \quad (10)$$

$$(11)$$

with  $V'_{sd}(i) = \sum_{\nu} V_{sd}(\nu) \alpha_{\nu}^i$ .

In this new Hamiltonian the states  $d^*$  and  $a_0^*$  are on equal footing. The state  $\Psi$  is built with these two states according to (7). The energy expectation value of this state is

$$E_0 = A^2 E(0) + B^2 E_d + 2ABV'_{sd}(0) + \sum_{i=1}^n E(i) \quad (12)$$

In our final step (5) we optimize the state  $a_0^* = \sum_{\nu=1}^N \alpha_{\nu}^0 c_{\nu}^*$ . For this purpose we rotate the state  $a_0^*$  in the Hilbert space until the energy expectation value  $E_0$  reaches its absolute minimum.

In the numerical calculation we use an energy band which extends from  $-1$  to  $1$ . In half of the numerical calculations we divide this band into a geometrical series of energy states as they were introduced by Wilson [2]. This yields the energies  $[\pm 3/4, \pm 3/8, \dots, \pm 3/2^{(N/2)}, \pm 1/2^{(N/2)}]$ . In the other half of the numerical calculation we use equidistant energy levels between  $-1$  and  $1$ . After several rounds of rotation we find the optimal  $a_0^*$  and the corresponding energy  $E_0$ .

It is, of course, easy to diagonalize the original Friedel Hamiltonian numerically and to calculate the groundstate energy of  $(n+1)$  electron states. This was done with an accuracy of better than  $10^{-13}$ . I will call the resulting energy the ‘‘exact’’ groundstate energy  $E_{00}$ . It turns out that the

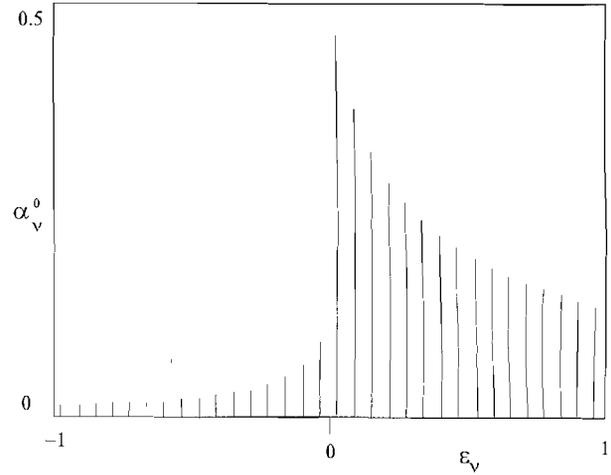


Fig. 1. The amplitudes of the ‘‘reverse Friedel’’ state  $a_0^*$  in terms of free electron states for 32 equidistant free electron states,  $V_{sd} = 0.25$ , and  $E_d = -0.5$

energy expectation value for our optimized state  $a_0^*$  agrees with the exact groundstate energy within the numerical accuracy of the calculation. As an example I choose a band of 40 equidistant levels in the energy range between  $-1$  and  $1$ , a d-level energy of  $E_d = -0.5$  and  $V_{sd} = 0.15$ . The ‘‘exact’’ Friedel groundstate energy for  $N/2 + 1 = 21$  electrons is determined. We subtract from this the energy  $E_m$  which is the sum of the lowest 20 free electron states (with the total energy 10) and the  $d^*$  state energy. (This represents the groundstate energy for  $V_{sd} = 0$  and removes the strong dependence of  $E_{00}$  on the levels of the conduction band). With this definition we find  $E_{00} = -0.0251584974013$ . Our iteration yield for  $E_0$  the same energy in all 13 digits. For the difference between the two energies the computer yields values which fluctuate around  $1 \cdot 10^{-14}$ , the internal accuracy of the computer.

Since the groundstate is not degenerated, any state which agrees with the groundstate in its energy must be the groundstate. Here it means that the constructed many-electron-state consists of the exact groundstate plus a small admixture of excited states whose overall concentration is less than  $10^{-10}$  for an equidistant energy spectrum. We take this as a numerical proof that the Friedel groundstate can be written in the form of (7). In Fig. 1 the coefficients  $\alpha_{\nu}^0$  of the artificial Friedel state  $a_0^*$  are plotted for an equidistant spectrum of  $N = 32$  levels. The following parameters were used in this calculation:  $V_{sd} = 0.25$ ,  $E_d = -0.5$ .  $(n+1) = (N/2 + 1) = 17$  electron states are occupied which corresponds to a half filled electron band plus one  $d^*$  electron. In Fig. 2 the energy spectrum  $E(i)$  of the states  $a_i^*$  is plotted for a free electron spectrum of 16 levels. The left ladder is the equidistant free electron energy ladder. The right ladder shows the energy  $E(i)$  of the new basis for  $1 \leq i \leq (N-1)$ . One observes that there is an additional separation of energy levels at the Fermi-energy and the energy of the artificial Friedel state,  $E(0)$ , is positive.  $E(0)$  and  $E_d$  have generally opposite signs. It should be emphasized that the new basis depends on the occupation number  $(n+1)$ .

We wish to better understand the mathematic behind this new wave-function of the groundstate. In order of the

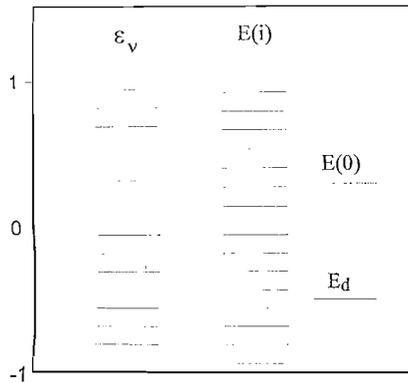


Fig. 2. The free electron spectrum  $\varepsilon_i$  on the left, the spectrum  $E(i)$  of the new basis, and the energy levels  $E(0)$  and  $E_d$ . An equidistant spectrum of 16 free electron states was used,  $V_{sd} = 0.25$  and  $E_d = -0.5$

groundstate to have the form of (7) it is first required that the state  $[Aa_0^* + Bd^*]$  must be an eigenstate of the part of the Hamiltonian which contains only the states  $a_0^*$  and  $d^*$ , i.e.  $H_{01} = E(0)a_0^*a_0 + E_d d^*d + V'_{sd}(0)[d^*a_0 + a_0^*d]$ . This yields the following secular equations:

$$\begin{aligned} E(0)A + V'_{sd}(0)B &= E'_0A \\ V'_{sd}(0)A + E_dB &= E'_0B \end{aligned} \quad (13)$$

These equations determine the energy of the state  $[Aa_0^* + Bd^*]$  and the coefficients  $A$  and  $B$ . (The secular equations have two solutions and the state with the lower energy yields the groundstate).

The other part of the Hamiltonian is  $H_{02} = \sum_i E(i)a_i^*a_i + \sum_i V_{fr}(i)[a_0^*a_i + a_i^*a_0] + \sum_i V'_{sd}(i)[d^*a_i + a_i^*d]$  which contains the new energy states  $E(i)$ , the transition matrix-elements between the states  $a_0^*$  and  $d^*$  on one side and the states  $a_i^*$  on the other side. In order for  $\Psi$  in (7) to be an eigenstate there should be no (non-zero) matrix-elements between the groundstate  $|0\rangle$  and any excited states. There are three classes of excited states which can be reached by a single electron transition:

- Both, the  $d^*$  state and the  $a_0^*$  state are empty and an electron is created above the Fermi energy. In this case either the  $a_0^*$  or the  $d^*$  state made a transition into an empty  $a_i^*$  state.
- Both, the  $d^*$  state and the  $a_0^*$  state are occupied and a hole is created below the Fermi energy. In this case an electron made a transition from an occupied  $a_i^*$  state into either the empty  $a_0^*$  or the empty  $d^*$  state.
- An electron-hole pair. This excited state can not be reached (directly) from the groundstate since the sub-Hamiltonian for  $a_i^*$  ( $1 \leq i \leq N-1$ ) is diagonal.

The transition from the groundstate  $|0\rangle$  to  $|a\rangle$  has the matrix-element  $[AV_{fr}(i) + BV'_{sd}(i)]$ . The transition from  $|0\rangle$  to  $|b\rangle$  has the matrix-elements  $[BV_{fr}(i) - AV'_{sd}(i)]$ . The effect of minimizing the energy expectation value  $E_0$  has the effect that the two above matrix-elements vanish (become less than  $10^{-9}$  in the numerical calculation). This yields the conditions

$$\begin{aligned} [AV_{fr}(i) + BV'_{sd}(i)] &= 0, \text{ for } 1 \leq i \leq n \\ [BV_{fr}(i) - AV'_{sd}(i)] &= 0, \text{ for } n+1 \leq i \leq N-1 \end{aligned} \quad (14)$$

Therefore the mathematical effect of introducing the artificial Friedel state  $a_0^*$  is to generate a new set of matrix-elements  $V_{fr}(i)$  which cancel the effect of the (now modified) s-d-interaction  $V'_{sd}(i)$ . The equation (14) represents  $(N-1)$  conditions and we have  $(N-1)$  free parameters. These parameters are essentially the amplitudes of the state  $a_0^*$  which has  $N$  components ( $(N-1)$  are independent).

The conditions (14) provide another way to construct the artificial Friedel state  $a_0^*$ . Instead of searching for the minimum of the energy expectation value  $E_0$  we square the matrix-elements in (14) and sum them. By minimizing this sum (until it reaches the value zero) while occupying the lowest  $n$  states  $a_i^*$  and choosing the lower state in the equations (13) we recover the same groundstate as before.

The significance of this new representation of the Friedel groundstate lies in the fact that it is well suited to describe the wave-function of interacting electron states, such as in the Friedel-Anderson model [3] for magnetic impurities. Here we can approximate the groundstate by a small sum of Slater determinants with either the  $a_0^*$  or the  $d^*$  state occupied. This ansatz is exact for zero Coulomb interaction as we have shown in this paper. Therefore it is a good starting point for the interacting case. As a matter of fact I observed the new groundstate of the Friedel Hamiltonian when I developed this method for the Anderson model and used the Friedel model as a test example for the numerical procedure as described above.

## References

- Friedel J., Philos.Mag. **43**, 153 (1952); Adv.Phys. **3**, 446 (1954); Philos.Mag.[Suppl.] **7**, 446 (1954); Can.J.Phys. **34**, 1190 (1956); Nuovo Cimento [Suppl.] **7**, 287 (1958); J.Phys.Radium **19**, 38 (1958)
- Wilson K.G., Rev.Mod.Phys. **47**, 773 (1975)
- Anderson P. W., Phys. Rev. **124**, 41 (1961)