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A sensible itinerant description for systems including highly correlated electrons: the intermediate valence state?

M W Long

Rutherford Appleton Laboratory, Chilton, Didcot, Oxon OX11 0QX, UK

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Abstract. We present a technique for building itinerant electron states as approximate ground states to the spin half Anderson lattice Hamiltonian. We choose one fermionic state per site from amongst the two initial states, in the most general mathematical manner. Restricting the application of the Hamiltonian to states where only this special state is non-empty, we minimise the restricted energy in the Hartree–Fock approximation. Treating the initial choice of the relevant fermion as a variable, we then minimise the Hartree–Fock energy over this choice. The resulting energy is an upper bound on the ground state energy because the variational principle underpins our technique. Since we are forcing an itinerant solution onto the problem, this technique fails when the solution involves localised electrons behaving as spins together with non-interacting electrons. There are however large regions of parameter space where the energy found is less than the best localised solutions. We treat on-site hybridisation, nearest-neighbour hybridisation and Coulomb repulsion between the two types of electron with equal ease. Finally we consider speculative applications to the α -Ce to γ -Ce phase transition and a more reasonable application to the magnetic phase transitions in $\text{CeNi}_x\text{Pt}_{1-x}$ and $\text{CeNi}_x\text{Pd}_{1-x}$ and the similar systems $\text{CeSi}_{2-x}\text{Ge}_x$ and $\text{CeSi}_{2-x}\text{Ge}_x$.

1. Introduction

Most systems with an unfilled shell of localised electrons show local moment behaviour at high temperatures and magnetic coherence at low temperatures. The simple physical picture is that of well defined atomic spins which interact with each other by superexchange or more commonly in metals, by the RKKY interaction.

Some such materials show quite different properties at low temperatures. There is a class of materials which go under the loose name of ‘intermediate valence’ (IV) [1], which can show itinerant behaviour at low temperatures, with the electrons at the Fermi surface having the character of the localised electrons. What do we mean by ‘localised’, when such electrons can yield a Fermi surface?

The ‘localised’ electrons in these systems are usually composed of nearly atomic states which have high angular momentum; namely the d electrons or the more interesting f electrons. The spatial wavefunctions for these states are normally compact and are often essentially zero outside of an atomic cell. This leads to two important physical consequences. Firstly the compact nature of the wavefunctions leads to very strong correlations between such electrons on the same site. The overlap of such electrons is large and so the Coulomb repulsion between such electrons is huge. Indeed one usually finds an energetic barrier of several electron volts separating the different

charge states of the localised shell. Secondly the overlap between orbitals on two nearest-neighbour sites is often negligible (the Hill limit) in which case the usual hybridisation effects leading to the electronic motion are absent and more subtle effects take over.

For most systems the chemical potential lies well away from any of the localised shell levels and the charge degrees of freedom are effectively ‘frozen out’. If the shell is only partially filled, then the residual spin degrees of freedom control the low-temperature physics and yield the normal magnetic coherence. For the intermediate valence systems, the chemical potential lies ‘near’ one of the localised atomic shell levels and one finds atoms with both of the relevant charge states. One expects the atomic shell to have a probability of being found in either of the two charge states. How does the charge degree of freedom for these highly correlated electrons behave?

Some mixed or intermediate valence materials show paramagnetic behaviour down to very low temperatures. Indeed, even for heavy-fermion materials one finds well defined Fermi surfaces with de Haas–van Alfen [2], and seemingly excellent Fermi liquid behaviour. The question we wish to address in this article is: how can we generate a natural single-particle description of a system which is composed predominately of highly correlated electrons?

The essential ingredient in a model which describes an intermediate valence system, is the existence of two types of states. Firstly one requires the highly correlated electrons with two energetically accessible charge states and secondly one requires the more mobile electrons that mediate the interaction between the localised states.

The simplest example of such a model is the Anderson lattice [3], which is a tight-binding Hamiltonian which includes only short-range Coulomb interactions. Longer-range Coulomb effects are assumed screened by ‘plasmon’-like collective motion of the other electrons. The Hamiltonian is:

$$\begin{aligned}
 H = S \sum_{i\sigma} c_{i\sigma}^\dagger c_{i\sigma} - S \sum_{i\sigma} f_{i\sigma}^\dagger f_{i\sigma} + U \sum_i f_{i\sigma}^\dagger f_{i\bar{\sigma}}^\dagger f_{i\bar{\sigma}} f_{i\sigma} - t \sum_{\langle ii' \rangle \sigma} c_{i\sigma}^\dagger c_{i'\sigma} + G \sum_{i\sigma\sigma'} c_{i\sigma}^\dagger c_{i\sigma} f_{i\sigma'}^\dagger f_{i\sigma'} \\
 + V \sum_{i\sigma} (c_{i\sigma}^\dagger f_{i\sigma} + f_{i\sigma}^\dagger c_{i\sigma}) - h \sum_{\langle ii' \rangle \sigma} (c_{i\sigma}^\dagger f_{i'\sigma} + f_{i'\sigma}^\dagger c_{i\sigma})
 \end{aligned} \tag{1.1}$$

where $f_{i\sigma}^\dagger$ is a creation operator for the localised electron with spin σ on site i , $c_{i\sigma}^\dagger$ is the corresponding operator for the nearly free ‘conduction’ electrons, $\bar{\sigma}$ denotes the complementary spin to σ and $\langle ii' \rangle$ denote all nearest-neighbour pairs of sites, i and i' . We are using the spin-half variant of this model. The large-spin-degeneracy version is much used in the study of heavy-fermion systems [4]. The restriction to two relevant charge states for the localised shell is enforced with the limit that the Coulomb repulsion between two electrons in the same localised orbital on the same site diverges, $U \mapsto \infty$. The two relevant charge states find the localised orbital either vacant or singly occupied. There are five relevant energy scales in this problem, but we will tend to consider them two or three at a time. We have the energy distance between the localised state and the centre of the conduction band, S , the half band width of the conduction electrons, $W = Xt$, where X is the number of nearest neighbours, the hybridisation energy between the localised and conduction electrons, V , the hybridisation between electrons of the two sorts on neighbouring sites, $H = Xh$, and the repulsion between a localised and conduction electron on the same site, G .

We are now in a position to address our problem, namely, how can we achieve a paramagnetic Fermi surface composed predominately of localised electrons? Firstly we

should ask: why is this a problem? In order to have a paramagnetic Fermi surface, one requires a charge degree of freedom and secondly one requires a spin symmetry for the paramagnetism. In essence this ensures *two* Fermi surfaces, one for spin up excitations and one for spin down excitations, which are mapped onto each other by the spin symmetry. For our simple model, if we restrict attention to the localised level, there is only *one* charge degree of freedom to make *two* Fermi surfaces out of. One would usually expect the spin symmetry to become broken and to associate a single spin with the charge degree of freedom. In this article we will show how to incorporate some of the conduction electrons charge degrees of freedom into a consistent paramagnetic description for the system.

There is another important physical fact to bear in mind. The localised electrons cannot hybridise directly with each other. In the model, the only way that they can move is by hybridising with the mobile conduction electrons through the hybridisation energy scales, V or H . If V is very small, then the induced motion will be very slow. This is the physical motivation behind heavy-fermion behaviour [5]. In fact the electrons are still an order of magnitude heavier than single-particle estimates of V would suggest and a reduction in the effective size of V from the local correlations imposed by U is required. In these systems the charge carriers move very slowly, which is translated into a very large effective mass. Even with two orders of magnitude mass enhancement over the free electron mass, one can still observe a paramagnetic Fermi surface. We must analyse whether a description predicts this mass enhancement or not, with a view to understanding the cause of the enhancement.

Other important physical effects are observed in intermediate valence systems. One of the most exciting effects is that of symmetry-preserving phase transitions. These are first-order changes including volume changes and sharp changes in conducting properties. These have been associated with changes in valence, electrons changing their character from localised states to itinerant states and vice versa. The Falicov–Kimball model has often been used in discussions of this problem [6]. The Falicov–Kimball model is the Anderson lattice with the Coulomb repulsion, G , between the localised and conduction electrons playing a dominant role. Although the transition is attributed to this additional repulsion, we will be able to apply our techniques to this generalised model with no appreciable change in order to test some of the conclusions of their work.

There have been numerous attempts at unravelling the physics of intermediate valence, but almost all have avoided the basic stability question: *what is the phase diagram of the Anderson lattice?* The major strength of our technique is that it gives an unbiased answer to this question, predicting magnetic, paramagnetic and even superconducting ground states as the parameters are varied. By using the optimal *single-particle* wavefunction, we can control the stability criteria using the well understood Hartree–Fock approximation. We are aware of no comparable work in the literature.

There are three exactly soluble limits for the Anderson lattice and our techniques will yield two of these. Firstly there is the limit where the localised level is empty and we find the non-interacting paramagnetic solution for the conduction electrons. Secondly there is the atomic limit where the hybridisation between neighbouring sites vanishes and we are left with independent atoms. Thirdly there is the limit where the hybridisation between the localised and conduction electrons vanishes and the two systems decouple. The last limit is that in which the charge carriers in the localised system become very slow and so this is the natural limit for studying heavy fermions. Oddly enough, the limit our technique fails to describe very well is the third limit.

The initial description involves both the localised operators, $f_{i\sigma}^\dagger$, and the dominant energy scale, U , in an intimately coupled way. The effect of the Coulomb repulsion, U , is to prohibit sites with double occupancy of localised electrons in real space. The solution we desire involves a reciprocal space Fermi surface. The basic technical problem is to develop a way simultaneously to ensure the real space constraint while building a wavefunction with reciprocal space phase coherence. The basic idea is to choose a 'variable' basis. We choose a local basis of fermionic states which is quite general and is allowed to vary. We then construct a single-particle state from this basis and determine its energy. We then allow the local basis to vary in such a way as to minimise the energy of the single-particle delocalised state. In this way, we not only choose the best reciprocal space phase coherence, we also choose to use the optimal local basis which avoids the prohibited double occupancy of localised levels. In our description we find that the choice of local basis depends strongly on the number of electrons in the system as well as the particular values that the parameters take.

Since our construction involves a single-particle state, we can also ask questions about the stability of the state. The most important stability criterion is whether the itinerant state is stable when compared to an atomic state. This comparison is between the 'normal' state with well defined spins and magnetic coherence and the more interesting itinerant paramagnetic state. This is a total energy calculation comparing the itinerant state with a typical atomic state. If the itinerant state is relatively stable in comparison to the atomic state, we can also ask whether it is locally stable with respect to other coherent states. The two obvious instabilities are with respect to itinerant magnetism and more interestingly towards a pairing instability and superconductivity.

There are four known heavy-fermion superconductors [7]. Some people think that the pairing mechanism finds its explanation in the correlations in these systems and *not* in the BCS phonon explanation [8]. Any pairing instability that we find can only be attributed to correlations.

One can also show that the most natural Hamiltonian with which to describe the electronic properties of the perovskite 'high- T_c ' superconductors, is an example of an Anderson lattice [22]. The special limit which best describes the copper oxide layer is restricted to *zero conduction electron band width*.

The Anderson lattice has been treated many times before. Most treatments involve sophisticated analysis of the original basis. One of the most favoured techniques is that of 'slave bosons' [9]. As with most sophisticated treatments, the mathematical analysis involves uncontrolled approximations. For 'slave bosons' a mean-field treatment of the local constraint is the dubious step. The most important aspect to our calculational technique is that the *variational principle* underpins our calculations. Although we physically motivate the states we use, they may be considered as simple trial wavefunctions in a variational calculation. Our calculation is technically Hartree-Fock applied to a basis which has further variational parameters associated with the choice of states on each atom. Hartree-Fock is equivalent to a variational calculation where the space of variations is all single-particle determinants. The final parameters which define the choice of on-site states are optimised directly. We end up with an *upper* bound on the exact ground state energy which can be compared directly with other calculations.

If the Hartree-Fock approximation were applied directly to the Anderson lattice, the infinite Coulomb repulsion, U , would either drive out the f electrons altogether or force them to become magnetic. Our technique obviates this problem.

One of the major 'mysteries' of the intermediate valence and heavy-fermion problems is 'coherence' [10]. Simple descriptions in terms of the single impurity or Kondo

effect seem valid at reasonably high temperatures, but at low temperatures, unlike real impurity systems, Fermi liquid ‘coherence’ is observed. There is a need for an association between this ‘coherence’ and an intrinsic energy scale in the material and further there is also a possible order parameter to be associated with this ‘coherence’. These ideas should be considered as the ‘theme’ to the present article. All we are trying to do is to obtain such a ‘coherent’ state.

In section 2 we will develop the paramagnetic state that we will associate with intermediate valence behaviour in cerium compounds. In section 3 we construct a magnetic intermediate valence state. This state has the properties of an itinerant strong-coupling magnet at low temperatures and not that of a ‘local moment’ magnet. In section 4 we analyse a few simple stability criteria for our intermediate valence phases and look in particular for pairing instabilities. In section 5 we calculate the properties of the states we have constructed and we include an analysis of relative stability and possible phase transitions to be expected. A simplistic discussion of the α - γ phase transition in cerium metal is found in section 6. The phase transitions in the systems $\text{CeNi}_x\text{Pt}_{1-x}$, $\text{CeNi}_x\text{Pd}_{1-x}$ and the similar compounds $\text{CeSi}_{2-x}\text{Ge}_x$, CeSi_{2-x} are modelled in sections 7 and 8, respectively. We draw conclusions in section 9.

2. The paramagnetic state

In this section we develop our variational wavefunction. Our physical motivation comes from the atomic limit where the hybridisation between conduction electrons on neighbouring sites vanishes and all the atoms become independent in real space. A single atomic Hamiltonian can be diagonalised exactly and the resulting basis of states can be used to consider the inclusion of a weak hopping potential. This was the method employed in our earlier work on this subject [11]. The powerful fact that underpins this work is that the diagonalisation of the atomic Hamiltonian is a *non-linear* fermion transformation which mixes up the localised and conduction electrons in such a way that a unique fermion can describe states which are predominately localised electrons *without* reference to the infinite local Coulomb repulsion, U . The problem with our earlier work is the implicit assumption that the band width, W , is small in comparison to the other relevant energy scales, S and V . The most interesting effects occur when the band width, W , becomes the same order as the hybridisation, V . In this article we will develop a description which involves the non-linear fermion transformation obviating the need for the Coulomb repulsion, U , *combined* with a variation which is usually *exact* when the band width becomes large. We can now leave the atomic limit.

We consider the general non-linear transformation mapping a Hilbert space of two fermions onto itself. The initial basis, $f_{i\sigma}^\dagger$ and $c_{i\sigma}^\dagger$, is mapped onto a new basis, $g_{i\sigma}^\dagger$ and $d_{i\sigma}^\dagger$. We force *all* states with two localised f electrons to belong to the subspace with non-zero g occupancy and then only consider the subspace of states with zero g occupancy from which to construct our variational wavefunction. The initial space has sixteen states. The infinite Coulomb repulsion ensures that four are energetically inaccessible. We are projecting away *eight* of the residual twelve states and this constitutes our approximation scheme. The remaining four states which constitute a single-fermion subspace are chosen quite generally, satisfying only the constraint that they are associated with a pure fermion, the d fermion.

This general d fermion can be defined in terms of two parameters which we choose

to be the angles, θ and ϕ :

$$d_{i\sigma}^\dagger | 0 \rangle = [\cos \theta c_{i\sigma}^\dagger + \sin \theta f_{i\sigma}^\dagger] | 0 \rangle \quad (2.1a)$$

for the single-fermion state and:

$$\sigma d_{i\sigma}^\dagger d_{i\bar{\sigma}}^\dagger | 0 \rangle = \left[\cos \phi \sigma c_{i\sigma}^\dagger c_{i\bar{\sigma}}^\dagger + \sin \phi \frac{1}{\sqrt{2}} \sum_{\sigma} \sigma c_{i\sigma}^\dagger f_{i\bar{\sigma}}^\dagger \right] | 0 \rangle \quad (2.1b)$$

for the two-fermion state. Note that we have not included a term from the doubly occupied localised orbital which is energetically inaccessible. These two angles are the variational parameters that we will determine by energy minimisation.

In this section we will determine a good paramagnetic state by employing the Hartree–Fock approximation for the d fermion. This is very simple for the present example, since it simply involves constructing a non-interacting free electron state from the d fermions and finding its energy.

Since we are dealing with nearest-neighbour interactions, there is only one function of wavevector from which to build the Fermi surface, and this may be chosen to be the normalised structure factor, γ_k :

$$\gamma_k = \frac{1}{NX} \sum_{\langle i' \rangle} \exp[i\mathbf{k} \cdot (\mathbf{R}_i - \mathbf{R}_{i'})] \quad (2.2)$$

where N is the number of atoms in the crystal. In terms of this quantity we can set up a density of states from which the energetics can be determined:

$$\rho(\gamma) = \frac{1}{N} \sum_k \delta(\gamma - \gamma_k) \quad (2.3)$$

The Fermi surface is independent of our choice of local basis and satisfies $\gamma_k = \gamma_F$ for some Fermi structure factor. The electron number per spin, D_0 , and hybridisation per spin, D_1 , are also independent of the particular choice of local basis we choose and at zero temperature satisfy:

$$D_0 = \int_{\gamma_F}^1 d\gamma \rho(\gamma) \quad (2.4a)$$

$$D_1 = \int_{\gamma_F}^1 d\gamma \rho(\gamma) \gamma \quad (2.4b)$$

In this article we will employ a uniform density of states assumption for which we have; $D_0 = \frac{1}{2}(1 - \gamma_F)$ and $D_1 = \frac{1}{4}(1 - \gamma_F^2) = D_0(1 - D_0)$.

In the absence of g occupancy we can determine the restricted definitions of the original operators in terms of the d fermion to find

$$c_{i\sigma}^\dagger = \cos \theta d_{i\sigma}^\dagger (1 + \eta d_{i\bar{\sigma}}^\dagger d_{i\bar{\sigma}}) \quad (2.5a)$$

with the non-linear hopping parameter which breaks particle–hole symmetry and leads to the interesting coherence effect:

$$\eta = \frac{1}{\sqrt{2}} \sin \phi \tan \theta + \cos \phi - 1 \quad (2.5b)$$

for the conduction electron and:

$$f_{i\sigma}^\dagger = \sin \theta d_{i\sigma}^\dagger (1 - \kappa d_{i\bar{\sigma}}^\dagger d_{i\bar{\sigma}}) \quad (2.6a)$$

with the corresponding non-linear hopping parameter:

$$\kappa = 1 - \frac{1}{\sqrt{2}} \sin \phi \cot \theta \quad (2.6b)$$

for the localised electron.

The Hamiltonian restricted to d occupancy becomes:

$$\begin{aligned} H = \epsilon \sum_{i\sigma} d_{i\sigma}^\dagger d_{i\sigma} + Z \sum_i d_{i\sigma}^\dagger d_{i\bar{\sigma}}^\dagger d_{i\bar{\sigma}} d_{i\sigma} - t \cos^2 \theta \sum_{\langle ii' \rangle \sigma} d_{i\sigma}^\dagger d_{i'\sigma} (1 + \eta d_{i\bar{\sigma}}^\dagger d_{i\bar{\sigma}}) (1 + \eta d_{i'\bar{\sigma}}^\dagger d_{i'\bar{\sigma}}) \\ - h \cos \theta \sin \theta \sum_{\langle ii' \rangle \sigma} d_{i\sigma}^\dagger d_{i'\sigma} (1 + \eta d_{i\bar{\sigma}}^\dagger d_{i\bar{\sigma}}) (1 - \kappa d_{i'\bar{\sigma}}^\dagger d_{i'\bar{\sigma}}) + \text{cc} \end{aligned} \quad (2.7a)$$

with the effective atomic one- and two-particle energies satisfying:

$$\epsilon = S \cos 2\theta + V \sin 2\theta \quad (2.7b)$$

$$Z + 2\epsilon = S + S \cos 2\phi + \sqrt{2}V \sin 2\phi + \frac{1}{2}G(1 - \cos 2\phi) \quad (2.7c)$$

We will need the particular form of this Hamiltonian for our discussion of stability in section 4, but now all we need to do is to determine the energy of our simple paramagnetic single-particle state:

$$|P\rangle = \prod_{\gamma k > \gamma_F} (\sigma d_{k\sigma}^\dagger d_{k\bar{\sigma}}^\dagger |0\rangle) \quad (2.8)$$

which is

$$\begin{aligned} \frac{1}{N} \langle P | H | P \rangle = 2\epsilon D_0 (1 - D_0) + (Z + 2\epsilon) D_0^2 - 2W \cos^2 \theta D_1 [(1 + \eta D_0)^2 - \eta^2 D_1^2] \\ - 4H \cos \theta \sin \theta D_1 [(1 + \eta D_0)(1 - \kappa D_0) + \eta \kappa D_1^2]. \end{aligned} \quad (2.9)$$

All that is now required is to minimise this energy over the two variational parameters.

In fact the variation over θ can be performed analytically if we expand (2.9) to obtain

$$\begin{aligned} \frac{1}{N} \langle P | H | P \rangle = D_0^2 [S + S \cos 2\phi + \sqrt{2}V \sin 2\phi + \frac{1}{2}G(1 - \cos 2\phi)] \\ - W D_1 [1 - 2D_0(1 - \cos \phi) + (D_0^2 - D_1^2)\{(1 - \cos \phi)^2 + \frac{1}{2} \sin^2 \phi\}] \\ - 2\sqrt{2} H D_1 \sin \phi \{D_0 - (1 - \frac{1}{2} \cos \phi)(D_0^2 - D_1^2)\} \\ + \cos 2\theta [2S D_0(1 - D_0) - \sqrt{2} H D_1 \sin \phi \cos \phi (D_0^2 - D_1^2)] \\ - \cos 2\theta [W D_1 \{1 - 2D_0(1 - \cos \phi) + (D_0^2 - D_1^2)[(1 - \cos \phi)^2 - \frac{1}{2} \sin^2 \phi\}] \\ + \sin 2\theta [2V D_0(1 - D_0) - W D_1 \sqrt{2} \sin \phi \{D_0 - (D_0^2 - D_1^2)(1 - \cos \phi)\}] \\ - \sin 2\theta [2H D_1 \{1 - D_0(2 - \cos \phi) + (D_0^2 - D_1^2)(1 - \cos \phi + \frac{1}{2} \sin^2 \phi)\}] \end{aligned} \quad (2.10)$$

which is readily minimised over θ . The remaining minimisation must be performed computationally and we present the results of this in section 5.

3. The localised state

In the last section we set up a paramagnetic variational wavefunction. This state was in fact a single-particle state and so has single-particle ‘statistics’. If there are D_0 electrons per spin per site, then the probability of finding a vacant, singly occupied and doubly occupied site are; $(1 - D_0)^2$, $2D_0(1 - D_0)$ and D_0^2 respectively in a single-particle state. As was pointed out by Gutzwiller, in highly correlated systems these probabilities can be severely modified. For the strong-coupling Hubbard model, the strong on-site repulsion yields a much reduced probability of finding a doubly occupied site. In order to determine whether a state with modified probabilities is relatively stable, we determine the Hartree–Fock energy of the strongly modified ferromagnetic state where the probability of finding either vacant or doubly occupied sites vanishes.

If there is less than half an electron per spin per site, $D_0 < \frac{1}{2}$, then we cannot avoid a vacant site and so we search for a ferromagnetic solution with no doubly occupied sites. We employ precisely the same technique as in section 2, where now the single-particle state is allowed to vary in order to optimise the energy of the ferromagnetic state:

$$|F\rangle = \prod_{\gamma k > \tilde{\gamma}_F} d_{k\uparrow}^\dagger |0\rangle \quad (3.1)$$

The Fermi surface is now quite different since it is unique and surrounds twice as many electrons. The total electron number, G_0 , and the total hybridisation, G_1 , satisfy the same equations as for the paramagnetic case

$$G_0 = \int_{\tilde{\gamma}_F}^1 d\gamma \rho(\gamma) \quad (3.2a)$$

$$G_1 = \int_{\tilde{\gamma}_F}^1 d\gamma \rho(\gamma)\gamma \quad (3.2b)$$

where the only change is the chemical structure factor. For our uniform density of states we find that $G_0 = 2D_0$ and $G_1 = 2D_0(1 - 2D_0)$.

The same effective Hamiltonian, (2.7), applies and the energy of this state is simply

$$\frac{1}{N} \langle F | H | F \rangle = -\frac{1}{2} W G_1 + \cos 2\theta [S G_0 - \frac{1}{2} W G_1] + \sin 2\theta [V G_0 - H G_1] \quad (3.3)$$

which is readily minimised over θ . We present the results of this in section 5.

If there is more than half an electron per state per site, $D_0 > \frac{1}{2}$, then we cannot avoid a doubly occupied site and so we search for a ferromagnetic solution with no vacant sites. Now we require both of the parameters of section 2 in order to optimise the energy of our variational state

$$|F\rangle = \left[\prod_{\gamma k > \tilde{\gamma}_F} d_{k\downarrow}^\dagger \right] \prod_q d_{q\uparrow}^\dagger |0\rangle. \quad (3.4)$$

Again the Fermi surface is a single quantity which is different from the paramagnetic case since it excludes twice as many holes. The total electron number, G_0 , and total

hybridisation, G_1 , now satisfy

$$G_0 = 1 + \int_{\tilde{\gamma}_F}^1 d\gamma \rho(\gamma) \quad (3.5a)$$

$$G_1 = \int_{\tilde{\gamma}_F}^1 d\gamma \rho(\gamma)\gamma \quad (3.5b)$$

which for our uniform density of states assumption becomes $G_0 = 2D_0$ and $G_1 = 2(1 - D_0)(2D_0 - 1)$.

The same effective Hamiltonian, (2.7), still holds true but now the energy takes the more complicated form

$$\begin{aligned} \frac{1}{N} \langle F | H | F \rangle = & (G_0 - 1) [S + S \cos 2\phi + \sqrt{2} V \sin 2\phi + \frac{1}{2} G(1 - \cos 2\phi)] \\ & - \frac{1}{2} W G_1 [\cos^2 \phi + \frac{1}{2} \sin^2 \phi] - \frac{1}{\sqrt{2}} H G_1 \sin \phi \cos \phi \\ & + \cos 2\theta [(2 - G_0)S - \frac{1}{2} W G_1 (\cos^2 \phi - \frac{1}{2} \sin^2 \phi) - \frac{1}{\sqrt{2}} H G_1 \sin \phi \cos \phi] \\ & + \sin 2\theta [(2 - G_0)V - \frac{1}{\sqrt{2}} W G_1 \cos \phi \sin \phi - \frac{1}{2} H G_1 \sin^2 \phi] \end{aligned} \quad (3.6)$$

the minimisation over θ is straightforward but again the minimisation over ϕ must be computed. The results of these calculations are given in section 5.

4. Stability against coherence

In the last two sections we have developed very particular states which are the Hartree–Fock solutions to the effective Hamiltonian, (2.7). We can compare the energies we derive in order to determine whether the itinerant solution is stable with respect to a ‘strong-coupling’ solution. If we discover that the itinerant solution is stable, we can also ask whether the state is stable with respect to the more interesting possibilities for coherence inherent in the form of the effective Hamiltonian (2.7). In particular we have the possibility of magnetic coherence, associated with particle–hole pairs, and pairing coherence associated with particle–particle or Cooper pairs. This last possibility might lead to an electronic explanation for heavy-fermion superconductivity.

The basic formalism for stability is the same in this treatment as it was for our work on the atomic limit [12]. Only the choice of local basis has changed. Since the effective Hamiltonian is similar and in the absence of H identical, we may simply read across the results.

For singlet spin pairing of fermions, both particle–particle and particle–hole, the best way of describing the results is in terms of two normalised Hubbard constants [13], U_{SC} and U_{FM} . A pairing instability is indicated by a negative U_{SC} and a ferromagnetic instability occurs when $U_{FM} > 1/\rho(\gamma_F)$, a form of Stoner criterion.

For the particular parameterisation in our model we find that both effective Hubbard constants satisfy

$$U_X = \frac{1}{\tilde{W}} [Z + b - \gamma_F a - R_X \{a - \gamma_F b\}] \quad (4.1a)$$

$$a = 2W \cos^2 \theta \eta (1 + \eta D_0) + 2H \cos \theta \sin \theta (\eta - \kappa - 2\eta \kappa D_0) \quad (4.1b)$$

$$b = 2W \cos^2 \theta \eta^2 D_1 - 4H \sin \theta \cos \theta \eta \kappa D_1 \quad (4.1c)$$

where \bar{W} is the renormalised band width which we are associating with the ‘heaviness’ of the d fermions:

$$\bar{W} = W [(1 + \eta D_0)^2 - 3\eta^2 D_1^2] \cos^2 \theta + 2H \sin \theta \cos \theta [(1 + \eta D_0)(1 - \kappa D_0) + 3\eta \kappa D_1^2] \quad (4.2)$$

and R_X is the ratio of the nearest-neighbour ‘pairing potential’ to the on-site ‘pairing potential’. For ferromagnetism:

$$R_{\text{FM}} = \gamma_F \quad (4.3a)$$

which comes directly from the Fermi surface whereas for pairing we find

$$R_{\text{SC}} = \frac{\bar{W} \gamma_F + (D_1 - \gamma_F (D_0 - \frac{1}{2}))a}{\bar{W} + (D_1 - \gamma_F (D_0 - \frac{1}{2}))b} \quad (4.3b)$$

because the pairing is different on different sides of the Fermi surface. For the uniform density of states, the density $\rho(\gamma) = \frac{1}{2}$, and the results are presented in the next section for these stability criteria.

Finally and perhaps of most interest, we should point out that the effective Hamiltonian *always* leads to an instability with respect to triplet or ‘d-wave’ pairing for the paramagnetic solution when stable. The usual stable pairing solution finds triplet spin character for the pair, and only if the off-site hybridisation, H , dominates the band width, W , is the ‘d-wave’ solution possible. As we said in previous work, there is experimental evidence that heavy-fermion superconductivity may have zeros in the gap function [14].

Our variational wavefunction is constructed solely with d fermions. This state is *not* an eigenstate of the Hamiltonian, but we believe that it has a large overlap with the ground state when it is relatively stable. If considered in the restricted space of d occupancy, we expect Fermi liquid behaviour with particle–hole excitations about the Fermi surface. Our next consideration is the subspace projected away; that with g occupancy. If our state were the ground state, then the states with g occupancy would make up part of the excitation spectrum. We will nominally interpret the g states as excitations, but if these excitations drop below the Fermi energy, then we would expect them to become filled in place of some of the d states. This then acts as a stability criterion, if we determine whether the g states are above the Fermi energy or not. The g fermions are subject to the infinite local Coulomb repulsion, U , and as such are necessarily strong coupling if occupied. When considered as an excitation spectrum, the g states are necessarily single particle in character since the many-body effects are strong. We now proceed to calculate the energy of a g fermion in our intermediate valence phase, $|P\rangle$:

$$\epsilon_{k\sigma}^f = \langle P | g_{k\sigma} H g_{k\sigma}^\dagger | P \rangle - \langle P | H | P \rangle \quad (4.4)$$

in order to compare it with our chemical potential

$$\mu = \epsilon + Z D_0 - W \cos^2 \theta D_1 2\eta(1 + \eta D_0) - 2H \sin \theta \cos \theta D_1 (\eta - \kappa - \eta \kappa D_0) - \bar{W} \gamma_F \quad (4.5)$$

which can be readily derived from (2.7).

In order to determine the energy of a g fermion, we must associate the different local basis states in the original basis to the corresponding states in the new basis. This requires a choice of relative phases, which we choose to be continuous with the description when the f states are empty and the d fermion becomes the c fermion identically. Our particular choice of basis is

$$g_{i\sigma}^\dagger | 0 \rangle = (-\sin \theta c_{i\sigma}^\dagger + \cos \theta f_{i\sigma}^\dagger) | 0 \rangle \quad (4.6a)$$

for the single g fermion state at energy $-\epsilon$:

$$\frac{1}{\sqrt{2}} \sum_{\sigma} \sigma d_{i\sigma}^\dagger g_{i\bar{\sigma}}^\dagger | 0 \rangle = \left(-\sin \phi \sigma c_{i\sigma}^\dagger c_{i\bar{\sigma}}^\dagger + \cos \phi \frac{1}{\sqrt{2}} \sum_{\sigma} \sigma c_{i\sigma}^\dagger f_{i\bar{\sigma}}^\dagger \right) | 0 \rangle \quad (4.6b)$$

for the two-particle singlet at energy $S(1 - \cos 2\phi) - \sqrt{2} V \sin 2\phi + \frac{1}{2}G(1 + \cos 2\phi)$

$$d_{i\sigma}^\dagger g_{i\sigma}^\dagger | 0 \rangle = c_{i\sigma}^\dagger f_{i\sigma}^\dagger | 0 \rangle \quad (4.6c)$$

$$\frac{1}{\sqrt{2}} \sum_{\sigma} d_{i\sigma}^\dagger g_{i\bar{\sigma}}^\dagger | 0 \rangle = \frac{1}{\sqrt{2}} \sum_{\sigma} c_{i\sigma}^\dagger f_{i\bar{\sigma}}^\dagger | 0 \rangle \quad (4.6d)$$

for the two-particle triplet at energy G and

$$g_{i\sigma}^\dagger \sigma d_{i\sigma}^\dagger d_{i\bar{\sigma}}^\dagger | 0 \rangle = f_{i\sigma}^\dagger \sigma c_{i\sigma}^\dagger c_{i\bar{\sigma}}^\dagger | 0 \rangle \quad (4.6e)$$

for the three-particle state at energy $S + 2G$. This constitutes a description for all the eight states projected away in our approximation scheme.

The contribution from the on-site Hamiltonian is straightforward, since we simply change the energy of the relevant site on which the g fermion sits, according to its new character and weighted with the probability of finding it in that configuration:

$$\begin{aligned} \epsilon_{k\sigma}^f &= (1 - D_0)^2(-\epsilon) + D_0(1 - D_0)(G - \epsilon) + D_0^2(S + 2G - 2\epsilon - Z) \\ &\quad + D_0(1 - D_0)\{S(1 - \cos 2\phi) - \sqrt{2} V \sin 2\phi + \frac{1}{2}G(1 + \cos 2\phi) - \epsilon\} - \tilde{W}\gamma_k \end{aligned} \quad (4.7)$$

where \tilde{W} is the effective half band width from the off-site contributions.

The off-site phase coherence is more involved. The Hamiltonian mixes in many different local configurations for the g fermion, including spin flips and other 'polaronic distortions'. We will not include such effects because such inclusions are against the spirit of this calculation. Any local change in environment will tend our 'excited' state towards the *true* ground state yielding more information about the deficiencies of our approximation scheme than about the likely excitation spectrum. We therefore only consider spin conserving 'hops' and the restricted definitions of the original basis to such 'hops' yields

$$c_{i\sigma}^\dagger = -\sin \theta g_{i\sigma}^\dagger (1 + \eta_1 d_{i\bar{\sigma}}^\dagger d_{i\bar{\sigma}} + \eta_2 d_{i\bar{\sigma}}^\dagger d_{i\bar{\sigma}} d_{i\sigma}^\dagger d_{i\sigma}) \quad (4.8a)$$

where we find two new non-linear parameters

$$\eta_1 = \frac{1}{\sqrt{2}} \sin \phi \cot \theta - \frac{1}{2}(1 + \cos \phi) \quad (4.8b)$$

$$\eta_2 = \frac{1}{\sqrt{2}} \sin \phi (\operatorname{cosec} \theta - \cot \theta) - \frac{1}{2}(1 - \cos \phi) \quad (4.8c)$$

for the conduction electron and

$$f_{i\sigma}^{\dagger} = \cos \theta g_{i\sigma}^{\dagger} (1 + \kappa_1 d_{i\bar{\sigma}}^{\dagger} d_{i\bar{\sigma}} + \kappa_2 d_{i\bar{\sigma}}^{\dagger} d_{i\bar{\sigma}} d_{i\sigma}^{\dagger} d_{i\sigma}) \quad (4.9a)$$

where we find two further new non-linear parameters

$$\kappa_1 = \frac{1}{2}(\cos \phi - 1) \quad (4.9b)$$

$$\kappa_2 = \cos \phi \sec \theta - \frac{1}{2}(1 + \cos \phi) \quad (4.9c)$$

for the localised electrons.

It is a simple matter to determine the effective band width from these results and we find

$$\begin{aligned} \tilde{W} = W \sin^2 \theta & [(1 + \eta_1 D_0 + \eta_2 \{D_0^2 - D_1^2\})^2 + (2\eta_2 - \eta_1^2) D_1^2] \\ & - 2H \sin \theta \cos \theta [(1 + \eta_1 D_0 + \eta_2 \{D_0^2 - D_1^2\})(1 + \kappa_1 D_0 + \kappa_2 \{D_0^2 - D_1^2\}) \\ & + (\eta_2 + \kappa_2 - \eta_1 \kappa_1) D_1^2] \end{aligned} \quad (4.10)$$

we will present the results of this excitation spectrum and related stability criterion in the next section.

5. Basic behaviour of the technique and solutions

Although our technique treats the atomic limit exactly, we know that in the limit of vanishing hybridisation between the localised and conduction electrons, when the two systems decouple, the technique fails. In order to verify that our solution has lower energy than this decoupled solution and is therefore relatively stable, we compare our upper bound with the energy of the ground state of the decoupled system

$$|D\rangle = \left[\prod_{i \in I} f_{i\sigma}^{\dagger} \right] \left[\prod_{\tilde{\gamma}k > \tilde{\gamma}_F} \sigma c_{k\sigma}^{\dagger} c_{k\bar{\sigma}}^{\dagger} \right] |0\rangle \quad (5.1)$$

where we can only treat the case of vanishing repulsion between the two types of electron, namely $G = 0$, and the set I and $\tilde{\gamma}_F$ are chosen to fill the lowest lying states. The energy of this state is simply

$$\frac{1}{N} \langle D | H | D \rangle = 2SD_0 - 2WD_0(1 - D_0) \quad D_S > D_0 \quad (5.2a)$$

$$\frac{1}{N} \langle D | H | D \rangle = -\frac{1}{2W}(W - 2S)^2 - 2SD_0 \quad \frac{1}{2} + D_S > D_0 > D_S \quad (5.2b)$$

$$\frac{1}{N} \langle D | H | D \rangle = 2S(D_0 - 1) - 2W(D_0 - \frac{1}{2})(\frac{3}{2} - D_0) \quad D_0 > \frac{1}{2} + D_S \quad (5.2c)$$

where $D_S = \frac{1}{2} - S/W$ and we are assuming the uniform density of states. Our solution is necessarily lower in energy than the state with an empty localised level. If our solution has lower energy than $|D\rangle$, then we believe that the ground state has the characteristics of an itinerant paramagnet *without* the local moments which can achieve magnetic coherence, if not then we believe that it will display characteristics of both.

If the local moment state, $|D\rangle$, has the lowest energy of the states considered, then we still expect a contribution from the hybridisation, V , but of a very special kind. The basic effect is that of virtual excitations into states with atoms empty of f electrons, yielding exchange interactions between neighbouring f moments. There is an energy contribution at order V^2 but the exchange interactions enter first at V^4 . If the hybridisation, V , is small, we expect only minor energetic modifications. The intermediate valence states we are considering are quite different, showing a definite reduction in valence due to charge transfer, combined with very different phase coherence.

The g fermions are subject to the infinite repulsion, U . As such we may think of them as 'local moments'. We find that our solution can behave in an identical fashion to the c and f basis, where the g fermion takes the place of the f fermion. Such behaviour is signalled in our treatment by an instability to g occupancy. The g fermions tend to have a non-trivial band width and so we find the problem of how to fill a strong-coupling band and what magnetic coherence is to be expected. Indeed this problem is first met in the infinitely strong-coupling Hubbard model where it has often been treated but not successfully dealt with. There is the possibility of continuous single filling of the g states and a continuous transition between itinerant and local moment behaviour. There is a second possibility which is not found in many other treatments; a first-order transition between itinerant and local moment behaviour. This is signalled by an energy degeneracy between the itinerant intermediate valence state and the local moment state prior to the instability to g occupancy.

We envisage *three* distinct types of states. Firstly the 'intermediate valence' states which are the paramagnetic metallic solutions of section 2. Secondly the strong-coupling magnetic solutions of section 3. Thirdly the decoupling solutions with well defined local moments which interact with each other via the conduction electrons to yield the 'normal' scenario of magnetic coherence induced by RKKY. The two types of magnetic solution are very different. In the strong-coupling solution only a certain fraction of the sites have magnetic moments, the other sites have singlet spin character, either being vacant or the two-particle mixed valence singlets. We would expect the saturated magnetisation to be reduced from the expected value of the free localised 'spins'. The moments associated with the decoupled solution should take their free localised values. This seems the natural experimental technique to differentiate an 'intermediate valence ferromagnet' from an RKKY local moment ferromagnet.

The next fairly general question we ask is: for what sort of physical situation does our model predict intermediate valence itinerancy? Our treatment predicts that the model is highly susceptible to strong-coupling magnetism. There are two regimes where such a strong-coupling magnetic solution is *not* to be expected. Firstly when the energy separation between the two levels, S , is small in comparison to the band width, W , and we expect a large number of conduction electrons in the ground state which then behaves as the intermediate valence paramagnet or the local moment decoupled system. Secondly when the hybridisation energy, V or H , dominates the level separation energy, S , we find that the local basis is strongly hybridised mixtures of localised and conduction electrons and the motion of the conduction electron component frustrates the magnetic coherence. This is the weakening of magnetism by 'charge transfer'. We should also note that by projecting away all triplet configurations of electrons on a site, we are losing spin fluctuations as a source of stabilisation for the paramagnetic state.

Now we consider some particular examples of the types of behaviour that our

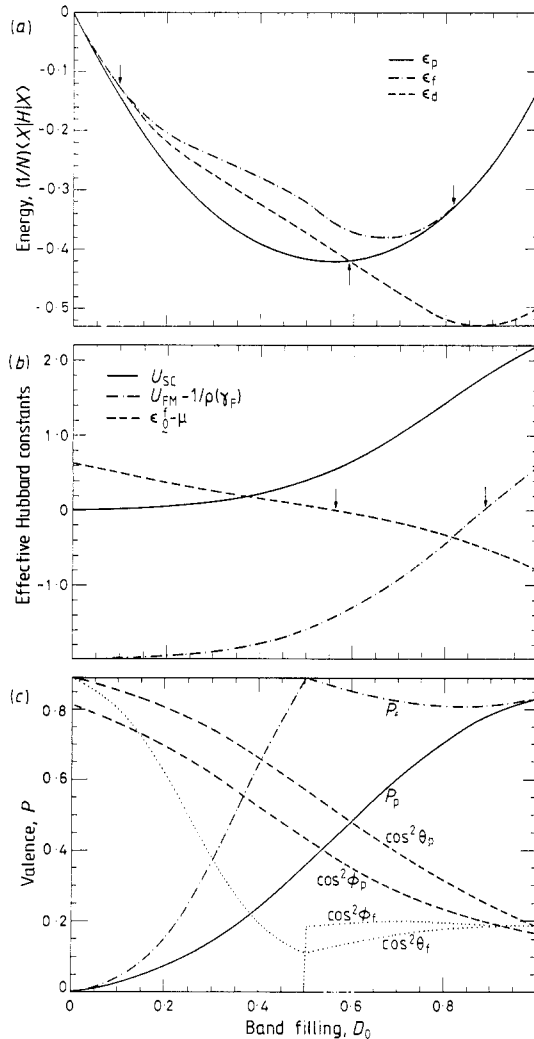


Figure 1. $W = 1.0$, $S = 0.25$, $V = -0.2$, $H = 0.0$, $G = 0.0$. (a) Total energy calculation showing an itinerant state at low band filling and a 'local moment' state at high band filling. (b) Stability criteria showing that instability to g occupancy occurs *prior* to the total energy transition suggesting a second-order 'transition' (i.e. continuous behaviour). (c) Valencies of the intermediate valence phases together with the many-body parameters, $\cos^2 \theta$ and $\cos^2 \phi$.

technique can display. First let us consider the case when the hybridisation between the two types of electrons is small. This is the case when our technique should be at its worst and we might expect the solution with well defined local moments to be preferred. In figure 1 we consider a case where the solution is predominately delocalised up to half filling while in figure 2 we consider a case where the solution is basically localised up to half filling.

The basic type of stable phase is discerned from the total energy calculation. We find at high electron concentrations, as expected, that the decoupled solution with local

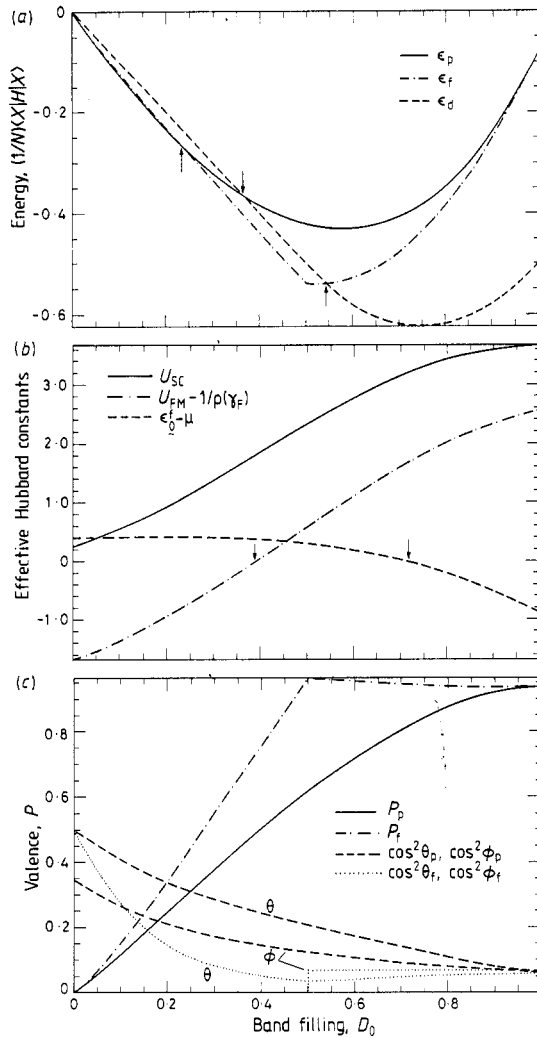


Figure 2. $W = 1.0$, $S = 0.5$, $V = -0.2$, $H = 0.0$, $G = 0.0$. (a) Total energy calculation showing an itinerant state at low band filling, a strong-coupling ferromagnetic solution at intermediate band filling and a 'local moment' state at high band filling. (b) Stability criteria showing that the total energies become degenerate *prior* to the instability to itinerant ferromagnetism and that the total energies become degenerate *prior* to g occupancy suggesting that both transitions are first order. (c) Valencies of the intermediate valence phases together with the many-body parameters, $\cos^2 \theta$ and $\cos^2 \phi$. Note that both transitions would involve a change in valence.

moments is relatively stable because the hybridisation energy, V , which would stabilise the intermediate valence phases is weak. For both cases we find that the paramagnetic intermediate valence state is relatively stable compared to the ferromagnetic strong-coupling state at low band filling but that this situation is reversed at concentrations with a higher number of localised electrons. Analysis of the stability criteria show that the strong-coupling ferromagnet is relatively stable prior to the instability to itinerant

ferromagnetism. Some of the most interesting quantities to consider are the variational parameters θ and ϕ . We present the fractional decompositions of the optimal basis in terms of the original states, together with the ‘valence’, P , defined by the number of localised electrons in the system:

$$P = 2D_0(1 - D_0) \sin^2 \theta + D_0^2 \sin^2 \phi \quad (5.3a)$$

for the itinerant paramagnet and

$$P = G_0 \sin^2 \theta \quad G_0 < 1 \quad (5.3b)$$

$$P = (2 - G_0) \sin^2 \theta + (G_0 - 1) \sin^2 \phi \quad G_0 > 1 \quad (5.3c)$$

for the strong-coupling ferromagnet. Note how in almost all the situations we depict, the valence of the strong-coupling magnetic state is higher than that of the intermediate valence paramagnet demonstrating, as expected, that it is easier to develop magnetic coherence with the localised electrons than without them.

6. Phase transitions in cerium metal

There is a symmetry-preserving phase transition in metallic cerium which is thought to be associated with a change in the number of localised f electrons on the cerium atom. The transition is between a ‘magnetic’ phase, γ -Ce, which under pressure at quite high temperature changes first order into a non-magnetic phase, α -Ce, with an appreciably smaller volume. The valencies of γ -Ce and α -Ce are thought to be 3.06 and 3.67, respectively [15]. The simple physical picture which explains these observations is that at the transition much of the single f electron in the Ce^{3+} core which makes up the γ -Ce phase transforms into the s,d-electron conduction band orbital leaving behind the Ce^{4+} core which makes up the α -Ce phase. This leaves two questions to be answered by theoretical physics: why? and what is the best way to model such a transition?

The simple descriptions of this transition have centred on the Falicov–Kimball model. Two pieces of physics emerged in the early treatments. Firstly the short-range Coulomb repulsion between the two types of electron, G , is crucial. The localised electrons are transformed into conduction electrons at low temperatures in order to avoid this energy penalty. Secondly the entropy associated with the spin degeneracy of the localised electrons competes with this at higher temperatures. As a function of temperature this competition is a physical explanation for the transition. When considered as a function of pressure, the dominant effect is modelled by a pressure dependence to the energy gap between the two types of electrons, S , because of the very different spatial character of the two wavefunctions and the dependence (or lack of it) on volume. Together these features give a consistent picture for the basic physics.

There are two quite important questions overshadowing this explanation. Firstly it is not clear whether the transition would be first or second order. The initial work suggested a first-order transition as required, but more sophisticated treatments have both laid doubt *and* confirmed this result which seems to be strongly dependent on the shape of the conduction band density of states [16]. Secondly and much more disturbing is the lack of hybridisation between the localised and conduction electrons which *only* interact via the Coulomb repulsion, G , in the early treatments. Weak hybridisation has been included by the standard ‘virtual bound state’ approach [17]

but this is essentially a perturbative addition to the existing picture. What is the likely effect of a stronger hybridisation, V , on the simple picture which has already emerged?

What does the technique developed in this article predict? Our work is predominately at zero temperature where the original treatments are trivial and do *not* allow first-order transitions. Even for the case of vanishing Coulomb repulsion between the two types of electrons, $G = 0$, we still find the possibility of a first-order transition which has a simultaneous change in localised electron number. The transition is the simple transition between the intermediate valence itinerant state and the strong-coupling magnetic state already mentioned. If we assume the simple correspondence between pressure and level separation, S , then the situation corresponding to that between figures 1 and 2 illustrates such a transition at half filling (namely $D_0 = \frac{1}{2}$). The transition described by our technique is in fact more akin to a simple 'Mott' transition. Discrete changes in the atomic configuration probabilities ensure that such a transition is first order if direct. There is the possibility of a second-order transition through an intermediate phase which for our analysis corresponds to itinerant magnetism. For the cases we have analysed the transition is always first order at zero temperature. The physical picture for our transition is that of the hybridisation, V , stabilising the itinerant intermediate valence state when the localised level is pushed close to the chemical potential by the pressure, but the strong-coupling magnetic phase is stable when the localised level is lower down below the chemical potential. The stabilisation of the itinerant state by the Coulomb repulsion, G , is replaced by the stabilisation of the itinerant state by charge transfer due to the hybridisation, V , which is related to the Kondo effect and mixed valence singlet.

When considered as a function of temperature, however, the technique cannot describe the entropy changes well at all. The simple choice of restricted basis does *not* allow much entropy for the strong-coupling state. Indeed we would expect straightforward loss of magnetism as a function of temperature and stabilisation of our itinerant state! The phase diagram of metallic cerium is opposite to this! The important missing element is entropy. Rather than being less entropy associated with the localised f electron, the large angular momentum degeneracy at the relevant temperature yields a higher entropy. We find that it is very difficult to associate the phase of γ -Ce with our simple strong-coupling magnet at higher temperatures and any inclusion of a large spin degeneracy immediately complicates a simple description for the hybridisation, V . In order to describe temperature dependence even for our over simplified model, one requires the states that have been projected away.

The conclusion from this discussion is that in order to get a first-order transition, it is not *necessary* to have the conduction electrons stabilised at low temperatures by the Coulomb repulsion, G . The low-temperature itinerant phase may also be stabilised by the hybridisation, V , and the first-order character of the phase transition would be attributed to a sharp change in many-body correlations, along the lines of a 'Mott' transition associated with a sudden decrease in the probability of one of the atomic configurations.

The model description of the α -Ce phase envisioned by Falicov at low temperatures is dominated by the repulsive energy, G . Let us consider what our technique would predict for this limit. For our model, our description in this limit should fairly well describe the two-particle states which ought to be pairs of conduction electrons. For the itinerant description with one electron per site, $D_0 = \frac{1}{2}$, this ensures that *half* of the electrons are conduction electrons at zero temperature! If the valence of α -Ce is 3.67 at low temperatures, then the single-particle states would need to be $\frac{2}{3}$ localised electrons

to make up the valence! We would need to be in a regime where the single-particle localised level were lower than the chemical potential! The Falicov–Kimball model tends to predict too high a valence for the α -Ce phase, essentially to obviate this rather unlikely scenario. The resolution of this paradox seems to be the hybridisation, V . Rather than transiting from the nearly localised γ -Ce phase into a nearly itinerant α -Ce phase, the system transits into an intermediate valence α -Ce phase. The large Coulomb repulsion, G , is *still* required to force the first-order transition in other treatments.

Our conclusion from this discussion is that α -Ce ought to be described as an intermediate valence state with paramagnetism stabilised by the hybridisation, V . Do we really need the Coulomb repulsion, G , to ensure a first-order transition? Surely a careful consideration of the intermediate valence phase will produce an ‘order parameter’, related to many-body correlations, to explain a first-order transition even in the absence of the repulsion, G .

To obtain a reasonable valence of 3.67 in our description, we need a fairly small value of G to ensure f character in the two-electron state at zero temperature.

7. Phase transitions in $\text{CeNi}_x\text{Pt}_{1-x}$ and $\text{CeNi}_x\text{Pd}_{1-x}$

There are several reasons why these particular materials might be a good testing ground for the Anderson lattice model restricted to spin half.

The lattice structure is orthorhombic and so at low enough temperatures, $T < 50$ K, the crystal field splitting of the relevant $J = \frac{5}{2}$ multiplet leads to only two relevant states for the localised f electron on the cerium atom. In most cerium compounds showing intermediate valence behaviour, the crystal field is cubic yielding less degeneracy breaking.

The compound CeNi [18] is known to be an intermediate valence material and based upon lattice parameters the cerium valence is predicted to be ≈ 3.3 – 3.5 yielding about 0.7–0.5 of an f electron over a temperature range of 300–4 K. Despite an even number of electrons in a unit cell, the material is a metal and it is believed that the conduction band states at the Fermi surface are strongly hybridised mixtures of nickel 3d which are below the Fermi surface and cerium 5d which are near the Fermi surface.

The compounds CePt and CePd do not show similar behaviour. On the contrary these materials become ferromagnetic at low temperatures, $T_c < 10$ K, well within the regime where there are only two relevant localised states. Once again these materials are metals but now the conduction electrons at the Fermi surface are thought to be strongly hybridised mixtures of platinum (palladium) 5d (4d) and cerium 5d electrons. The 5d (4d) electrons are higher in energy than the corresponding 3d electrons in nickel and so the simple physical picture is that the chemical potential has been raised from its value in CeNi making valence fluctuations on the cerium site less favourable and yielding fairly well defined localised spins which become magnetically aligned at low temperatures.

These two simple pictures are just the two natural states we have analysed for the Anderson lattice. A strongly hybridised mixed valence state showing metallic paramagnetism down to very low temperatures for CeNi and a strong-coupling metallic ferromagnet for CePt and CePd.

The fact that these two types of materials crystallise in the same structure allows the possibility of moving continuously from one type of behaviour towards the other by alloying. These experiments have recently been performed [19] with *very* similar

behaviour found for both systems. As one moves away from CePt, the magnetism is first strengthened, T_c weakly increases, and then collapses sharply at about a concentration of CePt_{0.1}Ni_{0.9}. The basic scenario presented with these data is that of a competition between the RKKY interaction inducing magnetic coherence and the Kondo effect stabilising a set of singlets made up of each of the localised 'spins' and the conduction band. The transition is viewed as 'smooth' and passes through some intermediate regime where both effects are present simultaneously. We have quite a different viewpoint.

We see the transition at zero temperature as being very sharp and not smooth at all. Firstly there is a well defined 'kink' in the cell volumes which seems to separate two very different volume dependences. Secondly the loss of magnetic coherence is *very* sharp occurring over a variation of less than five per cent. Thirdly and perhaps most instructive is the specific heat data. The materials with a supposedly high magnetic transition temperature near the intermediate valence transition show a tiny discontinuity in the specific heat. This is symptomatic of the magnetic transition being restricted to only a small fraction of the alloy. We believe that there is a fairly sharp transition at or around the stoichiometry of CePt_{0.2}Ni_{0.8} from a paramagnetic mixed valence phase to a ferromagnetic strong-coupling phase at zero temperature. The 'intermediate valence' behaviour of the materials at higher temperatures do not detract from this picture and only add to it, being associated with the extra entropy of the itinerant phase over the strong-coupling magnetic phase. We should bear in mind that there is no elastic energy built into our simple electronic model and this will severely effect the expected changes in valence and smoothness with which they occur.

8. Phase transitions in CeSi_{2-x} and CeSi_{2-x}Ge_x

The experimental situation in these alloys is very similar to that found in the CeNi_xPt_{1-x} alloy system. CeSi₂ [20] corresponds to CeNi and finds the cerium atom in an intermediate valence state. CeGe₂ corresponds to CePt where we find ferromagnetism but with a reduced saturated magnetisation from the free cerium ion value. Even the transition temperature is very similar being in the region of 10 K. Alloying Ge in place of Si is completely analogous to alloying Pt or Pd for Ni because the substitutions are for 'isoelectronic' elements lower down the same group in the periodic table. For the CeNi_xPt_{1-x} system we find a sharp transition at $x \approx 0.9$ whereas for CeSi_{2-x}Ge_x [21] we find a remarkably similar transition at $x \approx 0.6$.

Any explanation for one system should be applicable to the other *without* any significant changes.

One important point to realise is that a significant volume effect is missing in the CeSi₂ alloys, an effect which is central to any mixed valence determination for the Ce. We have nothing to say about this.

The omission of Si from the lattice in CeSi_{2-x} seems to have a very similar effect to replacing the Si by Ge and we also have little to say about this.

One of the pieces of experimental evidence that the simple RKKY picture finds very difficult to reconcile is the fact that the observed saturation magnetisation is much reduced from any reasonable free ion value, even one unreasonably crystal field split to minimise the expected moment! We are predicting two very different types of ferromagnetic state. As well as the state with local moments on all the sites, we are predicting a state with well defined moments on a much reduced fraction of the sites;

the strong-coupling ferromagnet. The remainder of the sites are found with 'mixed valence' singlet configurations where the local moment is locally compensated by a conduction electron spin. We suggest that the small moments observed in CeGe₂ and CePt are in fact strong-coupling ferromagnetic solutions rather than local moment ferromagnets, in which case the reduced moment is explained by the large quantity of sites which have singlet 'bound' local moments. Our calculations also suggest a likely change in the valence of the cerium atom at such a transition which ties in with the change in slope observed for the volume dependence of CeNi_xPt_{1-x} but *not* with the rather passive CeSi_{2-x}Ge_x system.

9. Conclusions

Before we go on to explain what we can do, let us survey the important physics that we most certainly *cannot* explain or model.

Firstly we are restricted to studying the case of a spin half local moment. The only materials that we can hope to get to grips with are those where crystal field effects restrict the relevant localised levels to a doublet. Secondly we are unable to model any of the important spin orbit effects for either the localised levels or the conduction electrons. In practice this means that there is no hope of any quantitative understanding of the systems coming from our work but only qualitative explanations and physical interpretation. Thirdly we totally ignore all volume effects and as such do not get any compensatory changes in elasticity to reduce our electronic predictions. Fourthly and by far the most important restriction of our work is to indecently low temperatures. Our technique involves a projection onto a subset of the initial states, a subset we believe to be relevant at low temperatures. Unfortunately we do not attempt to describe the states projected away, and the interesting changes in behaviour exhibited as functions of temperature ought to be associated with fluctuations into the very degrees of freedom we are not describing. The only temperature regime we can hope to describe is that for any magnetic coherence amongst the degrees of freedom remaining in our description. In practice we are restricted to $T < 50$ K.

The physical picture which we are attempting to establish is that of two very different regimes. The 'normal' situation where the localised levels are removed from the Fermi surface is that of well defined local moments on each site which interact via the conduction electrons yielding magnetic coherence at low temperatures. This is the picture of rare earth magnetism induced by RKKY interactions which has been established for several decades. The second regime which has the experimental label of mixed or intermediate valence is where the charge degrees of freedom of the localised electrons are relevant to the low temperature physics. They become mixed with the conduction electron charge degrees of freedom to form a single itinerant description with none of the properties of a local moment system. In our description this itinerant band composed predominately of localised electrons can show paramagnetic behaviour down to zero temperature as is observed in some systems or can show forms of strong- and weak-coupling magnetism, which have previously been described as a competition between RKKY and the Kondo effect in a rather unconvincing picture. Our description yields a natural reason for a much reduced magnetic moment for a system with an essentially filled localised level whereas the competing description sees a localised moment partly magnetised and partly in a singlet configuration with the surrounding conduction electrons. To some extent we have developed a way of describing a system

which can show a competition between magnetism and the 'Kondo effect' (and induced singlets) on a local level. It is important to realise that the mixing of states in our description is on a much shorter length scale than in the Kondo effect and is only connected to it in a very interpretative way and *not* directly.

We have developed a technique for describing the spin half Anderson lattice in terms of a single fermionic degree of freedom per site at low temperatures. We can justify our description for some parameterisations in the sense that we find lower energy for our ground state than any of the natural competing states that we have considered. The dominant contribution stabilising our intermediate valence state is the hybridisation between the localised and conduction electrons which must be strong enough to promote the localised electrons above the chemical potential, as might be expected.

There are four basic types of behaviour we consider. Firstly there is 'normal' local moment behaviour when our technique fails and pure itinerant behaviour is not stable. Secondly there is itinerant metallic paramagnetic behaviour corresponding to the intermediate valence state. Thirdly we have a strong-coupling magnetic solution, which does not have the usual local moment behaviour and yields reduced saturated magnetic moments. Lastly we have weak pairing instabilities in the intermediate valence state which ought to lead to a form of correlation mediated superconductivity.

Although we find great difficulty describing the change in behaviour between local moments and intermediate valence, we can readily describe a transition between magnetic and non-magnetic intermediate valence states. We suggest that these transformations yield a qualitative explanation for the phase transitions in the isoelectronic intermediate valence alloys $\text{CeNi}_x\text{Pt}_{1-x}$, $\text{CeNi}_x\text{Pd}_{1-x}$, $\text{CeSi}_{2-x}\text{Ge}_x$ and CeSi_{2-x} . Our description is a much more specific model, when compared to existing statements invoking competition between RKKY and Kondo effects, and gives predictions for very low temperature excitation spectrum which should be that of a Fermi liquid in both the paramagnetic and ferromagnetic phases.

We obtain an interesting pairing instability, but these correlations are restricted to a rather radical limit.

If we risk a sortie above absolute zero, we suggest that the breakdown of our description is due to the enormous amount of entropy in the f-moments and that we should expect a transition into a 'local moment' phase at quite low temperatures. Is this an explanation for the so-called coherence temperature in these systems?

Finally, let us return to the 'theme' of this article: 'coherence'. The energy scale for the intermediate valence state, in this article, is the hybridisation potential, V or H , and nothing to do with 'spin fluctuations'. The other major concern was for an 'order parameter' to mark the change of behaviour. How about θ and ϕ ?

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