

Direct Transition between a Singlet Mott Insulator and a Superconductor

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We argue that a normal Fermi liquid and a singlet, spin-gapped Mott insulator cannot be continuously connected, and that some intermediate phase must intrude between them. By explicitly working out a case study where the singlet insulator is stabilized by orbital degeneracy and an inverted Hund's rule coupling, mimicking a Jahn-Teller effect, we find that the intermediate phase is a superconductor.

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Understanding metal-insulator transitions driven by electron correlation, the so-called Mott transitions (MT), is a long standing problem. Renewed attention was recently aroused by the development of the so-called dynamical mean field theory (DMFT) [1], a quantum analog of classical mean field theories, which treats exactly local temporal fluctuations while freezing spatial correlations. The DMFT has provided us with a complete characterization of the MT for the single band Hubbard model (SBHM) within the paramagnetic sector, where magnetic instabilities are not allowed. The insulator-metal MT does not occur by gradual closing of the Mott gap between the Hubbard bands in the single-particle spectrum, but it is associated with the appearance (at a given value $U = U_{c2}$) of a narrow "Kondo" quasiparticle peak or resonance at the Fermi level [2,3]. The peak height is pinned to the noninteracting value $\rho_0(\mu_0)$, but its width is finite in the metal and vanishes continuously as the MT is approached. For $U < U_{c2}$ the metallic state is stable with respect to the metastable insulating solution which exists for $U > U_{c1}$ [2,3]. Roughly in the interval $U_{c1} < U < U_{c2}$, the spectral function presents both the broad Hubbard bands and the quasiparticle resonance, thus combining to some extent the properties of a narrow-band metal with those of the Mott insulator. For smaller U , the lower and upper Hubbard bands merge together, swamping the resonance away, and the correlated metal continuously turns into an ordinary metal. As soon as the constraint to the paramagnetic subspace is released, anti-ferromagnetism (AFM) appears, and everything changes. Even in partially frustrated models, where the effects of magnetism are attenuated and AFM usually sets in only above some $U_M < U_{c2}$, magnetism still "contaminates" the MT. The characteristic energy scale of the magnetic fluctuations, in proximity of a continuous MT, necessarily exceeds the width of the Kondo resonance, thus affecting the properties of the ensuing metallic phase, e.g., turning it into a spin-density wave.

A new and different situation is to be expected if one could realize a singlet, spin-gapped Mott insulator, such as, e.g., a spin-liquid insulator. The entropy of such a state is zero, as opposed to the extensive entropy of the Mott phase in the SBHM [2], and no symmetry, magnetic or other, is broken. In this Letter we discuss the consequences of the zero-entropy property on the MT and on the correlated metal just below the transition point. To this end, we consider a (threefold) orbitally degenerate model arising in the physics of the alkali-doped fullerides [4]. For densities $\langle n \rangle = 2$ or 4, the ground state (GS) of this model system is nonmagnetic both for small U (metallic) and for large U (singlet nondegenerate Mott insulator). We show that a third, intermediate phase actually intrudes between the Fermi liquid (FL) metal and the singlet Mott insulator. Remarkably, the intermediate phase is a superconductor.

The Hamiltonian reads

$$H = \sum_{ij\sigma} \sum_{a,b=1}^3 t_{ij}^{ab} d_{ia\sigma}^\dagger d_{jb\sigma} + \sum_i H_i^{\text{int}}. \quad (1)$$

The interaction term is local

$$H_i^{\text{int}} = \frac{U}{2} n_i^2 + \frac{2J}{3} \left[\sum_{a=1}^3 n_{ia}^2 - \sum_{a<b} n_{ia} n_{ib} + \frac{3}{4} \sum_{a<b} \Delta_{iab}^2 \right], \quad (2)$$

where $n_{ia} = \sum_{\sigma} d_{ia\sigma}^\dagger d_{ia\sigma}$ is the electron number on each orbital ($a = 1, 2, 3$) at site i , $n_i = n_{i1} + n_{i2} + n_{i3}$, and $\Delta_{iab} = \sum_{\sigma} (d_{ia\sigma}^\dagger d_{ib\sigma} + \text{H.c.})$. Besides the overall on-site repulsion U , the model includes a multiplet-exchange-splitting term J . In presence of a Jahn-Teller coupling to some high-frequency on-site vibration, as shown in Ref. [4], J may effectively change sign from positive (Hund's rule) to negative. When $\langle n \rangle$ corresponds to 2 or 4 electrons per site (the problem is electron-hole symmetric around $\langle n \rangle = 3$), the isolated ion has a nondegenerate GS which is simultaneously a spin and an orbital singlet.

With a negative effective J , it is quite natural that a MT from the paramagnetic metal towards a nondegenerate singlet insulator should take place increasing U [4,5].

We carry out a DMFT study of the dynamics of model (1) in proximity of the MT for $\langle n \rangle = 2, 4$ on a Bethe lattice with hopping diagonal in the orbital index, $t_{ij}^{\alpha\beta} = t\delta_{\alpha\beta}$. The bandwidth is $W = 4t$. The DMFT maps (1) onto a threefold-degenerate Anderson impurity model

$$H_I = \sum_{a=1}^3 \sum_{n,\sigma} \epsilon_{an} c_{an\sigma}^\dagger c_{an\sigma} + (V_n^a d_{a\sigma}^\dagger c_{an\sigma} + \text{H.c.}) - \mu \sum_{a\sigma} d_{a\sigma}^\dagger d_{a\sigma} + H_{\text{int}}, \quad (3)$$

where H_{int} is the interaction (2) for the impurity operators $d_{a\sigma}$'s. The self-consistency condition is

$$\sum_n \frac{|V_n^a|^2}{i\omega - \epsilon_{an}} = t^2 G_a(i\omega), \quad (4)$$

with $G_a(i\omega)$ being the impurity Green's function for orbital a [1]. We solve the impurity model by exact diagonalization [6]. The sums in Eqs. (3) and (4) are truncated to a finite and small number $N_s - 1$ of conduction "bath" orbitals [7]. A surprisingly small value of N_s is indeed enough to capture the qualitative features of the MT in the SBHM, and $N_s = 5$, the value used here, gives good quantitative results [6]. Although the Hamiltonian is $O(3)$ invariant under rotations in orbital space, we cannot exclude a spontaneous breaking of this symmetry. We explicitly studied solutions with orbital symmetry breaking (orbital ordering), but we found that the orbitally symmetric solution, $G_a(i\omega_n) \equiv G(i\omega_n)$, always has lower energy. In the following, we consider only such symmetric solutions.

In order to characterize the metallic phase close to the MT, we compute the single-particle spectral function $\rho(\omega) = -1/\pi \text{Im}G(\omega)$, and the quasiparticle weight $Z = m/m_*$ at the Fermi level, which is finite in the metallic phase but zero in the insulator, and thus determines the position of the MT. Within our numerical accuracy the vanishing of Z appears to be continuous [see Fig. 2(a) below], as in the SBHM [2]. In Fig. 1 we show the evolution of the spectral function across the transition, for different values of U/W but at fixed ratio $J/W = -0.02$.

The metallic phase close to the transition ($U \lesssim U_{c2}$) shows a coexistence between high-energy insulating features (Hubbard bands), and the low-energy metal feature (the Kondo resonance), whose width vanishes at the transition. In addition, the Hubbard bands display a well-defined multiplet structure, absent in the SBHM, and typical of the orbitally degenerate site. Surprisingly, the linewidth of these atomiclike excitations is not set by the bandwidth as in the SBHM [2], but by a much smaller energy scale, as if a kind of motional line narrowing were effectively at work. The coexistence of atomic and metallic features is therefore much more striking for our orbitally degenerate model than for the SBHM.

As in the SBHM, the single-particle density of states (DOS) at the chemical potential μ must coincide with the

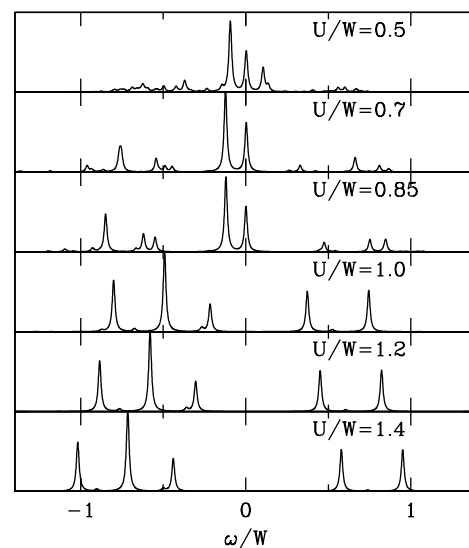


FIG. 1. U dependence of the single-particle spectral function for $\langle n \rangle = 4$ and $J/W = -0.02$ in the normal state (with gauge symmetry enforced).

bare DOS $\rho_0(\mu)$. Moreover, as a consequence of Luttinger's theorem, the chemical potential must coincide with the bare one, so that $\rho(\mu) = \rho_0(\mu_0)$ for every U , and the MT occurs by narrowing of the resonance peak. The peak width $E_F^* \approx ZW/2$ may be viewed as an effective Fermi energy for the interacting system, or a Kondo temperature T_K , below which the system may be described as a FL. As a consequence, the entropy $S(T)/N \sim T/T_K$ for $T \leq T_K$, so that $S(T_K)$ is of order 1 up to U_{c2} , where T_K vanishes. By continuity, one can expect this entropy to be released at the MT. This is indeed what happens in the SBHM, where the entropy of the paramagnetic insulator is $S/N = \log 2$. On the other hand, this is incompatible with our nondegenerate insulator, which has zero entropy. Therefore, it is hard to understand how a FL solution could continuously connect to the Mott insulator, despite the numerical evidence strongly pointing towards a continuous transition. This suggests that the metallic solution may be metastable close to the MT, and that some new phase may appear.

The above heuristic arguments, which apply in any dimension for a Brinkman-Rice-type transition, where the m_* diverges, can be generalized to other cases where the MT occurs towards a zero-entropy insulator. The main inadequacy of the metallic solution apparently lies in the constraint imposed by the Luttinger theorem. Without it, the chemical potential could gradually move towards the edge of the DOS, thus allowing one to smoothly connect the metal with a zero-entropy insulator, as for a metal-to-band insulator transition. This scenario would imply a breakdown of the Luttinger theorem before the MT. If the Mott insulator would break some symmetry of the Hamiltonian, e.g., the spin $SU(2)$ symmetry, the metallic phase close to the MT would likely break the same symmetry, allowing the transition to become of the metal-band insulator

type. This is what happens in the Hubbard model on a two-dimensional triangular lattice [8], and also corresponds to what is generally observed experimentally [9]. If, as in our system, the insulator does not break any symmetry, it is less clear what type of instability to expect. The presence of orbital degrees of freedom could suggest a possible orbital ordering, but, as mentioned before, solutions with broken orbital symmetry always have higher energies with respect to orbitally symmetric solutions, ruling out the possibility of orbital ordering. Moreover, being that the insulator is a spin singlet, there is no reason to expect a magnetic instability in the metal, as confirmed by the vanishing of the local spin susceptibility at the MT.

The only symmetry left, which we have so far enforced in solving the self-consistency equation, is the U(1) gauge symmetry. A deeper analysis of the metallic phase in the framework of Landau FL theory suggests that U(1) symmetry might be spontaneously broken. In our orbitally degenerate model, the Landau functional must be invariant under spin SU(2) and orbital O(3) symmetries. We define the local densities in momentum space,

$$\begin{aligned} n_k &= \sum_{a=1}^3 \sum_{\alpha=\uparrow,\downarrow} d_{a\alpha k}^\dagger d_{a\alpha k}, \\ \vec{\sigma}_k &= \sum_{a=1}^3 \sum_{\alpha,\beta=\uparrow,\downarrow} d_{a\alpha k}^\dagger \vec{\sigma}_{\alpha\beta} d_{a\beta k}, \\ l_{i,k} &= \sum_{a,b=1}^3 \sum_{\alpha=\uparrow,\downarrow} d_{a\alpha k}^\dagger L_{i,ab} d_{b\alpha k}, \\ \vec{l}_{i,k} &= \sum_{a,b=1}^3 \sum_{\alpha,\beta=\uparrow,\downarrow} d_{a\alpha k}^\dagger L_{i,ab} \vec{\sigma}_{\alpha\beta} d_{b\beta k}, \end{aligned}$$

where $\vec{\sigma}$ are Pauli matrices, and L_i ($i = x, y, z$) are the angular momentum operators in the $L = 1$ representation $d_1 \sim Y_{1,x}$, $d_2 \sim Y_{1,y}$, and $d_3 \sim Y_{1,z}$. We also need to introduce five additional densities $w_{i,k} = \sum_{a\alpha k} d_{a\alpha k}^\dagger W_{i,ab} d_{b\alpha k}$, $i = 1, \dots, 5$, where the matrices W_i 's are $\sqrt{3}(L_x^2 - L_y^2)$, $\sqrt{3}(L_x L_y + L_y L_x)$, $\sqrt{3}(L_y L_z + L_z L_y)$, $\sqrt{3}(L_z L_x + L_x L_z)$, and $(L_x^2 + L_y^2 - 2L_z^2)$, respectively, as well as their spin antisymmetric counterparts $\vec{w}_{i,k} = \sum_{a\alpha k} d_{a\alpha k}^\dagger W_{i,ab} \vec{\sigma}_{\alpha\beta} d_{b\beta k}$. In terms of these densities, the Landau functional reads

$$\begin{aligned} E &= \frac{1}{2} \sum_{k,k'} f_{kk'}^S n_k n_{k'} + f_{kk'}^A \vec{\sigma}_k \cdot \vec{\sigma}_{k'} \\ &+ \frac{1}{2} \sum_{i=x,y,z} \sum_{k,k'} h_{kk'}^S l_{i,k} l_{i,k'} + h_{kk'}^A \vec{l}_{i,k} \cdot \vec{l}_{i,k'} \\ &+ \frac{1}{2} \sum_{i=1}^5 \sum_{k,k'} g_{kk'}^S w_{i,k} w_{i,k'} + g_{kk'}^A \vec{w}_{i,k} \cdot \vec{w}_{i,k'}. \quad (5) \end{aligned}$$

The local spin susceptibility is given by $\chi/\chi_0 = m_*/[m(1 + F_0^A)]$, where χ_0 is the bare susceptibility, $F_0^A = 6V\rho_0 f_0^A m_*/m$, with f_0^A being the $l = 0$ Legendre transform of the Landau parameter. Since χ actually vanishes at the transition [as shown in Fig. 2(b)], then the antisymmetric Landau parameter F_0^A is positive and

diverges at the MT, probably as m_*^2 . This is surprising since, for small $U \gg |J|$, $f_0^A = -U/3 - 10/9J$ is negative. All local orbital and spin-orbital susceptibilities vanish at the transition, since the insulator has a total gap for spin and orbital excitations, so that the Landau parameters H_0^S , H_0^A , G_0^S , and G_0^A all diverge from the positive side. In addition, similar to the SBHM, the compressibility $\kappa/\kappa_0 = m_*/[m(1 + F_0^S)]$ vanishes like m_*^{-1} at the transition [Fig. 2(c)]. Hence $F_0^S \sim m_*^2$ also diverges. As a result, the (intraorbital) quasiparticle scattering amplitude in the singlet channel,

$$\begin{aligned} A_s &\simeq \frac{1}{m_*} \left(\frac{F_0^S}{1 + F_0^S} - 3 \frac{F_0^A}{1 + F_0^A} \right. \\ &\quad \left. + 4 \frac{G_0^S}{1 + G_0^S} - 12 \frac{G_0^A}{1 + G_0^A} \right), \end{aligned}$$

becomes negative close to the MT, finally vanishing as $(m_*)^{-1}$ for $U \rightarrow U_{c2}$, while, at weak coupling $t \gg U \gg |J|$, this quantity is positive ($A_s = U/2 + 2J/3 > 0$). This strongly suggests a pairing between quasiparticles. To check for this instability, we compute the dynamical pair susceptibility $\Pi(\omega) = \langle 0 | \Delta_0^\dagger(\omega - H)^{-1} \Delta_0 | 0 \rangle$, using as the pair wave function the singlet GS of the atomic limit $\Delta_0 = \sum_a d_{0a\uparrow}^\dagger d_{0a\downarrow}^\dagger$.

The static limit of the real part of $\Pi(\omega)$ [shown in Fig. 2(d)] changes sign in a narrow region just before the MT, turning from negative (stable metal) to positive (unstable). This is another clear indication of a superconducting instability of the FL. To confirm completely this hypothesis, we finally allow for a superconducting solution of the DMFT [1]. The lattice model is mapped onto

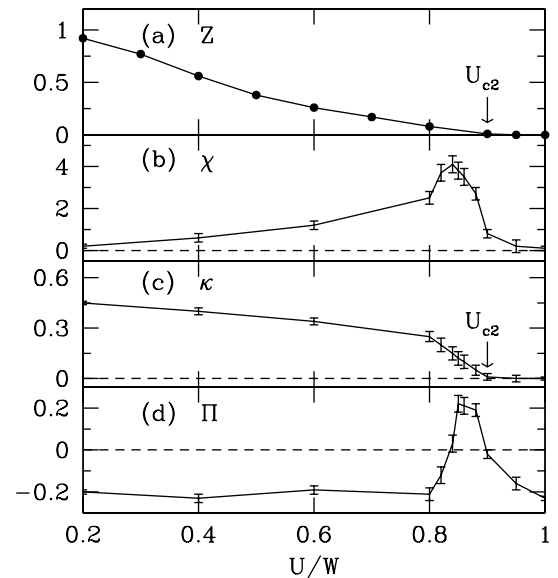


FIG. 2. U dependence of various relevant quantities in the normal state (with gauge symmetry enforced) for $J/U = -0.02$. In panel (a) we show the quasiparticle weight Z , in panel (b) the local spin susceptibility χ , in panel (c) the compressibility κ , and in panel (d) the real part of the zero-frequency pairing susceptibility $\Pi(0)$.

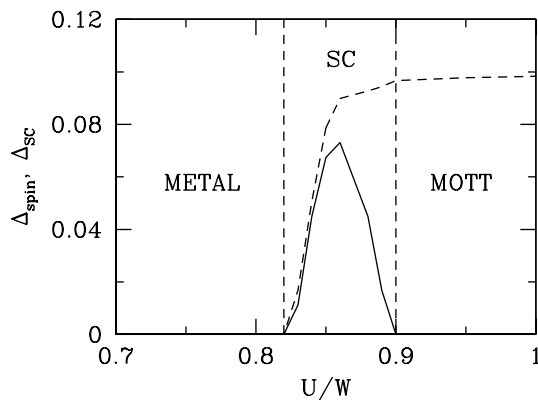


FIG. 3. Superconducting coupling Δ_{SC} (solid curve) and spin gap Δ_{spin} (dashed curve) as computed from the local spin susceptibility. The vertical dashed lines mark the boundaries of the various phases.

an impurity coupled to a superconducting bath or, equivalently, coupled to a normal bath through a normal and an anomalous term,

$$\begin{aligned}
 H_I^S = & \sum_{an,\sigma} \epsilon_{an} c_{an\sigma}^\dagger c_{an\sigma} + \sum_{an,\sigma} (V_n d_{a\sigma}^\dagger c_{an\sigma} + \text{H.c.}) \\
 & + \sum_{an} (\Delta_n d_{a1}^\dagger c_{an1}^\dagger + \text{H.c.}) - \mu \sum_{a\sigma} d_{a\sigma}^\dagger d_{a\sigma} + H_{int}.
 \end{aligned} \quad (6)$$

If the self-consistency equations,

$$\begin{aligned}
 \sum_n \frac{|V_n|^2}{i\omega - \epsilon_n} + \sum_n \frac{|\Delta_n|^2}{i\omega + \epsilon_n} &= t^2 G(i\omega), \\
 - \sum_n \frac{2V_n \epsilon_n \Delta_n}{\omega^2 + \epsilon_n^2} &= t^2 F(i\omega),
 \end{aligned}$$

stabilize a solution with a finite value of any Δ_n , then a superconducting solution is found. We find a stable superconducting GS in the interval $0.82 < U < 0.9$ (for $J/U = -0.02$) in close proximity of the MT, as shown in Fig. 3. We find that, while the superconducting order parameter vanishes at the MT, the spin gap of the superconductor, as computed from the local spin susceptibility, remains finite and joins continuously into that of the insulator, as shown in Fig. 3. Hence neither phase possesses spin entropy. A superconducting phase just before the MT is striking, as there is no sign of or reason for such an instability in the weak-coupling limit, where the intraorbital s -wave scattering amplitude is repulsive. The antiadiabatic electron-phonon coupling implicit in the choice $J < 0$, being unretarded, should be overwhelmed by a large $U \gg |J|$. As the repulsion U increases, the bare electrons turn into quasiparticles. An effective overscreening of U then takes place, generating the attraction that causes the s -wave pairing. This is reminiscent of phe-

nomena in other systems, such as the Hubbard chain with next-nearest-neighbor hopping and the two-leg Hubbard ladder [10]. Generation of an attractive interaction in the effective impurity model, which has an on-site mechanism of singlet formation competing with the Kondo screening, is similar to the two-impurity Kondo model [11]. For reasons of space we must defer pursuit of these analogies to a future paper. The heuristic arguments presented earlier suggest that superconductivity close to a singlet MT should be a phenomenon of wider generality than the simple model where we have uncovered it. Experimentally, in the $\langle n \rangle = 4$ alkali fulleride Rb_4C_{60} , which can be transformed by a pressure of about 10 Kbar from its narrow-gap, probably singlet Mott insulating state [4,5], to a metal, no superconductivity was reported as far down as 0.39 K [12]. Nonetheless, even if some features of our model (antiadiabatic Jahn-Teller effect, diagonal hopping) are quite unrealistic, we can expect, all the same, a narrow superconducting pocket sufficiently close to the critical insulator-metal pressure, at least if the transition is second order, or not too strongly first order. The small superconducting pocket for $\langle n \rangle = 4$ might be connected to the much larger one for $\langle n \rangle = 3$, the well-known case of superconducting fullerenes.

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