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Kondo atoms, double exchange molecules, and a novel large S expansion for the ordered Kondo lattice

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Abstract

Kondo lattice models are widely used to describe systems where local magnetic moments couple to itinerant electrons. We construct a novel large S expansion scheme for an ordered Kondo lattice, starting from the eigenstates of the Kondo coupling on a single site, and paying particular attention to the special case of two sites sharing a single electron, which we solve exactly. The expansion scheme which we introduce is shown to reproduce all features of this exact solution, to $O(1/S^2)$, and to offer a better physical starting point than previous approaches for calculating the properties of systems on a lattice in the ‘double exchange’ limit of strong Hund’s rule coupling.

1. Introduction

Systems of localized spins coupled to itinerant electrons are ubiquitous in the physics of rare earth and transition metal compounds. In the case of transition metal oxides with partially filled shells of d electrons, the first Hund’s rule coupling between the spin of the local moments and the itinerant electrons can be very large compared with the bandwidth of the delocalized electrons; it therefore plays a crucial role in determining the behaviour of the material. The ferromagnetic (FM) ground state of the widely studied colossal magnetoresistance (CMR) manganite $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$, for example, was explained by Zener [1] in terms of such a model; the essence of his ‘double exchange’ (DE) mechanism is that strong on-site Hund’s rule interaction between localized and itinerant electrons tends to favour states in which spins are locally aligned parallel to one another, as these maximize the kinetic energy of the itinerant electrons.

For the purposes of the article we will consider a sufficiently general Hamiltonian to be defined by

$$\mathcal{H} = -t \sum_{\langle ij \rangle \alpha} c_{i\alpha}^\dagger c_{j\alpha} - J \sum_i \vec{S}_i \cdot \vec{s}_i \quad \vec{s}_i = \frac{1}{2} \sum_{\alpha\beta} c_{i\alpha}^\dagger \vec{\sigma}_{\alpha\beta} c_{i\beta} \quad (1)$$

where t is an electron hopping integral, $J > 0$ is the strength of the exchange rule coupling, the sum i runs over all lattice sites and $\langle ij \rangle$ over all nearest neighbours. The Fermi operator

$c_{i\alpha}^\dagger$ creates an itinerant electron with spin α on site i , \vec{S}_i is the spin operator for the localized spin on that site, and the components of $\vec{\sigma}$ are Pauli matrices. In the limit $0 < -J \ll |t|$ this model is a simple generalization of the Kondo impurity model to a lattice (Kondo lattice model). Here we will, in the main, discuss results in the limit $0 < |t| \ll J$ relevant to Zener's DE model, but the calculation scheme developed here is *not* restricted to that limit.

While the physics of CMR materials is now understood to be very much more complicated than the simple DE picture would suggest, the Hamiltonian (1) still forms the basis of our understanding of their magnetic properties, and for finite J may equally be applied to many other systems. It is therefore desirable to find a convenient method of calculating the magnetic and electronic properties of such a model. In general this is very difficult, as the model possess both spin and charge degrees of freedom, and these are mixed by the Kondo coupling term. All possible spin and charge configurations of the model therefore play a role determining its ground state and excitation spectrum, and even in the DE model where the limit $J \rightarrow \infty$ can be used to project out many of these states, the most general quantization of (1) still leads to a rather involved gauge field theory.

It is much easier to make progress, however, if we start by assuming a classically ordered ground state and then expand fluctuations about that state using an appropriate small parameter. Furthermore it is convenient to work in the 'natural' coordinates of the system, so that a clear separation between the energy scale of excitations governed by the local (atomic) energy scale J and those governed by the kinetic energy scale t . In expanding magnetic excitations it is also desirable to use a coordinate system in which the important symmetries of the problem (for example the Goldstone mode) are manifest.

In what follows we will consider the length of the localized spin degree of freedom S to be a large parameter and expand all physical observables in powers of $1/S$. We will do so using an operator representation which has all of the properties described above. We will further argue that, if such an ordered classical ground state exists, it may be reduced to a network of bonds between neighbouring sites, each described by

$$\mathcal{H}^{ij} = -t \sum_{\alpha} c_{i\alpha}^\dagger c_{j\alpha} + c_{j\alpha}^\dagger c_{i\alpha} - J[\vec{S}_i \cdot \vec{s}_i + \vec{S}_j \cdot \vec{s}_j] \quad (2)$$

and that any expansion scheme which correctly reproduces the matrix elements of (2) can therefore be used to evaluate properties on the lattice.

Details of the actual calculations for lattice models will be presented elsewhere; here we concentrate on the mathematical structure of our expansion scheme (first introduced in [2]), and on the test case of a single bond described by (2), in the DE limit $J \gg t$. In this context we make comparisons with other possible expansion schemes, and show that the semi-classical mapping of the spin excitations of the DE model onto an effective Heisenberg model is flawed even at the level of two sites.

We begin in section 2 by considering the basic building block of a Kondo lattice, the 'Kondo atom' described by the Kondo coupling term on a single site. We explicitly construct an operator representation of the eigenstates of this Hamiltonian to fourth order in $1/\sqrt{S}$. To do this we must extend the usual Holstein–Primakoff representation of spin operators to the case where the length of the spin is not fixed, and introduce a 'composite spin' representation in which the fluctuations of the localized and itinerant electron spins are treated on an equal footing.

In section 3 we apply this composite spin representation to the simplest possible Kondo lattice model, the 'double exchange molecule' of two sites sharing a single electron, in the limit $J/t \gg 1$. The key point is that, having diagonalized the Kondo coupling term, we may expand the kinetic energy in powers of $1/S$, constructing a perturbation theory for interactions between the spin and charge based on the small parameter t/S , rather than the large parameter

JS . Our expansion scheme is shown to reproduce all features of an exact solution of the DE model on two sites. Details of the exact solution are included in the appendix.

In section 4, we discuss the advantages of our expansion scheme with respect to a few of the alternative methods which have been used to treat the FM DE model. We conclude in section 5 with an overview.

2. The Kondo atom

Let us start by considering the ‘Kondo atom’ of a single localized spin and an itinerant (spin degenerate) electron orbital, for which

$$\mathcal{H}_1 = -J_1 \vec{S} \cdot \vec{s}. \tag{3}$$

We can diagonalize this Hamiltonian in terms of eigenstates of charge, total spin, and the z -component of total spin. This is a natural generalization of the problem of spin–orbit coupling—we write

$$\begin{aligned} \mathcal{H}_1 &= -J_1 \vec{S} \cdot \vec{s} \\ &= -\frac{J_1}{2} [(\vec{S} + \vec{s})^2 - \vec{S}^2 - \vec{s}^2] \\ &= -\frac{J_1}{2} [S(S+1) - S(S+1) - s(s+1)]. \end{aligned} \tag{4}$$

Here $s = \{0, 1/2\}$ is the spin quantum number for the itinerant electron, and the total spin quantum number can take on values $\mathcal{S} = S \pm s = \{S + 1/2, S, S - 1/2\}$. We find three corresponding eigenvalues

$$\left\{ -\frac{J_1 S}{2}, 0, \frac{J_1 S}{2} \left(1 + \frac{1}{S}\right) \right\} \tag{5}$$

where the state with total spin S and eigenvalue zero is doubly degenerate and corresponds to zero or double occupancy of the itinerant electron state.

The families of eigenstates associated with the eigenvalues $-J_1 S/2$ and $J_1(S + 1)/2$ are easily found. We first determine the state with maximum S^z associated with each eigenvalue. Introducing the notation $u^\dagger = c_{\uparrow}^\dagger$ and $d^\dagger = c_{\downarrow}^\dagger$, these are

$$|\mathcal{S} = S + 1/2, S^z = S + 1/2\rangle = u^\dagger |S^z = S\rangle \tag{6}$$

$$|\mathcal{S} = S - 1/2, S^z = S - 1/2\rangle = \sqrt{\frac{2S}{2S+1}} \left[d^\dagger |S^z = S\rangle - \frac{1}{\sqrt{2S}} u^\dagger |S^z = S - 1\rangle \right] \tag{7}$$

(where $|S^z = S\rangle$ corresponds to the atom being prepared in a state with no itinerant electron and spin $S^z = S$, etc). The $2S + 1$ states associated with each value of total spin \mathcal{S} can then be found by acting on these with the total spin lowering operator

$$S^- = S^- + d^\dagger u^\dagger \tag{8}$$

we will return to this below.

At a classical level (to zeroth order in $1/S$) the states with $\mathcal{S} = S \pm 1/2$ correspond to aligning or anti-aligning the spin of a single itinerant electron with the localized spin on that site. At this level we can replace the Kondo coupling with a local magnetic field which defines a new z -axis and corresponding ‘up’ (f) and ‘down’ (p) states for that site. This corresponds to making an $SU(2)$ rotation of the electron spin coordinates such that the z -axis follows the direction of the instantaneous local magnetization, and one approach to deriving an action for this problem is to work in the $SU(2)$ rotated local frame and introduce a gauge field to describe

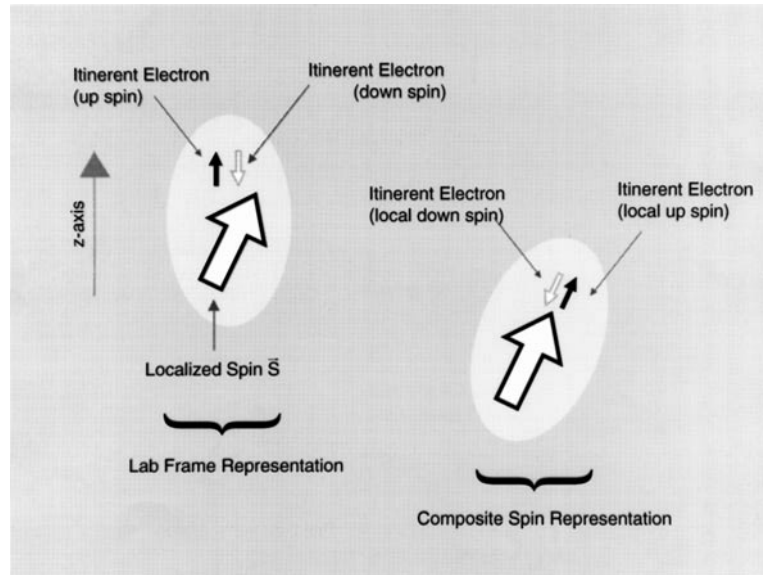


Figure 1. Schematic diagram of composite spin and lab frame representations. The electron operators $c_{\uparrow}, c_{\downarrow}$ and the spin boson a act in the lab frame representation, while f, p and \tilde{a} belong to the composite spin representation.

the rotation of coordinates for an electron hopping along any given bond of the lattice (see e.g. [5]). A schematic illustration of this local ‘composite spin’ representation of the Kondo atom is shown in figure 1.

In terms of the operators for local ‘up’ and ‘down’ spin electrons we obtain a representation of the Kondo coupling which depends on charge variables alone:

$$\tilde{\mathcal{H}}_1 \approx -\frac{J_1 S}{2} [f^\dagger f - p^\dagger p]. \quad (9)$$

However, this approach is meaningful *only* in the classical limit for which the orientation of the local magnetization is a variable and not an operator.

We obtain the correct eigenvalues of the full quantum mechanical problem by modifying this simple ‘Zeeman-splitting’ form to give

$$\tilde{\mathcal{H}}_1 = -\frac{J_1 S}{2} \left[f^\dagger f - p^\dagger p \left(1 + \frac{1}{S} \right) + \frac{f^\dagger f p^\dagger p}{S} \right]. \quad (10)$$

The new local interaction

$$-J_1 \frac{f^\dagger f p^\dagger p}{2} \quad (11)$$

comes from the fact that the eigenvalues of \mathcal{H}_1 for $S = S \pm 1/2$ are not symmetric about zero. For FM Kondo coupling $J_1 > 0$ (in the absence of any other on-site repulsion terms) if the system has both f and p electrons it can save energy by putting them on the same site.

This easy fix hides a deeper question—what does it mean to talk about a local up or down state relative to a quantum mechanical spin operator and not a classical vector? Since at least one component of a quantum mechanical spin must be undetermined, the obvious answer is ‘nothing’.

The classical picture breaks down as follows. If we classify the states of a single site in terms of eigenstates of the z -components of the electron and core spins (by specifying the

occupancy of c_\uparrow and c_\downarrow electrons and the S^z component of the localized ‘core’ spin) there are $2S + 1$ ‘vacuum’ states with eigenvalue 0 of the form

$$|u^\dagger u = 0, d^\dagger d = 0, S^z = m\rangle \quad m = S, S - 1, \dots, -S \quad (12)$$

on which f and p operators may act. The eigenstates of \mathcal{H}_1 are determined by specifying the occupancy of f and p electrons and the S^z component of the total spin. Clearly there are $2S + 2$ states with the eigenvalue $-J_1 S/2$ of the form

$$|f^\dagger f = 1, p^\dagger p = 0, S^z = \tilde{m}\rangle \quad \tilde{m} = S + \frac{1}{2}, S - \frac{1}{2}, \dots, -S - \frac{1}{2} \quad (13)$$

while there are only $2S$ states with the eigenvalue $-J_1 S/2(1 + 1/S)$ of the form

$$|f^\dagger f = 0, p^\dagger p = 1, S^z = \tilde{m}\rangle \quad \tilde{m} = S - \frac{1}{2}, S - \frac{3}{2}, \dots, -S + \frac{1}{2}. \quad (14)$$

From these simple counting arguments we see that there cannot exist simple scalar f and p operators which map the vacuum states for any given z -component of the localized spin S^z onto an eigenvalue of \mathcal{H}_1 with well defined z -component of the total spin S^z .

Let us instead ask a more restricted question. For small fluctuations of a localized spin \vec{S} of length $S \gg 1$, can we write down a one-to-one mapping between vacuum states and eigenstates of \mathcal{H}_1 such that we can define scalar Fermi operators f and p within this limited subset of states? The answer to this question is ‘yes’, and the prescription is very simple

$$\begin{aligned} f^\dagger |u^\dagger u = 0, d^\dagger d = 0, S^z = m\rangle &\equiv f^\dagger |f^\dagger f = 0, p^\dagger p = 0, S^z = m\rangle \\ &= |f^\dagger f = 1, p^\dagger p = 0, S^z = m + \frac{1}{2}\rangle \end{aligned} \quad (15)$$

$$\begin{aligned} p^\dagger |u^\dagger u = 0, d^\dagger d = 0, S^z = m\rangle &\equiv p^\dagger |f^\dagger f = 0, p^\dagger p = 0, S^z = m\rangle \\ &= |f^\dagger f = 0, p^\dagger p = 1, S^z = m - \frac{1}{2}\rangle. \end{aligned} \quad (16)$$

This choice corresponds to imposing the algebra

$$[f, S^z] = f/2 \quad [p, S^z] = -p/2 \quad (17)$$

and the procedure remains well defined at $1/S^2$ for $S \geq 3/2$.

We now turn to the spin algebra of the composite spin plus fermion object \vec{S} .

Provided the atom has a well defined preferred direction of magnetization (provided, for example, by a magnetic field or by its position in a magnetically ordered lattice), we can describe small fluctuations of the core spin \vec{S} using a Holstein–Primakoff transformation

$$S^z = S - a^\dagger a \quad (18)$$

$$S^+ = \sqrt{2S} \sqrt{1 - \frac{a^\dagger a}{2S}} a \quad (19)$$

$$S^- = \sqrt{2S} a^\dagger \sqrt{1 - \frac{a^\dagger a}{2S}} \quad (20)$$

where $[a, a^\dagger] = 1$. The Kondo term then reads

$$\mathcal{H}_1 = -\frac{J_1 S}{2} \left(\left(1 - \frac{a^\dagger a}{S}\right) [u^\dagger u - d^\dagger d] + \sqrt{\frac{2}{S}} \sqrt{1 - \frac{a^\dagger a}{2S}} a d^\dagger u + \sqrt{\frac{2}{S}} a^\dagger \sqrt{1 - \frac{a^\dagger a}{2S}} u^\dagger d \right). \quad (21)$$

For greater readability here and in what follows we use the notation $c_\uparrow = u, c_\downarrow = d$.

What we are interested in describing, however, is not fluctuations of the core spin alone, but of the core spin together with its local up and down spins—these are the true Goldstone modes of the system. To achieve this we generalize the Holstein–Primakoff representation to

the composite object \vec{S} by replacing the length of spin S with the operator \mathcal{S}

$$S^z = S^z + \frac{u^\dagger u - d^\dagger d}{2} = \mathcal{S} - \tilde{a}^\dagger \tilde{a} \quad (22)$$

$$S^+ = S^+ + u^\dagger d = \sqrt{2\mathcal{S}} \sqrt{1 - \frac{\tilde{a}^\dagger \tilde{a}}{2\mathcal{S}}} \tilde{a} \quad (23)$$

$$S^- = S^- + d^\dagger u = \sqrt{2\mathcal{S}} \tilde{a}^\dagger \sqrt{1 - \frac{\tilde{a}^\dagger \tilde{a}}{2\mathcal{S}}} \quad (24)$$

$$\mathcal{S} = S + \frac{f^\dagger f - p^\dagger p}{2} \quad (25)$$

where once again $[\tilde{a}, \tilde{a}^\dagger] = 1$. We know that the Kondo term \mathcal{H}_1 must commute with all rotations of the total spin \mathcal{S} . This constraint is automatically satisfied if the new spin boson \tilde{a} commutes with the new Fermi operators f and p . Note that this does *not* imply the commutation of f and p operators with the spin rotations S^+ and S^- .

Our goal is now to explicitly construct \tilde{a} , f and p operators in terms of a , u and d , which we do by expanding order by order in $1/\sqrt{S}$. The transformation is highly constrained by (I) the requirement that f , p and \tilde{a} are mutually (anti)commuting Fermi and Bose operators, (II) the need for them to correspond to the spin and charge algebra indicated above and (III) by the physical constraints that the total number of particles is conserved

$$f^\dagger f + p^\dagger p = u^\dagger u + d^\dagger d \quad (26)$$

and that double or zero occupancy of the electron orbital corresponds to the same two sets of states state in either representation

$$f^\dagger p^\dagger = u^\dagger d^\dagger \quad \text{etc.} \quad (27)$$

As well as satisfying each of these constraints order by order in $1/\sqrt{S}$, we must ensure an order-by-order identity between the desired spinless form of \mathcal{H}_1 (equation (10)) and the Holstein-Primakoff representation of the Kondo coupling (equation (21)).

This set of constraints is sufficient to uniquely define the transformation, and after lengthy algebra we find

$$\tilde{a} = a \left[1 + \frac{d^\dagger d - u^\dagger u}{4S} + \frac{3u^\dagger u - 5d^\dagger d + 2u^\dagger u d^\dagger d}{32S^2} \right] + \frac{u^\dagger d}{\sqrt{2S}} \left(1 - \frac{1}{4S} \right) - \frac{d^\dagger u}{\sqrt{2S}} \frac{aa}{4S} \quad (28)$$

$$f = u \left[1 - \frac{a^\dagger a + d^\dagger d}{4S} + \frac{3d^\dagger d + 3a^\dagger a - 2d^\dagger d a^\dagger a - a^\dagger a^\dagger aa}{32S^2} \right] + \frac{da^\dagger}{\sqrt{2S}} \left(1 - \frac{1}{4S} \right) \quad (29)$$

$$p = d \left[1 - \frac{a^\dagger a + uu^\dagger}{4S} + \frac{3uu^\dagger + 3a^\dagger a - 2uu^\dagger a^\dagger a - a^\dagger a^\dagger aa}{32S^2} \right] - \frac{ua}{\sqrt{2S}} \left(1 - \frac{1}{4S} \right). \quad (30)$$

We can compare the states created by the f^\dagger and p^\dagger operators acting on a spin S with given S^z directly with the exact eigenstates of (3), and find an exact correspondence, order by order in $1/\sqrt{S}$.

For purposes of developing a calculation scheme based on these coordinates we need the corresponding inverse transformation. This is found to be identical up to the sign of terms at odd order in $1/\sqrt{S}$:

$$a = \tilde{a} \left[1 + \frac{p^\dagger p - f^\dagger f}{4S} + \frac{3f^\dagger f - 5p^\dagger p + 2f^\dagger f p^\dagger p}{32S^2} \right] - \frac{f^\dagger p}{\sqrt{2S}} \left(1 - \frac{1}{4S} \right) + \frac{p^\dagger f}{\sqrt{2S}} \frac{\tilde{a}\tilde{a}}{4S} \quad (31)$$

$$u = f \left[1 - \frac{\tilde{a}^\dagger \tilde{a} + p^\dagger p}{4S} + \frac{3p^\dagger p + 3\tilde{a}^\dagger \tilde{a} - 2p^\dagger p \tilde{a}^\dagger \tilde{a} - \tilde{a}^\dagger \tilde{a}^\dagger \tilde{a}\tilde{a}}{32S^2} \right] - \frac{p\tilde{a}^\dagger}{\sqrt{2S}} \left(1 - \frac{1}{4S} \right) \quad (32)$$

$$d = p \left[1 - \frac{\tilde{a}^\dagger \tilde{a} + ff^\dagger}{4S} + \frac{3ff^\dagger + 3\tilde{a}^\dagger \tilde{a} - 2ff^\dagger \tilde{a}^\dagger \tilde{a} - \tilde{a}^\dagger \tilde{a}^\dagger \tilde{a}\tilde{a}}{32S^2} \right] + \frac{f\tilde{a}}{\sqrt{2S}} \left(1 - \frac{1}{4S} \right). \quad (33)$$

While these expressions may look formidable, all that is in fact needed to develop the zero temperature perturbation theories to $O(1/S^2)$ used in this paper are a subset of the leading terms of the inverse transformation

$$u = f \left[1 - \frac{\tilde{a}^\dagger \tilde{a}}{4S} \left(1 - \frac{3}{8S} \right) \right] - \frac{p \tilde{a}^\dagger}{\sqrt{2S}} + \text{irrelevant terms} \quad (34)$$

$$d = p + \frac{f \tilde{a}}{\sqrt{2S}} \left(1 - \frac{1}{4S} \right) + \text{irrelevant terms}. \quad (35)$$

In the next section we develop a practical example of an application of a perturbation theory based on this substitution.

3. The DE molecule

To demonstrate that our expansion scheme is valid, and to gain some insight into the validity of the many approximation schemes possible at $O(1/S)$, we first consider the smallest possible Kondo ‘lattice’ system—the two site ‘DE molecule’ described by

$$\mathcal{H}^{12} = -J_1 [\vec{S}_1 \cdot \vec{s}_1 + \vec{S}_1 \cdot \vec{s}_1] - t \sum_{\alpha} c_{1\alpha}^\dagger c_{2\alpha} + c_{2\alpha}^\dagger c_{1\alpha} \quad (36)$$

in the limit $0 < |t| \ll J_1$. In this limit, at fillings of less than one itinerant electron per site, the Kondo coupling acts as a principally as a projection operator, ensuring that the spin of an itinerant electron on any given site is aligned with the core spin on that site.

In the appendix we present an exact solution of this Hamiltonian in the subspace with the z -component of the total spin $S_0^z = 2S - 1/2$ and one itinerant electron, for arbitrary t , J_1 . We find six possible eigenstates, a pair with total spin $S_0 = 2S + 1/2$ and the eigenvalues $-J_1 S/2 \pm t$ and four with total spin $S_0 = 2S - 1/2$ and eigenvalues

$$E = \frac{J_1}{4} \pm \frac{\Delta E}{2} \sqrt{1 + \left(\frac{2t}{\Delta E} \right)^2} \pm 2 \left(\frac{2t}{\Delta E} \right) \cos \frac{\theta}{2} \quad (37)$$

where $\Delta E = J(S + 1/2)$ is the energy splitting between f and p electrons and θ is a parameter defined by

$$\cos \frac{\theta}{2} = \frac{2S}{2S + 1}. \quad (38)$$

In the limit $S \rightarrow \infty$ (and only in that limit), θ can be interpreted as the angle between two spins.

Expanding in powers of $1/S$ we find for the lowest energy eigenvalue

$$E_{-+} = -\frac{J_1 S}{2} - t \left[1 - \frac{1}{2S} + \frac{1}{4S^2} \right] - \frac{t^2}{J_1 S^2} + O\left(\frac{1}{S^3}\right). \quad (39)$$

We will use this as a starting point for checking perturbation theory based on our expansion scheme.

We can derive an effective Hamiltonian capturing the physics of the DE model on two sites using the inverse transformation (31) to express the electron (c_α) and spin (S^i) operators in (36) in terms of $\{f_1, p_1, \tilde{a}_1, f_2, p_2, \tilde{a}_2\}$ and then throwing away all terms containing p operators. To $O(1/S^2)$ this gives

$$\mathcal{H}^{12} = \mathcal{H}_0^{12} + \mathcal{V}_2^{12} + \mathcal{V}_4^{12} \quad (40)$$

$$\mathcal{H}_0^{12} = -\frac{J_1 S}{2} [f_1^\dagger f_1 + f_2^\dagger f_2] - t [f_1^\dagger f_2 + f_2^\dagger f_1] \quad (41)$$

$$\mathcal{V}_2^{12} = \frac{t}{4S} f_1^\dagger f_2 \left[(\tilde{a}_1^\dagger \tilde{a}_1 + \tilde{a}_2^\dagger \tilde{a}_2) \left(1 - \frac{3}{8S} \right) - 2\tilde{a}_1^\dagger \tilde{a}_2 \left(1 - \frac{1}{2S} \right) \right] + \text{h.c.} \quad (42)$$

$$\mathcal{V}_4^{12} = \frac{t}{32S^2} f_1^\dagger f_2 [\tilde{a}_1^\dagger \tilde{a}_1^\dagger \tilde{a}_1 \tilde{a}_1 + \tilde{a}_2^\dagger \tilde{a}_2^\dagger \tilde{a}_2 \tilde{a}_2 - 2\tilde{a}_1^\dagger \tilde{a}_1 \tilde{a}_2^\dagger \tilde{a}_2]. \quad (43)$$

Since we only wish to discuss spinwave-like excitations with one unit of angular momentum (relative to the ground state), at zero T we can drop \mathcal{V}_4^{12} entirely.

We first diagonalize the kinetic energy terms in the Hamiltonian and separate out physically distinct spin excitations by making the change of coordinates

$$f_0^\dagger = \frac{1}{2}(f_1^\dagger + f_2^\dagger) \quad f_\pi^\dagger = \frac{1}{2}(f_1^\dagger - f_2^\dagger) \quad (44)$$

$$p_0^\dagger = \frac{1}{2}(p_1^\dagger + p_2^\dagger) \quad p_\pi^\dagger = \frac{1}{2}(p_1^\dagger - p_2^\dagger) \quad (45)$$

$$\tilde{a}_0^\dagger = \frac{1}{2}(\tilde{a}_1^\dagger + \tilde{a}_2^\dagger) \quad \tilde{a}_\pi^\dagger = \frac{1}{2}(\tilde{a}_1^\dagger - \tilde{a}_2^\dagger) \quad (46)$$

Physically, \tilde{a}_0 is the Goldstone mode and \tilde{a}_π maps to the zone corner spinwave in the lattice case. In terms of these operators

$$\mathcal{H}^{12} = \mathcal{H}_0^{12} + \mathcal{V}_1^{12} + \mathcal{V}_2^{12} \quad (47)$$

$$\mathcal{H}_0^{12} = -\frac{J_1 S}{2} (n_{f_0} + n_{f_\pi}) + \frac{J_1 (S+1)}{2} (n_{p_0} + n_{p_\pi}) - t[(n_{f_0} + n_{p_0}) - (n_{f_\pi} + n_{p_\pi})] \quad (48)$$

$$\mathcal{V}_1^{12} = \frac{t}{\sqrt{2S}} (f_0^\dagger p_\pi - f_\pi^\dagger p_0) \tilde{a}_\pi + \text{h.c.} \quad (49)$$

$$\mathcal{V}_2^{12} = \frac{t}{4S} \left\{ (n_{f_0} - n_{f_\pi}) \left[\frac{N_0}{8S} + \left(2 - \frac{7}{8S} \right) N_\pi \right] - (f_0^\dagger f_\pi - f_\pi^\dagger f_0) (\tilde{a}_0^\dagger \tilde{a}_\pi - \tilde{a}_\pi^\dagger \tilde{a}_0) \right\} \quad (50)$$

where $n_{f_0} = f_0^\dagger f$, $N_0 = \tilde{a}_0^\dagger \tilde{a}_0$, etc. The ground state of the molecule at zeroth order in $1/S$ is

$$|\phi\rangle = f_0^\dagger |0\rangle \quad (51)$$

with energy $-J_1 S/2 - t$, where the vacuum state $|0\rangle$ is chosen to have $S_1^z = S_2^z = S$. We can find the energies of the excitations created by the operators \tilde{a}_0^\dagger and \tilde{a}_π^\dagger acting on this state using conventional perturbation theory. To $O(1/S^2)$ we find

$$E_0^{(0)} = 0 \quad (52)$$

$$E_\pi^{(0)} = -\frac{J_1 S}{2} - t \left[1 - \frac{1}{2S} + \frac{1}{4S^2} \right] \quad (53)$$

i.e. in exact agreement with equation (39).

To calculate leading order corrections in t/J_1 we need to include only the lowest order terms in p operators

$$\Delta \mathcal{H}_0^{12} = \frac{J_1 (S+1)}{2} [p_1^\dagger p_1 + p_2^\dagger p_2] + \frac{J}{2} [f_1^\dagger f_1 p_1^\dagger p_1 + f_2^\dagger f_2 p_2^\dagger p_2] - t[p_1^\dagger p_2 + p_2^\dagger p_1] \quad (54)$$

$$\mathcal{V}_1^{12} = \frac{t}{\sqrt{2S}} (f_2^\dagger p_1 - f_1^\dagger p_2) (\tilde{a}_1^\dagger - \tilde{a}_2^\dagger) + \text{h.c.} \quad (55)$$

in the Hamiltonian. The energies of the \tilde{a}_0^\dagger and \tilde{a}_π^\dagger excitations are then modified according to

$$\Delta E_0^{t/J_1} = 0 \quad \Delta E_\pi^{t/J_1} = -\frac{t^2}{J_1 S^2} \quad (56)$$

once again in perfect agreement with equation (39).

4. Comparison with alternative expansion schemes

We have demonstrated that a novel large S expansion scheme based on the (local) eigenstates of the Kondo coupling term can correctly describe certain low lying excitations of a ‘DE molecule’. However, as this simple two-site model can in any case be solved exactly, it is scarcely sufficient to justify the effort involved. We need therefore to show that, when it comes to evaluating quantum corrections in more complicated lattice models, our expansion scheme is either more rigorous, more intuitively appealing or easier to work with than the many alternatives. Considerable ingenuity has been brought to bear on the DE model alone over the 50 years for which it has been studied, and the DE model is only one of many possible Kondo lattice models. We do not pretend here to offer a complete review of previous work, but use some of the more obvious alternative ways of calculating the spinwave spectrum of a FM DE model to illustrate what we believe to be the advantages of our approach.

In fact it is not too hard to get the leading order ($1/S$) excitation energies of the DE model right on semi-classical arguments alone. If we treat the spins as classical vectors, then the transfer of a locally aligned f electrons from one site to another can be achieved by any operator which includes both the projection to remove local ‘down’ spins together the necessary $SU(2)$ rotation between local coordinate frames. Considering again the simplest case of two sites, we obtain

$$\mathcal{H}^{12} \sim -\frac{JS}{2}[f_1^\dagger f_1 + f_2^\dagger f_2] - t \cos \frac{\theta}{2}[f_1^\dagger f_2 + f_2^\dagger f_1]. \quad (57)$$

Since in this semi-classical picture θ corresponds to the angle between the two spins we can write

$$\cos \frac{\theta}{2} = \sqrt{\frac{1 + \cos \theta}{2}} = \sqrt{1 + \frac{1}{2} \left(\frac{\vec{S}_1 \cdot \vec{S}_2}{S^2} - 1 \right)} = \frac{3}{4} + \frac{\vec{S}_1 \cdot \vec{S}_2}{4S^2} + \dots \quad (58)$$

which clearly has the form of a (FM) Heisenberg coupling between sites 1 and 2. We can further expand spin excitations by substituting for components of \vec{S}_i in (58) in terms of the Holstein–Primakoff bosons a_i (to this order it makes no sense to distinguish between rotations of the localized spin \vec{S}_i and the composite spin \vec{S}_i). Doing this, we obtain an interaction between spinwaves and electrons of the form

$$\mathcal{V}_2 \sim \frac{t}{4S} f_1^\dagger f_2 (a_1^\dagger a_1 + a_2^\dagger a_2 - a_1^\dagger a_2 - a_2^\dagger a_1) + \text{h.c.} \quad (59)$$

To leading order in $1/S$, once again, we find the correct excitation energies

$$E_0^{(0)} = 0 \quad (60)$$

$$E_\pi^{(0)} = -\frac{J_1 S}{2} - t \left[1 - \frac{1}{2S} \right]. \quad (61)$$

However, this agreement is misleading—the Hamiltonian we have described is not really equivalent to the DE model as it contains the spurious operator

$$-\frac{t}{4S} f_1^\dagger f_2 a_2^\dagger a_1 + \text{h.c.} \quad (62)$$

and therefore if we go on to evaluate higher-order corrections, these will all be wrong. On closer examination we see that this mistake corresponds to neglecting the phase of the operator $f_1^\dagger f_2$ on the bond between sites 1 and 2.

It is then natural to ask whether the agreement between the exact eigenvalues and the predictions of our expansion scheme is more than a happy coincidence? We can check by

evaluating all of the matrix elements of the effective Hamiltonian explicitly, and, as shown in the appendix, the ‘effective’ Hamiltonian we derive in terms of f , p and \tilde{a} operators really is *identical* to the Hamiltonian \mathcal{H}^{12} (equation (36)) from which we started. This agreement is enough to justify applying the expansion scheme to ordered lattice models, since any lattice model can be thought of as a network of such bonds. Details of its application to lattice models will be described elsewhere [2]; here we briefly discuss the relative merits of different approaches, concentrating once again on magnetic excitations of FM lattice in the DE model limit $J \rightarrow \infty$.

One approach to the finding the spinwave spectrum on a lattice is to generalize the simple semi-classical mapping onto a Heisenberg model by applying approximation (58) to every bond in the lattice. If we assume FM order, and trace out (average over) the itinerant electrons we obtain a spinwave spectrum of the form

$$\omega_q = 2zJ_{DE}S[1 - \gamma_q] \quad J_{DE} = \frac{\bar{t}}{4S^2} \quad (63)$$

where \bar{t} is the expectation value of the kinetic energy per bond in the lattice and $\gamma_q = 1/z \sum_{\bar{\delta}} e^{i\vec{q}\cdot\bar{\delta}}$, where z is the lattice coordination number and the sum on $\bar{\delta}$ runs over nearest neighbours. This is the usual result for a FM Heisenberg model with nearest-neighbour coupling, and is also correct at leading order in $1/S$ for the FM DE model. However, because we have used the properties of a classical spin in deriving this approximation scheme, it cannot be used to evaluate quantum effects, as discussed above.

We can also derive the simple result of (63) using usual many-body techniques to treat the interaction between core spins and itinerant electrons. For a Kondo lattice in the limit $t \ll |J|$, it is natural to start with a band description of the itinerant electrons, and to introduce J as a perturbation; the Kondo coupling then leads to an effective RKKY interaction between spins determined by the details of the magnetic susceptibility of the itinerant electrons. One may also construct a perturbation theory in J in the limit $J \gg t$ and apply it to the FM DE model, using conventional Holstein–Primakoff bosons to quantize fluctuations of the core spin [6]. In this case the up-spin and down-spin electron bands are split by an energy JS and the important vertices for interaction between core spins and itinerant electrons are of the form

$$\frac{(JS)}{S} a^\dagger a [c_\uparrow^\dagger c_\uparrow - c_\downarrow^\dagger c_\downarrow] \quad \frac{(JS)}{\sqrt{S}} a^\dagger c_\uparrow^\dagger c_\downarrow + \text{h.c.} \quad (64)$$

This approach has two serious drawbacks. First, the spin excitations of the DE model have a characteristic energy scale t/S , once we have used the limit $J \rightarrow \infty$ to remove all minority spin electrons. However, the energy scale associated with each vertex above is JS , a product of two large parameters and in no sense a perturbation. In fact to obtain the correct physical energy scale for spinwave excitations we must rely on a cancellation between an infinite numerator and an infinite denominator in our ‘perturbation’ theory. Second, this approach does not respect our basic intuition about Hund’s rule physics, which is that the so far as magnetic excitations are concerned, it makes no sense to distinguish between core and localized electrons. Working in a basis which does not reflect the underlying physics of the model has important technical consequences; calculations of quantum effects at $O(1/S^2)$ require evaluation of diagrams at *fourth* order in $1/\sqrt{S}$, using a complex momentum dependent vertex.

A simple solution to the technical challenges presented by this conventional large- S expansion approach is to use a canonical transformation to remove terms linear in spinwave operators from the Hamiltonian [7]. This leads to a relatively straightforward scheme for calculating the properties of the FM DE model, which in the limit $J \rightarrow \infty$ is essentially equivalent to that obtained using our large- S expansion scheme. However the simplified vertices which remain after the canonical transformation still involve the ‘infinite’ energy

scale JS , and the nature of the physical excitations described by the transformed operators is far from transparent.

In the case of our novel large- S scheme the nature of the spinwave excitations of the FM DE model is immediately clear. We have quantized collective rotations of the combined spin of core and itinerant electrons on each site, and spinwaves are simply Bloch states of these collective modes. In a DE system the Goldstone mode is a rotation of the total magnetization of the core and itinerant electrons, and working in this collective basis it is evident how and why the Goldstone theorem is respected. Furthermore all vertices for interaction between spin and charge excitations have the prefactor t , and we expand in powers of S so the energy scale t/S associated with spinwave excitations emerges naturally from a calculation of self energy corrections for spin boson operators. Specifically, for the Hamiltonian, equation (1), in the limit $J \rightarrow \infty$, to $O(1/S^2)$ we obtain

$$\mathcal{H}_0 = \mathcal{H}'_0 + \mathcal{V}_2 + \mathcal{V}_4 \quad (65)$$

$$\mathcal{H}'_0 = -zt \sum_{\langle ij \rangle} f_i^\dagger f_j \quad (66)$$

$$\mathcal{V}_2 = \frac{zt}{4S} \sum_{\langle ij \rangle} f_i^\dagger f_j \left[(\tilde{a}_i^\dagger \tilde{a}_i + \tilde{a}_j^\dagger \tilde{a}_j) \left(1 - \frac{3}{8S} \right) - 2\tilde{a}_i^\dagger \tilde{a}_j \left(1 - \frac{1}{2S} \right) \right] \quad (67)$$

$$\mathcal{V}_4 = \frac{zt}{32S^2} \sum_{\langle ij \rangle} f_i^\dagger f_j [\tilde{a}_i^\dagger \tilde{a}_i^\dagger \tilde{a}_i \tilde{a}_i + \tilde{a}_j^\dagger \tilde{a}_j^\dagger \tilde{a}_j \tilde{a}_j - 2\tilde{a}_i^\dagger \tilde{a}_i \tilde{a}_j^\dagger \tilde{a}_j]. \quad (68)$$

The important vertex for the scattering of spinwaves from electrons is now of the form

$$\frac{t}{S} \tilde{a}^\dagger \tilde{a} f^\dagger f \quad (69)$$

which conserves separately the angular momentum of (collective) spin and itinerant electron excitations. Our physical intuition is that the hopping of electrons lifts the degeneracy between states with different spin textures on a scale t/S is manifest in the Hamiltonian before we even begin to calculate. In fact calculations of quantum and temperature corrections to the spinwave spectrum of the FM DE model starting from (65) are very straightforward, and show very different behaviour from corrections in a FM Heisenberg model. This is particularly true of the damping of spinwaves (which is non-zero even at zero temperature) and of the quantum corrections to the classical spinwave dispersion, which generate new long-range effective Heisenberg couplings at zero temperature. In addition, corrections the spinwave dispersion at finite temperature show departures from the simple $T^{5/2}$ scaling expected of a Heisenberg model. These issues will be discussed elsewhere [2].

The most powerful and technically sophisticated method which to have been applied to the FM DE model is gauge-field theory. The $SU(2)$ rotation associated with the local electron coordinate frame for each site in the lattice can be parametrized using a gauge field, and the spin operators for each site quantized using a coherent state representation. Since the resulting action is quadratic in Fermi operators, the itinerant electrons can be traced out to give an effective action for the gauge field and associated spin rotations. In principle this method may be applied in the absence of a small parameter $1/S$, or of a magnetically ordered ground state, since the gauge field carries all the information on the orientation of the localized spin, and is not just a parametrization of small fluctuations. However, it is hard to perform calculations in any limit other than that in which our expansion scheme may be applied, namely one in which the system is magnetically ordered and possess well defined semi-classical excitations (spinwaves). So far as we aware quantum corrections to the spinwave spectrum of the DE FM have not yet been calculated by this approach.

5. Conclusions

There are, in principle, many different ways of calculating the electronic and magnetic properties of Kondo lattice systems. Some, but not all, of the expansions used to derive semi-classical properties like spinwave spectra may also be used to reliably calculate quantum corrections to these properties. In this paper we developed a novel, fully quantum mechanical expansion scheme which is particularly convenient for the analysis of magnetically ordered systems where the Kondo coupling is large compared with the itinerant electron bandwidth. The scheme is found to be exact, up to $O(1/S^2)$ for the minimal model of two sites sharing a single electron, and to have a number of conceptual and technical advantages over alternative approaches when it comes to calculating the properties of lattice models.

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Appendix. Exact solution of the two site problem

In this appendix we solve exactly the two-site 'Kondo molecule' defined by

$$\mathcal{H}^{12} = \mathcal{H}_0^{12} + \mathcal{H}_1^{12} \quad (\text{A1})$$

$$\mathcal{H}_0^{12} = -t \sum_{\alpha} c_{1\alpha}^{\dagger} c_{2\alpha} + c_{2\alpha}^{\dagger} c_{1\alpha} \quad (\text{A2})$$

$$\mathcal{H}_1^{12} = -J_1 [\vec{S}_1 \cdot \vec{s}_1 + \vec{S}_1 \cdot \vec{s}_1] \quad (\text{A3})$$

in the subspace with one electron and z -component of total spin $S_0^z = 2S - 1/2$. The Hamiltonian \mathcal{H}^{12} commutes with the total spin S_0 of the molecule, with S_0^z and is invariant under the interchange of sites 1 and 2, so we expect to be able to simultaneously diagonalize all of these operators.

There are total of six independent states for the 'molecule' with one electron and $S^z = 2S - 1/2$; we can immediately write down six states which span this subspace, three with the electron on site one

$$|1\rangle = |\uparrow, S\rangle_1 |0, S-1\rangle_2 \quad (\text{A4})$$

$$|2\rangle = |\uparrow, S-1\rangle_1 |0, S\rangle_2 \quad (\text{A5})$$

$$|3\rangle = |\downarrow, S\rangle_1 |0, S-1\rangle_2 \quad (\text{A6})$$

and three with the electron on site two

$$|4\rangle = |0, S-1\rangle_1 |\uparrow, S\rangle_2 \quad (\text{A7})$$

$$|5\rangle = |0, S\rangle_1 |\uparrow, S-1\rangle_2 \quad (\text{A8})$$

$$|6\rangle = |0, S\rangle_1 |\downarrow, S\rangle_2 \quad (\text{A9})$$

where $|0, S\rangle_1$ denotes site one being prepared in a state with no itinerant electron, $S_1^z = S$, etc.

In terms of these states, the hopping term in the Hamiltonian reads

$$\mathcal{H}_0^{12} = -t(|1\rangle |2\rangle \dots |6\rangle) \begin{bmatrix} \mathbf{0} & \mathbf{h}_0 \\ \mathbf{h}_0 & \mathbf{0} \end{bmatrix} \begin{pmatrix} \langle 1| \\ \langle 2| \\ \vdots \\ \langle 6| \end{pmatrix} \quad (\text{A10})$$

where $\mathbf{0}$ is the empty (3×3) matrix and \mathbf{h}_0 is the matrix

$$\mathbf{h}_0 = \begin{bmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix} \quad (\text{A11})$$

which has determinate -1 .

The easiest way to find the eigenstates of \mathcal{H}^{12} is to construct a basis of simultaneous eigenstates of the on-site Kondo coupling \mathcal{H}_1^{12} and total spin S_0 , and then to allow intersite hopping \mathcal{H}_0^{12} to lift the degeneracy between these states. We construct the required basis in two steps. First we diagonalize \mathcal{H}_1 by the transformation

$$(|\phi_1\rangle |\phi_2\rangle |\phi_3\rangle) = (|1\rangle |2\rangle |3\rangle) \begin{bmatrix} 1 & 0 & 0 \\ 0 & \sqrt{\frac{2S}{2S+1}} & \frac{-1}{\sqrt{2S+1}} \\ 0 & \frac{1}{\sqrt{2S+1}} & \sqrt{\frac{2S}{2S+1}} \end{bmatrix} \quad (\text{A12})$$

together with an exactly equivalent rotation of the vector $(|4\rangle |5\rangle |6\rangle)$ into $(|\phi_4\rangle |\phi_5\rangle |\phi_6\rangle)$. The Hamiltonian in this intermediate basis reads

$$\begin{aligned} \mathcal{H}^{12} &= (|\phi_1\rangle |\phi_2\rangle \dots |\phi_6\rangle) \\ &\times \begin{bmatrix} -\frac{J_1 S}{2} & 0 & 0 & 0 & -t\sqrt{\frac{2S}{2S+1}} & \frac{t}{\sqrt{2S+1}} \\ 0 & -\frac{J_1 S}{2} & 0 & -t\sqrt{\frac{2S}{2S+1}} & -\frac{1}{2S+1} & -\frac{\sqrt{2S}}{2S+1} \\ 0 & 0 & \frac{J_1(S+1)}{2} & \frac{t}{\sqrt{2S+1}} & -\frac{\sqrt{2S}}{2S+1} & -\frac{2S}{2S+1} \\ 0 & -t\sqrt{\frac{2S}{2S+1}} & \frac{t}{\sqrt{2S+1}} & -\frac{J_1 S}{2} & 0 & 0 \\ -t\sqrt{\frac{2S}{2S+1}} & -\frac{1}{2S+1} & \frac{t}{\sqrt{2S+1}} & 0 & -\frac{J_1 S}{2} & 0 \\ \frac{t}{\sqrt{2S+1}} & -\frac{\sqrt{2S}}{2S+1} & -\frac{2S}{2S+1} & 0 & 0 & \frac{J_1(S+1)}{2} \end{bmatrix} \\ &\times \begin{pmatrix} \langle \phi_1| \\ \langle \phi_2| \\ \vdots \\ \langle \phi_6| \end{pmatrix}. \end{aligned} \quad (\text{A13})$$

We will return to this result below.

The next step is to construct a basis of eigenstates of S_0 , in which case the two sectors with total spin $S_0 = 2S + 1/2$ and $S_0 = 2S - 1/2$ decouple completely. The two p states $|\phi_3\rangle$ and $|\phi_6\rangle$ already have well defined total spin $S_0 = 2S - 1/2$, but the states $|\phi_1\rangle, |\phi_2\rangle, |\phi_3\rangle$ and $|\phi_4\rangle$ do not. We can easily construct an f state on site 1 with total spin $S_0 = 2S + 1/2$ and

$S_0^z = 2S - 1/2$, by acting with a total spin lowering operator on the (unique) eigenstate with $S_0 = 2S + 1/2$ and $S_0^z = 2S - 1/2$

$$\phi_0 = |\uparrow, S\rangle_1 |0, S\rangle_2. \quad (\text{A14})$$

This gives the state

$$|\phi_1^*\rangle = \frac{\sqrt{2S}|1\rangle + \sqrt{2S}|2\rangle + |3\rangle}{\sqrt{4S+1}} \quad (\text{A15})$$

$$= \sqrt{\frac{2S}{4S+1}}|\phi_1\rangle + \sqrt{\frac{2S+1}{4S+1}}|\phi_2\rangle \quad (\text{A16})$$

We now form an orthogonal f state with total spin $S_0 = 2S - 1/2$ and $S_0^z = 2S - 1/2$. It turns out to be convenient to make the choice

$$(|\phi_1^*\rangle |\phi_2^*\rangle |\phi_3^*\rangle) = (|\phi_1\rangle |\phi_2\rangle |\phi_3\rangle) \begin{bmatrix} \sqrt{\frac{2S}{4S+1}} & \sqrt{\frac{2S+1}{4S+1}} & 0 \\ \sqrt{\frac{2S+1}{4S+1}} & -\sqrt{\frac{2S}{4S+1}} & 0 \\ 0 & 0 & 1 \end{bmatrix} \quad (\text{A17})$$

for site 1 and the alternative choice

$$(|\phi_4^*\rangle |\phi_5^*\rangle |\phi_6^*\rangle) = (|\phi_4\rangle |\phi_5\rangle |\phi_6\rangle) \begin{bmatrix} \sqrt{\frac{2S}{4S+1}} & -\sqrt{\frac{2S+1}{4S+1}} & 0 \\ \sqrt{\frac{2S+1}{4S+1}} & \sqrt{\frac{2S}{4S+1}} & 0 \\ 0 & 0 & 1 \end{bmatrix} \quad (\text{A18})$$

for site 2. The product of the two combined transformation matrices for the two sites with the states chosen in this way has determinate -1 , which means that the determinate of the off-diagonal block of hopping matrix elements is 1 and can be interpreted as a rotation. The more obvious choice of identical rotations on sites 1 and 2 makes this simple identity impossible. The physics of the problem is of course independent of our choice of sign for the determinate.

The sector with $S_0 = 2S + 1/2$ can be trivially diagonalized by constructing even and odd (binding and antibinding) combinations of $|\phi_1^*\rangle$ and $|\phi_4^*\rangle$ with the eigenvalues $-J_1 S/2 \pm t$. Within the sector $S_0 = 2S - 1/2$ we find

$$\mathcal{H}^{12} = (|\phi_2^*\rangle |\phi_3^*\rangle |\phi_5^*\rangle |\phi_6^*\rangle) \times \begin{bmatrix} -\frac{J_1 S}{2} & 0 & -t \cos \frac{\theta}{2} & -t \sin \frac{\theta}{2} \\ 0 & \frac{J_1(S+1)}{2} & t \sin \frac{\theta}{2} & -t \cos \frac{\theta}{2} \\ -t \cos \frac{\theta}{2} & t \sin \frac{\theta}{2} & -\frac{J_1 S}{2} & 0 \\ -t \sin \frac{\theta}{2} & -t \cos \frac{\theta}{2} & 0 & \frac{J_1(S+1)}{2} \end{bmatrix} \begin{pmatrix} \langle \phi_2^* | \\ \langle \phi_3^* | \\ \langle \phi_5^* | \\ \langle \phi_6^* | \end{pmatrix} \quad (\text{A19})$$

where the parameters $\cos \theta/2$ and $\sin \theta/2$ are defined by

$$\cos \frac{\theta}{2} = \frac{2S}{2S+1} \quad \sin \frac{\theta}{2} = \sqrt{1 - \cos^2 \frac{\theta}{2}}. \quad (\text{A20})$$

This matrix has the eigenvalues

$$vE = \frac{J_1}{4} \pm \frac{\Delta E}{2} \sqrt{1 + \left(\frac{2t}{\Delta E}\right)^2} \pm 2 \left(\frac{2t}{\Delta E}\right) \cos \frac{\theta}{2} \quad (\text{A21})$$

where $\Delta E = J_1(S + 1/2)$ is the energy difference between the f and p electrons.

The matrix, equation (A19), was first derived by Anderson and Hasegawa [3] using the group theoretical methods outlined in [4], and is valid for all S_0 if we make the identity

$$\cos \frac{\theta}{2} = \frac{2S_0 + 1/2}{2S + 1}. \tag{A22}$$

In the classical limit $S \rightarrow \infty$, the off-diagonal blocks of the matrix have the form of an $SU(2)$ rotation and the parameter θ therefore has the interpretation of the angle between the two spins.

It is possible to express the intermediate basis $\{|\phi_1\rangle, \dots, |\phi_6\rangle\}$ directly in terms of the f and p states used in our expansion scheme,

$$|\phi_1\rangle = |f(S + 1/2)\rangle_1 |0(S - 1)\rangle_2 = \tilde{a}_2^\dagger f_1^\dagger |0\rangle \tag{A23}$$

$$|\phi_2\rangle = |f(S - 1/2)\rangle_1 |0(S)\rangle_2 = \tilde{a}_1^\dagger f_1^\dagger |0\rangle \tag{A24}$$

$$|\phi_3\rangle = |p(S - 1/2)\rangle_1 |0(S)\rangle_2 = p_1^\dagger |0\rangle \tag{A25}$$

$$|\phi_4\rangle = |0(S - 1)\rangle_1 |f(S + 1/2)\rangle_2 = \tilde{a}_1^\dagger f_2^\dagger |0\rangle \tag{A26}$$

$$|\phi_5\rangle = |0(S)\rangle_1 |f(S - 1/2)\rangle_2 = \tilde{a}_2^\dagger f_2^\dagger |0\rangle \tag{A27}$$

$$|\phi_6\rangle = |0(S)\rangle_1 |p(S - 1/2)\rangle_2 = p_2^\dagger |0\rangle \tag{A28}$$

where $|f(S + 1/2)\rangle_1$ corresponds to a state in which site 1 has total spin $\tilde{S}_1 = S + 1/2$, with $\tilde{S}_1^z = S + 1/2$, and $|0(S - 1)\rangle_2$ corresponds to a state in which site 2 has total spin $\tilde{S}_2 = S$, with $\tilde{S}_2^z = S - 1$. The vacuum $|0\rangle$ corresponds to the state with no itinerant electron and $S_0^z = 2S$. This enables us to make a direct comparison between the matrix elements of (A13) with the matrix elements of the effective Hamiltonian found by expanding (A1) using the inverse transformation, equation (31). Since by definition the f^\dagger and p^\dagger operators create eigenstates of the on-site Kondo coupling, the diagonal blocks of the two Hamiltonians must agree; in the case of the off-diagonal blocks, after some algebra, we find

$$-t \begin{bmatrix} 0 & 1 - \frac{1}{4S} + \frac{3}{32S^2} & \frac{-1}{\sqrt{2S}} \left(1 - \frac{1}{4S}\right) \\ 1 - \frac{1}{4S} + \frac{3}{32S^2} & \frac{1}{2S} - \frac{1}{4S^2} & \frac{1}{\sqrt{2S}} \left(1 - \frac{1}{4S}\right) \\ \frac{-1}{\sqrt{2S}} \left(1 - \frac{1}{4S}\right) & \frac{1}{\sqrt{2S}} \left(1 - \frac{1}{4S}\right) & 1 - \frac{1}{2S} + \frac{1}{4S^2} \end{bmatrix}. \tag{A29}$$

If we expand the matrix elements of equation (A13) in powers of $1/\sqrt{S}$ we see the effective Hamiltonian in the transformed coordinate system is identical to \mathcal{H}_{12} at each order in $1/\sqrt{S}$, and so the expansion scheme *must* correctly reproduce all features of the exact solution in this subspace.

The physics of the models which we are interested in, however, is determined almost exclusively by the lowest energy eigenstate. This is easy to understand in the limit $t/J_1 \rightarrow 0$ for which we can restrict ourselves to f electron states and work with the (2×2) matrix

$$\mathcal{H} = (|\phi_2^*\rangle |\phi_5^*\rangle) \begin{bmatrix} -\frac{J_1 S}{2} & -t \cos \frac{\theta}{2} \\ -t \cos \frac{\theta}{2} & -\frac{J_1 S}{2} \end{bmatrix} \begin{pmatrix} \langle \phi_2^* | \\ \langle \phi_5^* | \end{pmatrix} \tag{A30}$$

which has the two eigenvalues

$$E(S_0) = -\frac{J_1 S}{2} \pm t \frac{2S_0 + 1/2}{2S + 1} \tag{A31}$$

corresponding to odd and even (binding and antibinding) combinations of f electron states. The lowest energy eigenstate has $S_0 = 2S - 1/2$ and, for the choice of coordinates made

above, is the ‘binding state’

$$|\phi_B^*\rangle = \frac{1}{\sqrt{2}}(\langle\phi_2^*| + \langle\phi_5^*|) \quad (\text{A32})$$

$$= \frac{1}{\sqrt{2}} \left(\frac{\sqrt{2S+1}}{4S+1} [|\phi_1\rangle - |\phi_4\rangle] - \frac{\sqrt{2S}}{4S+1} [|\phi_2\rangle - |\phi_5\rangle] \right) \quad (\text{A33})$$

with eigenvalue

$$E_B^* = -\frac{J_1 S}{2} - t \left[1 - \frac{1}{2S} + \frac{1}{4S^2} \right] + \mathcal{O}\left(\frac{1}{S^3}\right). \quad (\text{A34})$$

At leading order in t/J_1 there is a further admixture of the p electrons states $|\phi_3\rangle$ and $|\phi_6\rangle$ and the eigenvalue is modified to

$$E_B^* = -\frac{J_1 S}{2} - t \left[1 - \frac{1}{2S} + \frac{1}{4S^2} \right] - \frac{t^2}{J_1 S^2} + \mathcal{O}\left(\frac{1}{S^3}\right). \quad (\text{A35})$$

We use these results to make comparison with a perturbation theory in section 3.

We note that the lowest energy excitation in our expansion scheme for $t/J_1 \rightarrow 0$ is associated with the ‘spinwave’ operator \tilde{a}_π . If we transcribe this in terms of the states $|\phi_i\rangle$ we see that it corresponds to

$$|\phi_\pi^{(0)}\rangle = \frac{1}{2}([|\phi_1\rangle - |\phi_4\rangle] - [|\phi_2\rangle - |\phi_5\rangle]) \quad (\text{A36})$$

which is identical to the exact state, to leading order in $1/S$.

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