The Friedel-Anderson and Kondo Impurity Problem for Arbitrary s-Band Density of States and Exchange Interaction.

Gerd Bergmann
Department of Physics
University of Southern California
Los Angeles, California 90089-0484
e-mail: bergmann@usc.edu

February 1, 2008

Abstract

In his renormalization paper of the Kondo effect Wilson replaced the full band of s-electrons by a small number of "Wilson states". He started from a rather artificial symmetric band with constant density of states and constant interaction with the impurity. It is shown in the present paper that with a minor modification the Wilson states are optimally suited to treat the interaction of an impurity with an arbitrary s-band. Each Wilson state represents electrons of a whole energy range $\Delta \varepsilon$. It carries the interaction of all these electrons with the impurity. All the other electron states in this energy range have zero interaction with the impurity and are neglected in the calculation. The resulting error is minor. As an example the singlet-triplet excitation energy of a Kondo impurity is numerically calculated for a tight-binding band with a strongly energy dependent density of states.

PACS: 75.20.Hr, 72.15.Rn
1 Introduction

The description of metal electrons as plane waves \( \psi_k(r) = e^{i k r} \sqrt{V} \) has been extremely successful during the past. However, if one wants to manipulate the whole electron basis one runs into problems. For example, a rotation of the whole basis in Hilbert space requires a number of Euler angles which is equal to \( N (N - 1) / 2 \) where \( N \) is the number of basis states. Such a rotation is rather difficult for \( N = 10^{23} \) in a macroscopic metal sample. Wilson [1] encountered a similar problem when he treated the Kondo effect where the impurity mixes the plane waves in complex ways. For his numerical evaluation Wilson strongly reduced the number of states to a few states and only included these ”Wilson”-states in his treatment. (Wilson called these states ”Kondo”-states).

The purpose of this paper is to illuminate some of the physics behind the use of the Wilson states and to introduce a generalization. We will consider a host with a d-impurity. Wilson used a band of electrons with constant density of states and a constant interaction with the impurity. This may appear to be rather artificial and far removed from a real system. This is far from true. With a minor modification the Wilson states can be applied to bands with arbitrary energy density of states and impurity interaction. This generalization does not increase the complexity of the calculation.

To demonstrate the method two examples will be treated quantitatively in this paper. Our group developed recently a new and very compact approximate solution for the Friedel-Anderson and the Kondo impurity problems [2], [?, 3]. This method yields remarkably accurate results for the ground-state energy and the singlet-triplet excitation energy. The ground state requires the construction of one localized s-electron state (per spin) \( a^\dagger_0 = \sum k \alpha^k_0 c^k \) while the remaining electron states are rearranged into states \( a^i \) so that the new basis \( \{ a^i \} \) is orthonormal. Since this requires an orthogonal transformation of the whole electron basis Wilson’s state reduction is essential in the numerical procedure. In section IV the ground-state energy and the singlet-triplet excitation energy for a Kondo impurity is numerically calculated for (i) a free electron system with \( \rho(\varepsilon) \propto \sqrt{\varepsilon} \) and (ii) a tight-binding metal. For both electron systems the density of states is not constant. Particularly in the tight binding band \( \rho(\varepsilon) \) show a strong variation (see Fig.2).
2 The Wilson States

Let us first start (like Wilson) with the somewhat artificial energy band having the half-band width $D$, i.e., the range $[-D : D]$ with a constant density of states. It is half filled and the Fermi level lies at zero energy. We divide all energies by the half-width $D$ of the band (see Fig. 1). Then the band extends from $-1$ to $+1$. The full band can accommodate one electron per atomic volume (and spin). The density of states (per spin) is $\rho_0 = 1/2$ per atomic volume $v_A$.

Wilson sub-divided the positive and negative parts of the energy band into $N$ cells. This is done on an exponential scale. The boundaries of the cells are for $\nu < N/2$ at $\xi_\nu = -1/2^\nu$, i.e. $-1$, $-1/2$, $-1/2^2$, ..., and for $\nu > N/2$ at $\xi_\nu = +1/2^{N-\nu}$, i.e. $+1/2^2$, $+1/2$, $1$. (Wilson used originally $\pm \Lambda^{\nu}$ with the parameter $\Lambda$ but generally chose the value $\Lambda = 2$). With these discrete points $\xi_\nu$ one obtains a sequence of intervals or cells. The interval $\nu$ (for $\nu < N/2$) is given by $\xi_{\nu-1} = -1/2^{\nu-1} < \varepsilon < -1/2^\nu = \xi_\nu$ or $[\xi_{\nu-1} : \xi_\nu]$. (The equivalent intervals for positive $\xi$-values are treated completely analogously).

The new Wilson states $\psi_\nu$ lie in the center of the energy interval $(\xi_{\nu-1}, \xi_\nu)$ and have an energy of $\varepsilon_\nu = (\xi_\nu + \xi_{\nu-1}) / 2$, i.e. $-3/4$, $-9/8$, $-27/16$, $-27/8$, $-27/4$ (for $\nu \leq N/2$). One essential property of the Wilson basis is that it has an arbitrarily fine energy spacing at the Fermi energy. In his normalization treatment of the Kondo effect Wilson entangled these states numerical with the Kondo impurity.

The first cell $C_1$ extends from $(-1 : -1/2)$. This cell contains $Z_1(\approx 10^{22})$ electron states which we denote as $\varphi_\mu (r)$. They all interact with the impurity. Now these states are transformed with the matrix $A$ where $A$ has the simple form $A_{\lambda\mu} = \exp (i2\pi \lambda \mu / Z_1) / \sqrt{Z_1}$. With $A_{\lambda\mu}$ one obtains the new states

$$\chi_\lambda (r) = \frac{1}{\sqrt{Z_\nu}} \sum \varphi_\mu (r) e^{i2\pi \lambda \mu / Z_\nu}$$

where $0 \leq \lambda < Z_1$ and the sum is taken over all states $\varphi_\mu (r)$ in $C_1$. 

3
Fig. 1a: Left side: Wilson’s rectangular symmetric energy band. It is divided into energy cells whose width decrease exponentially towards the Fermi energy. Each energy cell $\nu$ is represented by a state $\psi_{\nu}$ whose energy lies in the center of the cell. It represents the full interaction of all states in the cell with the impurity.

Fig. 1b: A realistic band with energy dependent density of states. The division into energy cell is completely analogous. The construction of the Wilson states is modified to accommodate the energy dependence of density of state and s-d-interaction.

If all states $\varphi_{\mu}(r)$ have the same s-d matrix element $v_{sd}$ with the impurity then only the state for $\lambda = 0$ has a finite interaction with the impurity. For all other states with $\lambda \neq 0$ the s-d interaction is zero. These states are ignored in the calculation. Then the cell $\mathcal{C}_1$ is represented by a single state $\psi_1(r)$ where

$$\psi_1(r) = \frac{1}{\sqrt{Z_1}} \sum \varphi_{\mu}(r)$$  \hspace{1cm} (1)
The energy (expectation value) of this state follows from the energies $e_\mu$ of the states $\varphi_\mu$

$$\varepsilon_1 = \sum e_\mu / Z_1 = \frac{1}{2} (\xi_0 + \xi_1)$$

This state has the s-d-matrix element $V_{sd}(1) = \sqrt{Z_1 v_{sd}}$.

The same procedure is then applied to all the other cells $\mathcal{C}_\nu$. In other words each energy cell is represented by just one state $\psi_\nu$ which carries the full interaction with the impurity. The neglected states have no interaction with the impurity.

For the discussed case (constant density of state and constant interaction) the s-d-matrix elements $V_{sd}(\nu)$ of the Wilson states are proportional to $\sqrt{Z_\nu}$ and given by

$$V_{sd}(\nu) = V_{sd}^0 \sqrt{\frac{\Delta \xi_\nu}{2}}$$

where $\Delta \xi_\nu = \xi_\nu - \xi_{\nu-1}$ is the width of the energy cell and $|V_{sd}^0|^2 = \sum_\nu |V_{sd}(\nu)|^2$.

The size of the energy cells is about equal to the distance from the Fermi level. From perturbation theory one realizes that each Wilson state has about the same coupling to the impurity. (The ratio of the square of the matrix element divided by the energy denominator $|V_{sd}(\nu)|^2 / \Delta \varepsilon_\nu$ yields about the same contribution as long as $\Delta \varepsilon_\nu$ can be replaced by $\varepsilon_\nu$ itself.)

Wilson’s philosophy was somewhat different when he introduced the "Kondo"-states. In his renormalization approach he considered the wave functions of these states as spherical shells, like in an onion, surrounding the impurity. The states $\psi_\nu, \psi_{N+1-\nu}$ belonged to the $(\nu - 1)$-th shell. During the renormalization procedure he first coupled the states $\psi_1, \psi_N$ directly to the impurity. Then he progressed step wise outwards by coupling the impurity complex (consisting of the impurity plus $(\nu - 1)$ shells) to the shell $\nu$. In our pragmatic application we consider the Wilson states as representatives of a finite energy range which contain the complete s-d-interaction of all the (neglected) states in the energy range with the impurity. The square of the resulting $V_{sd}(\nu)$ is proportional to the total number of states in that energy interval.

The neglected states which do not interact with the impurity cause a small error since they interact through the kinetic energy with the states $\psi_\nu$. But Wilson pointed out that this error is very small, a result that our calculations confirm.
3 Generalization of Wilson States

The Wilson concept can now be applied to an s-band with arbitrary density of states and state-dependent s-d-interaction. Numerically it is a trivial extension of the Wilson rectangular band. Let us consider a band that extends from $-D_1$ to $+D_2$ with the Fermi energy at zero energy. The density of states depends strongly on the energy and the matrix elements for the s-d-interaction $v_{sd}$ are not only a function of the energy but depend on the exact quantum numbers of the state. To simplify the discussion we normalize the energy with $D = \max(D_1, D_2)$ so that the band lies within $[-1 : +1]$ (see fig.1b). Then we subdivide the band as before obtaining the same energy cells $C_\nu$. Again we use the cell $C_1$ to demonstrate the new procedure. This cell contains $Z_1$ electron states $\varphi_\mu(r)$.

3.1 Friedel-Anderson impurity

Let us first consider the case where the electrons interact with the impurity through the s-d-interaction. Now this interaction $v_{sd,\mu}$ with the impurity depends on the state $\varphi_\mu$. In this case we define the Wilson state $\psi_1(r)$ as

$$\psi_1(r) = \sum v_{sd,\mu} \varphi_\mu(r) / \sqrt{\sum |v_{sd,\mu}|^2}$$

(2)

(The sum over $\mu$ is taken over all states $\varphi_\mu$ within the energy cell $C_1$.) The energy $\varepsilon_1$ of this state $\psi_1$ follows from the energies $e_\mu$ of the states $\varphi_\mu$:

$$\varepsilon_1 = \frac{\sum |v_{sd,\mu}|^2 e_\mu}{\sum |v_{sd,\mu}|^2}$$

(3)

This state has the full s-d-interaction of the cell $C_1$ with impurity. All other ($Z_1 - 1$) states which can be constructed from the states $\varphi_\mu$ within cell $C_1$ (being orthonormal to each other and to $\psi_1(r)$) have zero interaction with the impurity. This can be easily seen with the following argument. The state $\psi_1$ has the coefficients $\alpha_1^\mu = v_{sd,\mu} / \sqrt{\sum |v_{sd,\mu}|^2}$ in the basis of $\{\varphi_\mu\}$. If $\chi = \sum \beta^\mu \varphi_\mu$ is a state orthogonal to $\psi_1$ (built from the same basis $\{\varphi_\mu\}$) then the scalar product $\langle \chi | \psi_1 \rangle$ has to be zero, i.e.

$$\langle \chi | \psi_1 \rangle = \sum \alpha_1^\mu \beta^\mu = \frac{1}{\sqrt{\sum |v_{sd,\mu}|^2}} \sum v_{sd,\mu} \beta^\mu = 0$$
The s-d-matrix element between the state $\chi$ and the impurity is equal to the sum of its components, i.e.

$$V_{sd}(\chi) = \sum \nu_{sd,\mu} \beta^\mu = 0$$

From the orthogonality with respect to the state $\psi_1$ follows the disappearance of the interaction. Therefore all other states built from the $\{\varphi_\mu\}$-basis have no interaction with the impurity.

So now we have a new Wilson basis $\{\psi_\nu\}$ with the energies $\varepsilon_\nu$ and the s-d-interaction $V_{sd}(\nu)$. The energies $\varepsilon_\nu$ don’t lie anymore in the center of the cells and the s-d-matrix elements are no longer proportional to the square root of the cell width. (There may be even a cell or two with no Wilson state in it. Then one can either reduce the number of Wilson states or one gives these states zero s-d-interaction.) For a numerical evaluation this generalization of the Wilson states to arbitrary density of states and interaction causes no additional complications.

### 3.2 Kondo impurity

For a Kondo impurity the situation is slightly more difficult because the interaction matrix element $\langle \varphi_\mu(r) | J(r) | \varphi_\mu'(r) \rangle$ is taken between two s-electrons. We restrict ourselves here to the case where the exchange potential is a $\delta$-function $J(r) = J \delta(r)$. In this case the matrix element takes the value $J \varphi_\mu^*(0) \varphi_\mu'(0)$ and can be separated. Therefore the role of $\nu_{sd,\mu}$ in eq. (2) is replaced by $\varphi_\mu(0)$. Then the Wilson state $\psi_1$ for the Kondo impurity is

$$\psi_1(r) = \sum \varphi_\mu(0) \varphi_\mu(r) / \sqrt{\sum |\varphi_\mu(0)|^2}$$ (4)

These Wilson states have a maximal amplitude at the origin. All other states in $\mathbf{C}_1$ vanish at the origin and therefore they don’t interact with the $\delta$-exchange potential.

The matrix element between two Wilson states is

$$J_{\nu,\nu'} = J \sqrt{\sum_{\nu \in \varepsilon_\nu} |\varphi_\mu(0)|^2} \sqrt{\sum_{\nu' \in \varepsilon_{\nu'}} |\varphi_\mu'(0)|^2}$$ (5)

This means that treatment of the Friedel-Anderson and the Kondo impurity can be directly combined, for example, with density functional theory calculations of the s-electron band, the Coulomb and s-d-exchange interaction. One has just to extract from the band-structure calculation the energies and matrix-elements of a relatively small number $N$ of states (where $N$ is of the order 40)
4 Application of the Modified Wilson States in the Kondo Impurity Problem

As an example I calculate the Kondo ground state and its singlet-triplet excitation energy for three examples and compare the results. For the calculation I choose (i) the Wilson spectrum with \( \rho(\varepsilon) = 1/2 = \text{const} \), (ii) a three-dimensional free electron band with \( \rho(\varepsilon) \propto \sqrt{\varepsilon} \) and (iii) a tight-binding band for an fcc lattice. The density of states of the latter is sketched in Fig.3. These calculations are an extension of a recent paper on the Kondo effect [3]. In the appendix the authors ansatz for the Kondo solution is briefly sketched. It is discussed in detail in [3].

![Energy band for an fcc lattice in the tight binding model. The dark shaded region represents the half-filled band.](image)

4.1 Comparison between the different band-structures.

4.1.1 Rectangular Wilson band

Wilson’s original rectangular band, extending from \((-1 : +1)\) with \( \rho_0 = 1/2 \), is used. The singlet-triplet excitation energy is plotted in Fig.3a as a function of \( 1/(2\rho_0 J) \). It follows essentially an exponential law: \( \Delta E_{st} \propto \exp[-1/(2\rho_0 J)] \).
4.1.2 Free electron band.

Here the s-electrons are treated as free electrons. However, the s-band is defined as full (i.e. cut off) at the energy where the electron density of one electron per spin and atom is reached. Then the s-band is occupied with 1/2 electron for spin up and down. This defines the Fermi energy which can be expressed in terms of the atomic volume

\[ \varepsilon_F = \frac{\hbar^2}{2m} \left( \frac{3\pi^2}{v_a} \right)^{2/3} \]

When the energy is normalized by the Fermi energy and the Fermi level adjusted to zero the upper band edge lies at \( 2^{2/3} - 1 \approx 0.5874 \). The density of states at the Fermi energy per atom and spin is \( \rho_0 = 3/4 \). The singlet-triplet excitation energy is plotted in Fig.2 as stars. The (almost) straight line lies below the results of the rectangular Wilson band but is parallel to it.

4.1.3 Three dimensional tight binding

For a face centered cubic metal the tight binding energy is given by

\[ \varepsilon(k) = E_0 - 4t \left[ \cos \left( \frac{1}{2} k_x a \right) \cos \left( \frac{1}{2} k_y a \right) + \cos \left( \frac{1}{2} k_y a \right) \cos \left( \frac{1}{2} k_z a \right) + \cos \left( \frac{1}{2} k_z a \right) \cos \left( \frac{1}{2} k_x a \right) \right] \]

where \( E_0 \) is a constant energy, \( t \) is the coupling between nearest neighbors, i.e., the hopping matrix element, \( a \) is the cubic lattice constant and \( k = (k_x, k_y, k_z) \) is the wave number of the electron. By calculating the energy for all \( k \)-states in the first Brillouin zone (for a crystal of roughly \( 10^6 \) atoms or \( k \)-points in the 1BZ) one obtains a density of state which, after some smoothing, is shown in Fig.2. The actual values of \( E_0 \) and \( t \) cancel out through the normalization with the Fermi energy. The density of states per spin and atom at the Fermi energy is \( \rho_0 = 1.36 \) and is much larger than in the rectangular Wilson band. The singlet-triplet excitation energy is plotted in Fig.3 as triangles. The (almost) straight line lies below the results of the rectangular Wilson and the free electron band but is parallel to both.

All three curves follow essentially the exponential law \( \Delta E_{st}/D \propto \exp \left[ -1/(2J\rho_0) \right] \). For the half-band width \( D \) the value \( D = 1 \) is used in all three curves.
Fig. 3a: The logarithm of the singlet-triplet excitation energy \( \ln(\Delta E_{st}/D) \) is plotted as a function of \( 1/(2J\rho_0) \) for three different spectra with different density of states \( \rho_0 \) at the Fermi energy. For the half-band width \( D \) the value of one is used.

The fact that the three curves in Fig. 3a are essentially parallel to each other demonstrates that the density of states \( \rho_0 \) at the Fermi energy is the appropriate parameter because otherwise the different curves would form a finite angle. On the other hand the fact that the curves for the free electrons and the tight binding are shifted with respect to the rectangular band can be described by an effective half-band width \( D^* \) which is different from one. The shift is just equal to \( \ln(D^*) \). After adjusting an effective half-band width \( D^* \) the plots of \( \ln(\Delta E_{st}/D^*) \) yield a universal curve for the three cases as shown.
in Fig.3b.

Fig.3b: The same plot as in Fig.3a but using an effective half-band width $D^*$. 

In table I the effective values for the half-band width are collected in column 3. In column 4 the effective band width $2D^*$ is multiplied with $\rho_0$. The result is rather surprising. It yields the value one in all three cases.

The Kondo energy is essentially given by

$$k_B T_K \approx D^* \exp \left( -\frac{1}{2J\rho_0} \right)$$

The density of states $\rho_0$ appears in denominator of the exponent while the half-band width $D^*$ is just a pre-factor to the exponential function. From the numerical calculation follows that for the very different bands the product of $\rho_0$ and $2D^*$ is constant and equal to the number of states (per spin and
atom) in the whole band which is one.

\[ \rho_0 \]

| Spectrum        | \( \rho_0 \) | \( D^* \) | \( 2D^*\rho_0 \) |
|-----------------|--------------|----------|------------------|
| Wilson spectrum | 0.5          | 1        | 1                |
| Free Electrons  | 0.75         | 0.66     | 0.98             |
| Tight Binding   | 1.36         | .37      | 1.01             |

Table I: The density of states \( \rho_0 \) at the Fermi level, the effective half-band width \( D^* \) obtained from the Kondo calculation and the product \( 2D^*\rho_0 \) for bands with very different band structure.

5 Conclusion

The Wilson states are generalized to electron bands with energy dependent density of states and s-d-interaction. These state represent a finite energy range and possess the full interaction with the impurity. The Wilson states permit us to introduce band-structure data into numerical calculations of the Friedel-Anderson impurity and the Kondo impurity. This is demonstrated in three examples. These calculations show that the properties of the singlet- and triplet state of the Kondo impurity for an arbitrary band can be deduced from the results for a rectangular Wilson band and the actual density of states at the Fermi level.

Acknowledgement: The research was supported by the National Science Foundation DMR-0439810.


A Appendix

A.1 Friedel-Anderson impurity

With the Wilson bases the Friedel-Anderson Hamiltonian has the form

$$H_{FA} = \sum_{\sigma} \{ \sum_{\nu=1}^{N} \varepsilon_{\nu} c_{\nu\sigma}^* c_{\nu\sigma} + E_{dd}^* d_{\sigma}^* d_{\sigma} + \sum_{\nu=1}^{N} V_{sd}(\nu) [d_{\sigma}^* c_{\nu\sigma} + c_{\nu\sigma}^* d_{\sigma}] \} + U n_d + n_d^- \quad (6)$$

The author introduced a magnetic solution $\Psi_{MS}$ of the form

$$\Psi_{MS} = [A a_{0+1}^* a_{0+1} + B d_{0+1}^* d_{0+1} + C a_{0-1}^* d_{0+1} + D d_{0-1}^* d_{0+1}] |0_{a+1} 0_{a-1}\rangle$$

The states $a_{0+}$ and $a_{0-}$ are optimized localized states formed from the Wilson states. They determine the full bases $\{a_{i+}\}$ and $\{a_{i-}\}$. The many-electron state $|0_{a+1} 0_{a-1}\rangle$ is given by $\prod_{i=1}^{n-1} a_{i+}^* \prod_{i=1}^{n-1} a_{i-}^* \Phi_0$ where $\Phi_0$ is the vacuum state.

This solution has a considerably lower energy than the mean-field solution and yields lower magnetic moments than the mean-field solution. The threshold of the Coulomb interaction $U$ to form a magnetic moment is almost twice as large as in mean-field theory $[?]$. However, the real ground state is a symmetric state. It is obtained by reversing all spins in $\Psi_{MS}$ and superimposing the two solutions. Then one obtains

$$\Psi_{SS} = \Psi_{MS} (\uparrow \downarrow) \mp \Psi_{MS} (\downarrow \uparrow) \quad (7)$$

$$= [A a_{0+1}^* a_{0+1} + B d_{0+1}^* a_{0-1} + C a_{0-1}^* d_{0+1} + D d_{0-1}^* d_{0+1}] |0_{a+1} 0_{a-1}\rangle$$

$$\mp [\overline{A} a_{0-1}^* a_{0+1} + \overline{B} d_{0-1}^* a_{0+1} + \overline{C} a_{0-1}^* d_{0+1} + \overline{D} d_{0-1}^* d_{0+1}] |0_{a-1} 0_{a+1}\rangle$$

The final solution is obtained by minimizing the ground-state energy by optimizing the two localized states $a_{0+}^*$ and $a_{0-}^*$. The construction of the localized states $a_{0\pm}$ and the full basis $\{a_{i\pm}\}$ as well as the optimization are described in appendix A3.

This ground state is determined by the components of the two localized states $a_{0+}^*$ and $a_{0-}^*$. Since we generally use 40 Wilson states this requires 80 components. The resulting ground-state energy and the occupation of the d-states is of the same accuracy as a large $(1/N)$ expansion up to second order which requires the calculation of more than $10^7$ self-consistent amplitudes.
A.2 Kondo wave-function

The Kondo impurity has a magnetic moment. Therefore either the spin-up or spin-down d-state is occupied. Zero or double occupancy of the d-states is forbidden. Then the Coulomb interaction transforms into an exchange interaction of the form

\[ H_{\text{ex}} = v_a J \left[ \left( S_+ \Psi_+^\dagger(0) \Psi_+^\dagger(0) + S_- \Psi_-^\dagger(0) \Psi_-^\dagger(0) \right) \right. \]

\[ \left. + S_z \left( \Psi_+^\dagger(0) \Psi_+^\dagger(0) - \Psi_-^\dagger(0) \Psi_-^\dagger(0) \right) \right] \quad (8) \]

where \( S_+, S_-, S_z \) are the spin operators of the impurity with spin \( S = 1/2 \) and \( \Psi_+^\dagger(0) \) and \( \Psi_-^\dagger(0) \) represent field operators.

In ref. [3] the approximate solution for the Kondo impurity was introduced. It is given by equ. (9).

\[ \psi_K = (B a_{0+1}^* d_{i+1}^* + C d_{i-1}^* a_{0+1}^*) |0_{a+1}0_{a-1}\rangle + (C a_{0-1}^* d_{i-1}^* + B d_{i+1}^* a_{0-1}^*) |0_{a-1}0_{a+1}\rangle \quad (9) \]

It uses two sets a bases, \( \left\{ a_{i+}^\dagger \right\} \) and \( \left\{ a_{i-}^\dagger \right\} \) which are orthogonal transformed versions of a Wilson basis \( \left\{ c_{\nu}^\dagger \right\} \). Again the many-electron state \( |0_{a+1}0_{a-1}\rangle \) is given by \( \prod_{i=1}^{n-1} a_{i+1}^\dagger \prod_{i=1}^{n-1} a_{i-1}^\dagger \Phi_0 \). The first part of the ansatz consists of the product of two \( n \)-electron state \( |0_{a+1}0_{a-1}\rangle \) multiplied with the two-particle state \( (B a_{0+1}^* d_{i+1}^* + C d_{i-1}^* a_{0+1}^*) \). If one reverses all spins in this term one obtains the second term (after rearranging the operators). This solution is derived from the solution of the Friedel-Anderson impurity in the limit where zero and double occupancy of the d-level is zero (for infinite Coulomb potential \( U \) and \( E_d = -U/2 \)).

The final solution is obtained by minimizing the ground-state energy by optimizing the two localized states \( a_{0+}^\dagger \) and \( a_{0-}^\dagger \). The construction of the localized states \( a_{0\pm}^\dagger \) and the full basis \( \left\{ a_{i\pm}^\dagger \right\} \) as well as the optimization are described in appendix A3.

If one sets \( \overline{C} = C \) and \( \overline{B} = B \) one obtains the singlet ground state. If one permits a free variation of all four coefficients one obtains besides the singlet ground state also the excited triplet state with \( \overline{C} = -C \) and \( \overline{B} = -B \). We denote this state as the unrelaxed triplet state. One obtains the relaxed triplet state when the opposite signs of the coefficients are locked \( (\overline{C} = -C \) and \( \overline{B} = -B \)). Then the minimization of the energy yields the triplet state with the lowest energy. In present paper the unrelaxed singlet-triplet excitation is plotted for the different bands.
A.3 Construction of the Basis $a_0^\dagger$, $a_i^\dagger$

For the construction of the state $a_0^\dagger$ and the rest of basis $a_i^\dagger$ one starts with the s-band electrons $\{c_\nu^\dagger\}$ which consist of $N$ states (for example Wilson’s states). The $d^\dagger$-state is ignored for the moment.

- In step (1) one forms a normalized state $a_0^\dagger$ out of the s-states with:

$$a_0^\dagger = \sum_{\nu=1}^{N} \alpha_0^\nu c_\nu^\dagger$$  

(10)

The coefficients $\alpha_\nu^0$ can be arbitrary at first. One reasonable choice is $\alpha_\nu^0 = 1/\sqrt{N}$

- In step (2) $(N - 1)$ new basis states $a_i^\dagger$ ($1 \leq i \leq N - 1$) are formed which are normalized and orthogonal to each other and to $a_0^\dagger$.

- In step (3) the s-band Hamiltonian $H_0$ is constructed in this new basis. One puts the state $a_0^\dagger$ 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 $a_0^\dagger$ is diagonalized. The resulting Hamilton matrix for the s-band then has the form

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

(11)

The creation operators of the new basis are given by a new set of $\{a_i^\dagger\}$, $(0 < i \leq N - 1)$. Again the $a_i^\dagger$ can be expressed in terms of the s-states; $a_i^\dagger = \sum_{\nu=1}^{N} \alpha_i^\nu c_\nu^\dagger$. After the state $a_0^\dagger$ is constructed the other states $a_i^\dagger$ are uniquely determined. The additional s-d hopping Hamiltonian can be expressed in the terms of the new basis, and one obtains the Friedel Hamiltonian as given in eq. (??). The state $\Psi_{SS}$ is formed, and the energy expectation value (of the full Hamiltonian) is calculated.
• In the final step (5) the state $a_0^\dagger$ is rotated in the $N$-dimensional Hilbert space. In each cycle the state $a_0^\dagger$ is rotated in the $(a_0^\dagger, a_i^\dagger)$ plane by an angle $\theta_{i_0}$ for $1 \leq i_0 \leq N - 1$. Each rotation by $\theta_{i_0}$ yields a new $a_0^\dagger$

$$a_0^\dagger = a_0^\dagger \cos \theta_{i_0} + a_i^\dagger \sin \theta_{i_0}$$

The rotation leaves the whole basis $\{a_0^\dagger, a_i^\dagger\}$ orthonormal. Step (4), the diagonalization of the $(N - 1)$-sub Hamiltonian, is now much quicker because the $(N - 1)$-sub-Hamiltonian is already diagonal with the exception of the $i_0$-row and the $i_0$-column. For each rotation plane $(a_0^\dagger, a_i^\dagger)$ the optimal $a_0^\dagger$ with the lowest energy expectation value is determined. This cycle is repeated 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 [4]. For the Friedel-Anderson impurity the procedure is stopped when the expectation value changes by less than $10^{-10}$ during a full cycle.
References

[1] K.G.Wilson, Rev.Mod.Phys. 47, 773 (1975), The renormalization group: Critical phenomena and the Kondo problem

[2] G.Bergmann, Phys.Rev. B 74, 144420 (2006), Compact Approximate Solution to the Friedel-Anderson Impurity Problem

[3] G.Bergmann and Liye Zhang, Phys.Rev. B 76, 064401 (2007), A Compact Approximate Solution to the Kondo Problem

[4] G.Bergmann, Z.Physik B102, 381 (1997), A new many-body solution of the Friedel resonance problem

[5] G.Bergmann, Eur.Phys.J.B2, 233 (1998), Geometrical derivation of a new groundstate formula for the n-electron Friedel resonance