

Fermi Sea of Heavy Electrons (a Kondo Lattice) is Never a Fermi Liquid

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I demonstrate a contradiction which arises if we assume that the Fermi surface in a heavy-electron metal represents a finite jump in occupancy. Therefore it does not and the resulting density of states has a sharp, deep anomaly at the Fermi energy which will appear in vacuum tunneling and many other experiments.

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The striking quantum phenomenon of heavy-electron formation occurs in intermetallic compounds of the rare earth and actinide metals (usually Ce, Yb, Lu, and U, but occasionally others). The f -shell electrons, which are, at room temperature, to all intents localized spins, scattering a conventional sea of free metallic electrons, cross over at low temperature into mobile band electrons, albeit with very heavy effective masses, and change the Fermi surface radically in order to accommodate precisely the number of electrons—or, in the case of Yb, holes—which accounts for the number of spins [1].

From a fundamental point of view the most surprising feature of this observation is that the dimensionality of the Hilbert space which we must use to describe the wave function has radically changed. N sites on which we may have a spin up or down have 2^N possible states; but if we can occupy each of these N sites with 0, 1, or 2 real electrons that amounts to 4^N possible states. (If there is orbital degeneracy that merely changes the arithmetic, not the enormous discrepancy in dimension.) It turns out that this is the crucial feature: enforcing the requisite constraints on the 4^N degrees of freedom causes a characteristic anomaly. The net effect is to make the $T = 0$ axis into a critical line, having a continuously variable exponent for some properties, but not to invalidate Luttinger's theorem and the existence of a Fermi surface.

It is essential to go into the physics of why Ce f electrons, for example, normally act as spins. The $5f$ shell is deeply localized within the atom, so that two f electrons on the same atom will interact strongly via their Coulomb repulsion, which is not effectively screened by outer-shell, metallic electrons. Although the f electrons can hybridize to an extent with the metal band electrons, the breadth of the f band caused by this will undoubtedly be small compared to the repulsion. There will be no more than one f electron per site, which may have up or down spin. This is often modeled as simply a spin (the “Kondo lattice” model), but one should not forget that in condensed matter situations spins are always electrons. One correct way to express this fact is to describe the spin as a projected electron, i.e., to project away the possibility of double occupancy of the f shell from a wave function

written nominally in the full Hilbert space of four possible occupancies.

If the spins are dense, as we lower the temperature they will tend to order magnetically, and indeed the rare earth elements are almost all magnetic. But in a sufficiently dilute compound the magnetic interactions may not dominate, and the hybridization with the metallic electrons may lead to the formation of narrow f bands. In fact, naive band calculations always predict f bands much less narrow than are observed, and that the mobilization of the f electrons should be much easier than it is, but spectacularly, wrong as such calculations are quantitatively, they predict the correct size, and often shape, of the Fermi surface which eventually appears at low temperature.

I said we must project out double occupancy; when there is one electron per atom this has the effect of requiring one spin per site. When the bands form, a percentage of the f sites will empty because they are hybridized with the band electrons, and one can show that the chemical potential will be such that the energy of an empty site is not far from that of a singly occupied one, and should not be excluded by projection; so in fact we must project down to a space of 3 states per f site, not 2. This implies that the ground state wave function may be written

$$\Psi(r_1, \sigma_1; r_2, \sigma_2; \dots) = P_G \Phi(r_1, \sigma_1; \dots), \quad (1)$$

$$\text{with } P_G = \prod_i (1 - n_i^f n_{i\downarrow}^f).$$

Here Φ is a general function in the full Hilbert space of all electrons' coordinates and spins, and the “Gutzwiller” projector P_G projects out all doubly occupied atomic states. A great deal of misinformation is in the literature about this projection process, and we should emphasize two points. The first is that it can be derived in principle by a perturbation procedure as a nonsingular canonical transformation of the Hamiltonian into block-diagonal form. The transformation can, of course, be thought of as acting on the wave function or the Hamiltonian equivalently; for the canonically transformed Hamiltonian, the Gutzwiller form of the wave function is necessary. Second, any perturbative admixture between the two subspaces of states can only increase the separation to the “upper Hubbard

band” of doubly occupied states and make the projection more efficient.

The theory of the “freezing-out” process for the spins, (sometimes called “Kondoization”), has been the subject of a considerable amount of literature, but that is not our concern here. The introduction of the Gutzwiller projection referred to above into the theory is due to Rice and Ueda [2]; and the most reliable quantitative account of the process of forming heavy-electron bands is given by the approximate dynamical mean field theory of Kotliar and Georges [3]. But what we are here concerned with is the end product at low temperatures: the ground state and low elementary excitations.

Most of the heavy-electron materials have either superconducting or magnetically ordered ground states. (Often called “animal” and “mineral.”) A few, however, persist as supposed Fermi liquids to absolute zero; while also a number have competing and incompatible magnetic and superconducting orderings and therefore at the critical point between them have, again, no order at all (vegetable). While the effects we will discuss persist in altered form into the other phases, it simplifies matters to study the case of no ordering. Our method of proof is to assume there is a Fermi liquid ground state and show that leads to a contradiction.

A Fermi liquid may be treated as a noninteracting system with quasiparticles described by Fermion operators $c_{i,\sigma}^*$, $c_{i,\sigma}$ in site representation, and correspondingly

$$c_{k,\sigma} = \frac{1}{\sqrt{N}} \sum_i e^{-ik \cdot r_i} c_{i,\sigma}, \quad (2)$$

etc., in momentum representation. The Green’s function is defined in space-time as (omitting spin indices as irrelevant)

$$G_{ij}(t; t') = -i \langle 0 | T(c_i(t) c_j^*(t')) | 0 \rangle; \quad (3)$$

$|0\rangle$ is the ground state. (Most of what follows refers to the site-diagonal Green’s function G_{ii} , but the analytic structure is general.) G may also be represented in frequency-momentum space by its Fourier transform $G(k, \omega)$. G has a well-known representation in terms of the densities $A(\omega)$ and $B(\omega)$ of excited states accessed by adding or removing one Fermion:

$$G_{ij}(\omega) = \int_0^\infty \left[\frac{A_{ij}(E)}{\omega - E + i\delta} + \frac{B_{ij}(E)}{\omega + E - i\delta} \right] dE \quad (4)$$

(we set the Fermi level at $\omega = 0$). Here A and B are defined by

$$\begin{aligned} A_{ij}(E) &= (2\pi)^3 \sum_s \langle 0 | c_i | s \rangle \langle s | c_j^* | 0 \rangle \delta(E - \varepsilon_s), \\ B_{ij}(E) &= (2\pi)^3 \sum_{s'} \langle 0 | c_i^* | s' \rangle \langle s' | c_j | 0 \rangle \delta(\varepsilon_{s'} + E). \end{aligned} \quad (5)$$

That is, they are the densities of, respectively, electron and

hole eigenstates s and s' at energy E accessed by applying an electron or hole creation operator to the ground state. From (4) and (5) we can derive the real and imaginary parts of G and a dispersion relation between them:

$$\begin{aligned} \text{Im} G_{ij}(\omega) &= \{-\pi A, \omega > 0; \pi B, \omega < 0\} \\ \text{and } \text{Re} G_{ij}(\omega) &= \frac{P}{\pi} \int_{-\infty}^{\infty} \frac{\text{Im} G(\omega')(\omega')}{\omega' - \omega} d\omega'. \end{aligned} \quad (6)$$

Equation (6) is not the conventional Hilbert transform because the singularities of G cross the real axis at $\omega = 0$; but correspondingly the coefficients of A and B change sign at $\omega = 0$ and the integrand is normally nonsingular. This absence of singularity is only assured if $A(0) = B(0)$, a requirement which is taken for granted in the standard texts [4] and is obviously true in the Fermi liquid, where the hole quasiparticle is simply the negative of the electron at the same momentum. What will be shown here is that this is not true for projected electrons, i.e., spins, and that therefore (6) is logarithmically infinite: the assumption that there is a Fermi liquid with a finite step at the Fermi surface can thus be shown to be mathematically inconsistent.

Let us consider the fermion creation and destruction operators for an electron in the f shell on a particular site i : $c_{i,\sigma}^*$ and $c_{i,\sigma}$. The presumed band state $|k, \sigma\rangle$ will be created or destroyed by a linear combination of these operators as in Eq. (2). The matrix elements which enter into the definitions (5) of A and B are those of these operators, acting on the projected wave function Ψ . The reason for a difference is almost obvious: a hole can always be created without violating the constraint, but an electron often encounters an already-occupied site.

Formally,

$$c_{i,\sigma}^* \Psi = (1 - P_G) c_{i,\sigma}^* P_G \Phi + P_G c_{i,\sigma}^* P_G \Phi$$

and the first term is finite but creates states in the upper, split-off Hilbert space which cannot contribute to A near $\omega = 0$; these states have ε_s near or above the large repulsion U . On the other hand, $c_{i,\sigma} \Psi = P_G c_{i,\sigma} P_G \Phi$, since it cannot create double occupancy. Note that

$$P_G c_{i,\sigma}^* P_G = (P_G c_{i,\sigma} P_G)^*. \quad (7)$$

These operators are conjugates of each other and would have equal A and B densities; c^* and c do not.

To illustrate the difference let us make the “Gutzwiller approximation” of assuming that Φ , like a simple Slater determinant of Bloch waves, has no correlation of site occupancies for opposite spins. (If there is a “correlation hole” the numbers are modified but the structure is the same. The basic point is that site occupancy probabilities are not singularly dependent on momentum.) Let us define a parameter x which is the number of holes relative to the case of $1f$ electron per site. Every state s is equally accessed by the local Fermion operator, and there are $(1 - x)/(1 + x)$ fewer full states below E_F than empty ones above it, in the state Φ .

In the state Ψ , on the other hand, there are only x empty ones to $(1-x)/2$ full ones, so that the weight of the terms of Eq. (5) in A is reduced relative to those in B by the ratio

$$A/B = g = \frac{x}{(1-x)/2} \frac{1-x}{1+x} = 2x/(1+x). \quad (8)$$

There will thus be a logarithmic singularity in the real part of G , according to Eq. (6), proportional to $1-g = (1-x)/(1+x)$ (times the renormalization constant Z which gives the height of the Fermi discontinuity, in case there are many-body corrections).

The reasoning here is so close to simple arithmetic that it seems difficult for trained theorists to comprehend. The sum rule which follows from the commutator of c and c^* tells one that the total integral from $-\infty$ to ∞ of $A_{ii} + B_{ii}$ must be fixed at unity. By its definition, the integral of A is the number density of holes and B that of electrons (assuming for simplicity a single band). If we did not have any strong interactions indeed these will match at k_F . But B , and not A , has amplitude in the split-off upper Hubbard band, and this amplitude is not singularly dependent upon k ; so B must be less than A in the low-energy region, specifically at the Fermi surface.

This singularity is obviously not allowable. In order to demonstrate this I demonstrate that the wave-function renormalization vanishes.

$$\begin{aligned} Z(\omega) &= (1 - \partial \Sigma / \partial \omega)^{-1} \text{ since } G^{-1} \\ &= \omega - H_0 - \Sigma, \\ Z &= [\partial(G^{-1}) / \partial \omega]^{-1} \\ &= [-(\partial G / \partial \omega) / G^2]^{-1} \\ &\approx \omega(\ln^2 \omega) \rightarrow 0 \quad \text{as } \omega \rightarrow 0. \end{aligned}$$

Since Z at the Fermi surface $\omega = 0$ measures the discontinuity in $n(k)$, this contradicts the original assumption.

If $A(\omega = 0)$ is related to B by a constant ratio, as in (8), the only way in which this singularity can be avoided is if $A = B = 0$. The conjecture I have arrived at through more

complicated and less rigorous reasoning [5] is that the real and imaginary parts of G have primarily a power law dependence on ω for small values, with a small but finite positive exponent. There is strong experimental evidence for such a power law singularity in the case of the cuprates (see Ref. [5]) but the direct measurement of the Green's function has not yet been carried out for heavy-electron materials or the cuprates. Indirect evidence in the form of transport anomalies does exist [6].

In the heavy-electron case, there has been much discussion in the literature of possible "quantum critical point" effects. I feel that one must first clear up the effects of the above universal critical behavior before speculating about QCP's. A question which will occur to many readers is why the transport properties often resemble those of a Fermi liquid except near QCP's. As in the cuprates, this has to do with details of the transport theory; our conjecture is that there is a "hidden Fermi liquid" [7] which can constitute a "bottleneck" for relaxation processes in some circumstances, and make the latter look like those of a Fermi liquid.

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