

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^* , (Φ_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 δ -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 Φ_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 Ψ_n consists of $\binom{N}{n}$ Slater determinants and Ψ_{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 Ψ_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 Ψ_{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 Ψ 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

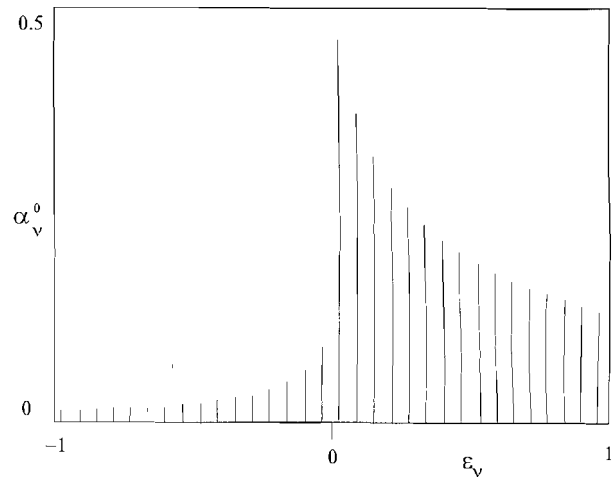


Fig. 1. The amplitudes of the ‘‘reverse Friedel’’ state a_0^* in terms of free electron states for 32 equidistant free electron states, $V_{sd} = 0.25$, and $E_d = -0.5$.

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 α_{ν}^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

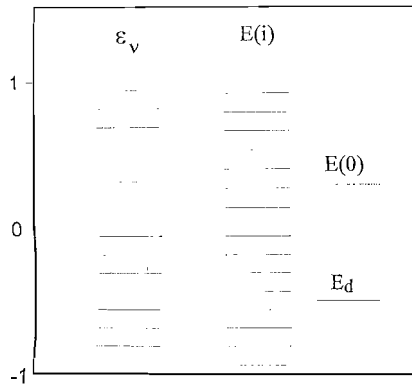


Fig. 2. The free electron spectrum ε_i on the left, the spectrum $E(i)$ of the new basis, and the energy levels $E(0)$ and E_d . An equidistant spectrum of 16 free electron states was used, $V_{sd} = 0.25$ and $E_d = -0.5$

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 Ψ 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.

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