Is the Mott transition relevant to f-electron metals?

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We study how a finite hybridization between a narrow correlated band and a wide conduction band affects the Mott transition. At zero temperature, the hybridization is found to be a relevant perturbation, so that the Mott transition is suppressed by Kondo screening. In contrast, a first-order transition remains at finite temperature, separating a local moment phase and a Kondo-screened phase. The first-order transition line terminates in two critical endpoints. Implications for experiments on f-electron materials such as the Cerium alloy Ce0.8La0.1Th0.1 are discussed.

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The Mott transition, i.e., how electrons evolve from localized to itinerant as a function of an external parameter such as pressure, is a fundamental problem in condensed matter physics. It is a key phenomenon in d-electron materials, such as transition-metal oxides, in which a set of bands with d-character is well separated and close to the Fermi level. In this case, the phase with localized electrons is insulating, and that with itinerant electrons is metallic. Dynamical mean-field (DMFT) studies have deepened our understanding of this phenomenon, and led to many interesting experimental predictions which have been recently verified experimentally.

In several f-electron materials, a transition between a phase where f-electrons are more localized and another in which they are more itinerant is also observed (such as the isostructural γ-α phase transition of Cerium). In these materials however, there is a broad band with spd-character close to the Fermi level (in addition to the f-orbitals), and both phases are metallic. It was suggested early on by B. Johansson that the concept of a Mott transition within the f-electron subspace may still be relevant in this context. A different view is the Kondo volume collapse (KVC) model, in which the transition is driven by the change in the hybridisation between the two phases with different unit-cell volumes. In this picture, the broad band of conduction electrons plays a key role, while it is merely a spectator in the Mott picture. The interplay of these two mechanisms in Cerium have recently received a great deal of attention, since DMFT provides a comprehensive framework in which these problems can be studied systematically.

In this article, we study the localization-delocalization transition within a simple model, which nevertheless retains the key ingredients present in f-electron materials. The model interpolates between a Hubbard model for the f-orbital and the periodic Anderson model (PAM) in which this orbital is hybridized to a broad band. Our goal is to understand whether, in a purely electronic model, the Mott transition present when the f-band is isolated remains a robust feature in the presence of a finite hybridization to a broad band. Our key finding is that the answer to this question depends on temperature in a crucial manner. At zero-temperature, the Kondo effect always sets in and screens the local moment. As a result, in a purely electronic setting, the Mott transition is suppressed by an arbitrarily small hybridization. In contrast, a first-order transition remains at finite temperature.

The similarities between the phase diagram of the PAM and that of the Hubbard model at finite temperature have been pointed out in previous work. However, the distinction between a first-order transition with coexisting electronic phases and a mere crossover was not addressed. More importantly, the zero-temperature case was investigated in the case where the hybridisation vanishes at the Fermi level: this is a non-generic case in which the transition survives down to T = 0. In the generic case of a finite hybridisation, the connection between the smooth behaviour at T = 0 and the finite-temperature transition has not been addressed before. Our model study also has direct implications for the volume-collapse transition of materials such as Ce0.8La0.1Th0.1, and its dependence on magnetic field, as explained at the end of this paper. We study a generalization of the periodic Anderson Model (PAM) defined by the Hamiltonian:

\[
H = -t \sum_{\langle ij \rangle} \sum_{\sigma} c_{i\sigma}^\dagger c_{j\sigma} + V \sum_{i\sigma} c_{i\sigma}^\dagger f_{\sigma} - \alpha t \sum_{\langle ij \rangle} f_{i\sigma}^\dagger f_{j\sigma} + U \sum_{i} \left( n_{i\uparrow} - \frac{1}{2} \right) \left( n_{i\downarrow} - \frac{1}{2} \right)
\]

In addition to the usual hybridisation and interaction terms, it contains a direct hopping between the f-orbitals: \( t_{ff} = \alpha t \). The model reduces to the PAM when \( \alpha = 0 \). When \( V = 0 \), it describes two independent fluids: free conduction electrons, and a narrow band of f-electrons described by the Hubbard model. For simplicity, our study is restricted to the particle-hole symmetric case where both bands are half-filled (\( n_f = n_c = 1 \)). In this case, one has a (renormalised) hybridisation-gap insulator when the direct \( f-f \) hopping is small, as studied in [15] (for \( \alpha = 0 \) and large \( U \) this is the Kondo insulator). For \( \alpha \) large enough however, the hybridisation gap...
closes and the model describes a metal. As shown below, the criterion for a metallic ground-state is essentially independent of $U$ and reads: $\alpha > (V/D_c)^2$ (with $D_c$ the conduction electron bandwidth).

In this article, we study this metallic regime within DMFT, focusing on the paramagnetic phase. When $V = 0$, the situation is well-documented [1,2]: the f-electrons are described by a Hubbard model which undergoes a Mott transition. The transition is first-order at finite temperature, with a transition line $U_c(T)$ ending at a critical endpoint $(U_c, T_c)$. The transition line separates two different regimes: on one side the f-electrons are itinerant while on the other side the f-electrons behave as local moments. These two behaviors correspond to two locally stable mean-field solutions, which coexist in the domain $U_{c1}(T) < U < U_{c2}(T)$ delimited by two spinodal lines. The transition persists down to $T = 0$: there, the quasiparticle weight of the correlated itinerant solution vanishes continuously at $U_{c2}(T = 0)$. The main issue we want to address is whether a regime with unscreened local moments survives in the presence of a finite hybridisation $(V \neq 0)$ to the broad conduction electron band, and what happens to the phase transition.

DMFT associates to this lattice model a single-impurity Anderson model for the f-orbital, subject to an effective hybridisation function $\Delta_{\text{eff}}(i\omega_n)$ which must be determined self-consistently. For the case of semicircular densities of states for both the c- and f-electrons (corresponding to a large-connectivity Bethe lattice), this self-consistency condition can be written, using the cavity construction [1], as:

$$\Delta_{\text{eff}}(i\omega_n) = \alpha^2 t^2 G_{ff}(i\omega_n) + \frac{[V - \alpha^2 G_{cf}(i\omega_n)]^2}{i\omega_n - t^2 G_{cc}(i\omega_n)}. \quad (2)$$

In this expression, $G_{ff}$, $G_{cf}$ and $G_{cc}$ are the effective components of the on-site interacting Green’s function, which must be computed self-consistently from the effective impurity model. This expression has a transparent interpretation: The screening of the f-moment on a given site in the local picture of the lattice model has two origins reflected in each term of this equation. The first term describes the screening due to the motion of the f-electrons onto other sites: it is effective only when the f-electrons are itinerant, and its vanishing at low-energy is associated with the Mott phenomenon. The second term describes the local screening due to the conduction electrons. This screening is affected by the f-electron motion, resulting in a reduced frequency-dependent effective hybridization $V_{\text{eff}}(i\omega_n) = V - \alpha^2 G_{cf}(i\omega_n)$.

Let us consider first the case $T = 0$. Physical intuition suggests that an arbitrarily small hybridisation $V$ is enough to screen the local moment through the formation of a Kondo singlet with the conduction electrons. The energy scale associated with screening will be very small, but finite, at small $V$. Hence, at $T = 0$, the hybridization is a singular perturbation when starting from the paramagnetic Mott phase, suggesting that the $T = 0$ Mott transition is unstable against the introduction of hybridization. This intuition is supported by a low-frequency analysis of Eq. (2). In a Mott phase with unquenched f-moments, the Green’s function and self-energy behave as: $\Sigma_f(i\omega) \sim 1/i\omega$, $G_{ff}(i\omega) \sim \omega$ at small $\omega$. Inserting this into (2), one sees that $\Delta_{\text{eff}}(i\omega) \sim \omega$ as $\omega \to 0$ if $V = 0$, which is consistent with the original assumption of a local moment as it implies a gap in the hybridisation density of states $\text{Im}\Delta_{\text{eff}}(\omega + i0^+)$. However, as soon as $V \neq 0$, $\Delta_{\text{eff}}(i\omega)$ tends to a finite (imaginary) value as $\omega \to 0$ because of the second term in (2). This implies a finite value of $\text{Im}\Delta_{\text{eff}}(\omega + i0^+)$ at low-frequency, which is inconsistent with a free local moment. Hence, at $T = 0$ and when $V \neq 0$, the self-energy has a local Fermi-liquid form $\Sigma_f(i\omega) \sim \omega(1 - 1/Z) + ...$ for all values of $U$, with $Z$ the f-quasiparticle weight. At large $U$, $Z$ is very small and sets the scale for screening. This yields two quasiparticle bands, which read (neglecting lifetime effects): $2\omega_k^\pm = (1 + \alpha Z)\omega_k \pm [(1 + \alpha Z)\omega_k^2 + 4VZ^2]^{1/2}$.

This corresponds to the non-interacting bandstructure, with renormalized parameters: $\alpha_{\text{eff}} = Z\alpha$, $V_{\text{eff}} = \sqrt{Z} V$. It is easily seen that a hybridisation gap is present only if $V_{\text{eff}} > \sqrt{\alpha_{\text{eff}} D_c}$. The quasiparticle weight $Z$ drops out from this criterion: hence, the two quasiparticle bands overlap and one has a metal when $V < \sqrt{\alpha D_c}$, independently of $U$ as announced above. Accordingly, it follows from this low-frequency analysis that, at $T = 0$, the f-spectral function is pinned at $\omega = 0$ to its non-interacting value: $A_{ff}(0) = \alpha^{-1}\rho_0(V/\sqrt{\alpha})$, for all $U$, as long as $0 < V \leq \sqrt{\alpha D_c}$ (with $\rho_0$ the non-interacting density of states of the conduction band). In this Fermi-liquid state, the “large” Fermi surface encounters $n_c + n_f = 2$ electrons per site. This low-frequency analysis can be illustrated by a simple calculation using the Gutzwiller approximation (GA). In this approach, one optimizes a variational energy depending on the probability of double occupancy $d$, and the quasiparticle residue is obtained as $Z = 16d(1/2 - d)$. The results of this approximation for our model are displayed in Fig. 1. This figure clearly shows that the Brinkman-Rice transition (analogous to the $U_{c2}$ found in DMFT), at which $Z$ vanishes in the Hubbard model $(V = 0)$, is no longer present at finite $V$. We showed analytically that, because $V$ introduces a logarithmic singularity ($\propto Z \ln Z$) in the variational energy at small $Z$, the minimum is always found at a finite value of $Z$. This also allows us to estimate the behaviour of $Z$ at large $U \gg U_{c2}$, which has the expected exponential suppression characteristic of the Kondo effect: $Z \sim c_{\alpha,V} e^{-eU_c D_c/32V^2}$ (the prefactor $c_{\alpha,V}$ depends only weakly on $\alpha$ and $V$). We performed a full quantitative solution of the DMFT equations at $T = 0$, in order to confirm and extend this analysis. For this purpose, we used an exact diagonalization (ED) scheme based on the Lanczos algorithm and an adaptive discretization of the effective bath degrees of freedom [1]. The Green’s func-
tion and self-energy obtained from ED (not shown) do obey $G(i\omega) \sim -i\alpha^{-1}\rho_0(V/\sqrt{\alpha})$, $\Sigma(i\omega) \sim i\omega(1-1/Z)$ at low-frequency for all $V \neq 0$, from which we obtained the quasiparticle weight displayed in Fig. 1. Besides confirming the analysis above, we also performed ED calculations for increasing and decreasing sweeps in $U$ in order to check that no other solution of the DMFT equation is present at $T = 0$ when $V \neq 0$, besides the Fermi-liquid one with screened $f$-moments and a large Fermi surface. This is in contrast to the Hubbard model ($V = 0$) which has a coexistence region $[U_{c1}, U_{c2}]$ between a Mott-localized and an itinerant solution extending down to $T = 0$.

While Kondo screening always sets in at $T = 0$ and suppresses the Mott transition, we expect the situation to be qualitatively different at finite temperature. Indeed, on general grounds, the effect of a perturbation (even if singular for the ground-state) is expected to be smooth at $T \neq 0$. As a result, the first-order transition and the coexistence region should be robust features of the present model as long as $V$ is not too large. Since small energy scales are involved ($T_c$ is of order $D_c/40$ for the pure Hubbard model, and the Kondo screening scale is tiny at large $U$), an exact numerical study is difficult and we approached the problem using two approximate impurity solvers. The first is the iterated perturbation theory (IPT) approximation [21], which has proven to be semi-quantitatively very successful in the study of the Mott transition. IPT is known to overestimate low-energy scales, and will not be accurate in the Kondo regime. The second method is the (dynamical) “slave-rotor” (DSR) integral equations [21], which is able to resolve low-energy scales and reproduces the correct exponential Kondo scale at large $U$. The phase diagram found within IPT is displayed in Fig. 2. As anticipated, the coexistence (hysteretic) region is still present for the smaller values of $V$. As $V$ increases, its extension is drastically reduced, and $T_c$ decreases, as also found with the more accurate DSR solver (Fig. 2 compares the estimates of $T_c$ in the two methods). The spectral functions of two coexisting solutions are displayed in Fig. 2: one has a well-formed Kondo peak corresponding to good screening of the local moment while the other one has very small (but finite) spectral weight at low energy. In contrast to the $V = 0$ case, we find that the two spinodals no longer extend down to $T = 0$ and that, within IPT, another critical endpoint is found at low temperature at which the actual first-order transition line terminates. Note that, in view of the above analysis at $T = 0$, the two spinodal lines must indeed either end at a lower critical point or run away towards infinite coupling. Unfortunately, because of the low energy scale involved, we have not been able to push the DSR method to low enough temperatures and firmly establish the existence of a lower critical endpoint within this technique.

We have also studied the effect of a magnetic field on the transition between the screened (low-$T$, itinerant) and unscreened (high-$T$, local moment) regimes. This is motivated by recent experiments on the $\gamma - \alpha$ transition of the Ce$_{0.5}$La$_{0.5}$Th$_{0.1}$ alloy, showing that the transition temperature is decreased by an applied magnetic field [17]. Dzero et al. [22] pointed out that this can be rationalized by approximating the high-$T$ $\gamma$-phase as a collection of almost free localized magnetic moments, while assuming that the free-energy of the low-$T$ $\alpha$-phase does not change appreciably with magnetic field. In Fig. 3D, we display our findings for the temperature associated with the local moment spinodal line (lower boundary of the coexistence region), as a function of applied field. This demonstrates, within the simple microscopic model.
is diagonal, with $\bar{Z}$ corresponding simply to the vanishing of $\omega$. We emphasize that self-energy $\hat{\Sigma}$ takes a matrix form and the Mott transition is suppressed by Kondo screening. This is qualitatively consistent with the KVC picture. These findings can be put in the broader context of the orbital-selective Mott transition (OSMT), which attracted a lot of attention recently [23, 24]. In a general two-band case, the Mott transition (OSMT) is characterized by $\hat{\Sigma}(\omega) = 0$ (dashed lines) and $\hat{\Sigma}(\omega) = 0$ (Hubbard Model, full lines), in the screened phase (A) and in the unscreened one (B). Upper $T_c$ with DSR (dashed line). D. Transition temperature as a function of an applied magnetic field $H$ for $U=2.7$, calculated at $T = 0$ within ED.

studied here, that indeed the transition is suppressed by a magnetic field as observed experimentally.

To summarize, we have studied a model which retains the key aspects of f-electrons metals, i.e. a narrow correlated band hybridized with a wide uncorrelated conduction band. We found a first-order transition at finite temperature between a screened phase and a localisation-delocalisation transition at lower temperatures than in pure Cerium. We emphasize that our results also imply that a $T = 0$ quantum-critical valence transition is a non-generic case that requires the tuning of an extra parameter.

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FIG. 3: Left panel: comparison between spectral densities for $V \neq 0$ (dashed lines) and $V = 0$ (Hubbard Model, full lines), in the screened phase (A) and in the unscreened one (B). Highlighted endpoints are shifted upwards and downwards, respectively, by elastic terms. We therefore conclude that there are two generic situations that are consistent with our results: either the material displays a first-order transition down to $T = 0$ (for softer materials, with smaller values of $B_0$) or it will display two critical-endpoints (for harder materials) (see also [4]). Experimental studies [10] suggest that the latter case may be realized in the Cerium alloy Ce$_{0.8}$La$_{0.1}$Th$_{0.1}$, in which alloying acts as a “negative pressure”, thus allowing for an investigation of the localization-delocalization transition at lower temperatures than in pure Cerium. We emphasize that our results also imply that a $T = 0$ quantum-critical valence transition is a non-generic case that requires the tuning of an extra parameter.

Finally, we comment on the qualitative relevance of our results for f-electron materials. There, the contribution ($F_e$) to the free-energy from the electronic degrees of freedom that are active close to the transition have to be added to the contributions from all other bands and ions, which can be approximated by an elastic contribution (see e.g. [4]). As a result, the volume-collapse transition does not correspond to a true divergence of the response function $\chi_e = -d^2 F_e/dv^2$ of the active electronic degrees of freedom (with $v$ the unit-cell volume). Rather, it will take place [22] when $\chi_e = B_0/v_0$, with $B_0$ and $v_0$ a typical bulk modulus and unit-cell volume. Hence the critical temperatures of the upper and lower endpoints are shifted upwards and downwards, respectively, by elastic terms. We therefore conclude that there are two generic situations that are consistent with our results: either the material displays a first-order transition down to $T = 0$ (for softer materials, with smaller values of $B_0$) or it will display two critical-endpoints (for harder materials) (see also [4]). Experimental studies [10] suggest that the latter case may be realized in the Cerium alloy Ce$_{0.8}$La$_{0.1}$Th$_{0.1}$, in which alloying acts as a “negative pressure”, thus allowing for an investigation of the localization-delocalization transition at lower temperatures than in pure Cerium. We emphasize that our results also imply that a $T = 0$ quantum-critical valence transition is a non-generic case that requires the tuning of an extra parameter.

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