Janus-Faced Influence of Hund's Rule Coupling in Strongly Correlated Materials

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We show that in multiband metals the correlations are strongly affected by Hund's rule coupling, which depending on the filling promotes metallic, insulating or bad-metallic behavior. The quasiparticle coherence and the proximity to a Mott insulator are influenced distinctly and, away from single- and half-filling, in opposite ways. A strongly correlated bad metal far from a Mott phase is found there. We propose a concise classification of $3d$ and $4d$ transition-metal oxides within which the ubiquitous occurrence of strong correlations in Ru- and Cr-based oxides, as well as the recently measured high Néel temperatures in Tc-based perovskites are naturally explained.

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Hund's rules determine the ground-state of an isolated atom by accounting for the dependence of the Coulomb repulsion between electrons on their relative spin and orbital configurations. In insulating solids, their role is to select the relevant atomic multiplets, which are then coupled by intersite magnetic interactions. In contrast, the effects of the Hund's rule coupling in metallic compounds are less understood. The difficulty lies in dealing with the localized (atomic) and itinerant characters of electrons on equal footing, a key issue for materials with strong electron correlations [1]. Despite increasing awareness of the physical relevance of the Hund's rule coupling for such materials [2–8], a global view is still lacking.

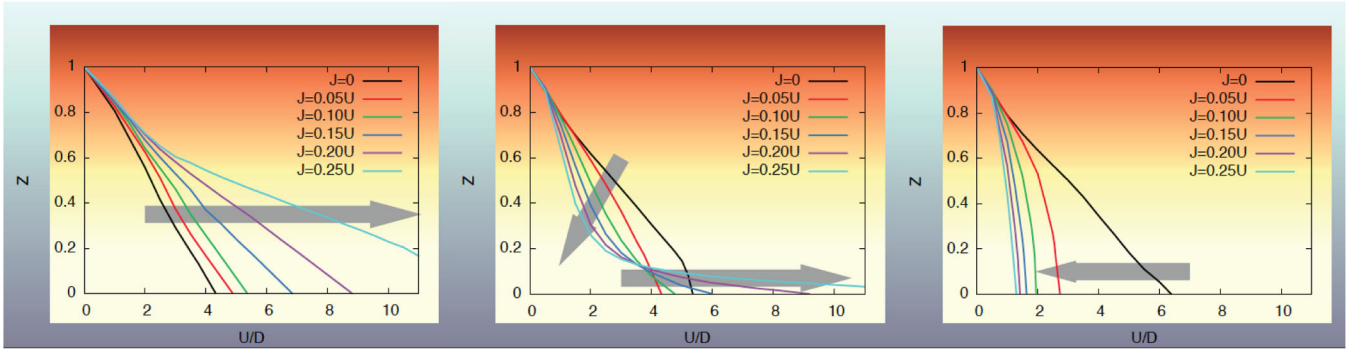
In this Letter, we fill this gap and provide a classification with respect to the number of electrons filling the active orbitals. We show that, aside from the case of a singly occupied shell (where metallicity is favored [4,8]), or a half-filled shell (where it promotes Mott-insulating behavior [9,10]) the Hund's rule coupling induces conflicting tendencies and thus causes strong correlations far from the insulating state (''bad-metal'' behavior). This picture explains the observed physical properties of a number of transition-metal oxides and allows for predictions on novel ones, such as Technetium compounds.

In order to describe all these possibilities and illustrate our key point in a simple context, we consider a model of three identical bands with semicircular density of states of half-bandwidth D filled by N electrons per site. This is relevant, for example, to transition-metal oxides with cubic symmetry and a partially filled t_{2g} shell well separated from the empty e_g shell. The standard interaction Hamiltonian [1] can be written as

$$H_{\text{int}} = (U - 3J)\frac{\hat{N}(\hat{N}-1)}{2} - 2J\vec{S}^2 - \frac{1}{2}J\vec{T}^2, \qquad (1)$$

where $\hat{N}$ denotes total charge, $\vec{S}$ spin and $\vec{T}$ the angular momentum operators. U is the intraorbital interaction and J is the Hund's rule coupling. The Hund's rule coupling favors, in decreasing order: configurations with parallel spins in different orbitals, with opposite spins in different orbitals, and with opposite spins in the same orbital, maximizing S and then T. We solve the model using dynamical mean-field theory (DMFT) [11] which maps a correlated electron system onto a quantum-impurity problem: an effective atom coupled to a self-consistent environment. This approach handles the on-site atomic physics and the itinerant motion of electrons on equal footing. Both the limit of an isolated atom with its multiplet structure and that of a noninteracting band are correctly reproduced.

In Fig. 1, we display the quasiparticle spectral weight Z as a function of coupling U, for several values of J, in the paramagnetic state. Z characterizes the degree of correlations of the metallic state. For example, the Drude weight measured from optical conductivity is proportional to Z [11]. It also sets the energy or temperature scale T^* above which the lifetime of quasiparticles becomes short and coherence is lost. Z and T^* diminish progressively as U/D is increased and a vanishing Z signals the Mott-insulating state, reached for $U > U_c$. We observe that the case of one electron ($N = 1$) is in striking contrast to the case of a half-filled shell ($N = M = 3$): upon increasing J/U the critical coupling U_c in the former is increased [8] while in the latter it is reduced [9,10]. Correspondingly, for a fixed U in the metallic phase, Z increases with J for $N = 1$ while it decreases for $N = M$. Hence, as summarized in Table I, correlations are increased by the Hund's



(a) $N = 1$ (b) $N = 2$ (c) $N = 3$

FIG. 1 (color online). Quasiparticle weight Z vs U for $N = 1$, 2, 3 electrons in $M = 3$ orbitals. The grey arrows indicate the influence of an increasing Hund's rule coupling J/U.

rule coupling for a half-filled shell, and diminished for a singly occupied one.

In contrast, we find that the Hund's rule coupling has a more complex influence in the case of two electrons (or two holes) in 3 orbitals. On the one hand, the critical coupling U_c is strongly increased (and the Mott gap reduced) at the largest values of J/U. As a result, the range of coupling U/D with metallic behavior is enlarged as compared to the case with $J = 0$. On the other hand, for a wide range of coupling strengths, Z is suppressed upon increasing J [7,12,13]. To accommodate these antagonistic effects, Z displays a long tail as a function of U. The small values of Z found there indicate a very low quasiparticle coherence scale T^*, below which the system is expected to show a conventional Fermi liquid physics. An incoherent regime with a Curie-like magnetic response [3] and bad-metal behavior [3,7] is found for temperatures above $T*$ (see the supporting material [14]). This was reported in Ref. [3] and coined "spin-freezing" regime. These considerations are not specific to 2 electrons in 3 orbitals: the Hund's coupling is "Janus-faced" for N electrons in M degenerate orbitals, except for a singly occupied or half-filled band, as summarized in Table. I.

We calculated also away from integer fillings and display the data as a contour plot of the quasiparticle weight as a function of coupling strength U/D and band filling, for a fixed typical value of the ratio J/U (Fig. 2). The extended region of strongly correlated bad-metallic behavior (small Z) around $N = 2$ appears clearly. In contrast, the half-filled case favors insulators (except at weak U/D) and the single-electron case favors good metals (except at strong U/D).

These numerical results can be corroborated and explained by analytical considerations in the simplified limits. In order to understand the influence of J on the Mott gap, we start from the limit of an isolated atom. The charge gap $\Delta_{\mathrm{at}} = E_{\mathrm{at}}(N+1) + E_{\mathrm{at}}(N-1) - 2E_{\mathrm{at}}(N)$ takes two different values depending on whether the relevant orbitals are half-filled or not: $\Delta_{\mathrm{at}} = U - 3J$ for $N < M$ or $N > M$ and $\Delta_{\mathrm{at}} = U + (M-1)J$ for $N = M$. Including hopping perturbatively leads to a correction $\Delta_{\mathrm{Mott}} = \Delta_{\mathrm{at}} - cD + \cdots$, where c is of order unity. Hence, we see that the Mott gap is increased by J (and U_c decreased) at half-filling [9,10], while it is decreased in all other cases [4,8,15]. This localized limit explains the distinction between $N = 3$ and $N = 1$ (and the insulating side of $N = 2$) but does not account for the bad-metal, small-Z, part of the phase diagram around $N = 2$.

To understand this regime we consider the itinerant limit. Studying a correlated metallic phase within DMFT translates mainly in characterizing the coherence scale of the effective impurity problem (self-consistent atom). Here we focus on how it is affected by the Hund's coupling. The key distinction between different cases is the degeneracy of the atomic ground state which is, except for a single electron or hole, reduced by J, as the state with aligned angular momenta is selected (Table S1 in the supporting material [14]). Lower degeneracy enhancing the quantum fluctuations and weaker tunneling from or

TABLE I. The effects of an increasing Hund's rule coupling on the degree of correlations.

Number N of electrons in M orbitals	Degeneracy of atomic ground state	Mott gap	Correlations	Materials behavior promoted by J
one electron or one hole ($N = 1$, $2M-1$)	unaffected	reduced	diminished	metallic
half-filled ($N = M$)	reduced	increased	increased	insulating
All other cases ($N \neq 1$, M, $2M-1$)	reduced	reduced	Conflicting effect (see text)	bad metallic

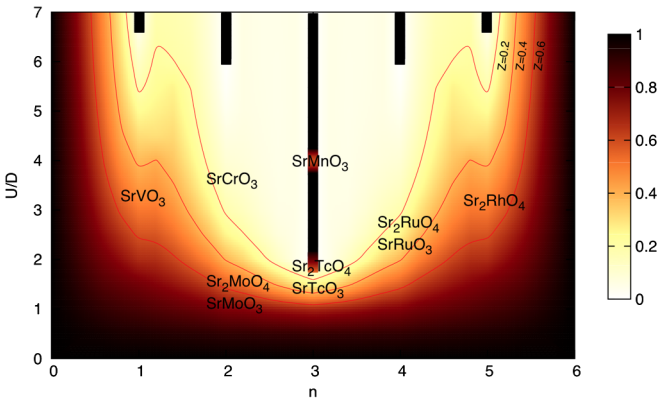


FIG. 2 (color online). Quasiparticle weight Z in a model with 3 orbitals, for $J/U = 0.15$, as a function of the interaction strength U and the number of electrons—from empty (0) to full (6). Darker regions correspond to good metals and lighter regions to bad metals. The black bars signal the Mott-insulating phases. One notes that, among integer fillings, the case of 2 electrons (2 holes) displays bad-metal behavior in an extended range of coupling. Specific materials are schematically placed on the diagram (see text).

onto the composite object suppress the coherence scale [16–20], which corresponds to the Kondo scale of the effective impurity model below which the atomic multiplet is screened out. Further numerical and analytical results are given in the supporting material [14].

Now we examine how the different influences of the Hund's rule coupling are manifested in the physical properties of transition-metal oxides. First, a word of warning. Often these materials do not have perfect cubic symmetry. The distortions mix the orbitals, reduce the bandwidths and induce crystal fields which lower the atomic degeneracy further. These effects usually enhance the correlations and promote insulating behavior, which can often be described by an effective model with a smaller number of orbitals (as some are emptied or filled by the crystal fields) [21–23]. For illustrative purposes, we choose a set of materials indicated on Fig. 2. In [14], the discussion is extended to other materials for which the lifting of orbital degeneracies is stronger.

We begin with oxides of $3d$ transition metals with a half-filled t_{2g} shell, such as $SrMnO_3$ and $LaCrO_3$. A typical ratio of the Coulomb repulsion to half-bandwidth for these materials is $U/D \simeq 4$ eV/1 eV. This exceeds substantially the insulating limit for this case, explaining why no metallic $3t_{2g}^3$ oxides are known [1,24]. Conversely, at a comparable value of U/D, the $3t_{2g}^1$ cubic $SrVO_3$ is a moderately correlated metal with $Z^{-1} = m^*/m \simeq 2$ [1]. LDA + DMFT explicitly demonstrates (see [14]), that $SrVO_3$ would be significantly more correlated [4] were it not for the decorrelating action of Hund's rule at this filling. For $3t_{2g}^2$ materials, still within the same range of U/D (Fig. 2), strongly correlated bad-metal behavior caused by the Janus-faced action of J is found. Observable signatures of bad-metals are large values (beyond the Mott limit [25]) of the non-T^2 but metalliclike resistivity in the extended temperature range above a very low T^* and a large, poorly screened moment, prone to itinerant magnetism. A possible realization among $3d$ oxides is $SrCrO_3$ [26,27].

Oxides of $4d$ transition metals are characterized by smaller values of $U/D \simeq 2$, due to the larger bandwidths and smaller screened interaction associated with the more extended $4d$ orbitals. We consider the series $SrMO_3$ and Sr_2MO_4 with $M =$ Mo, Tc, Ru, and Rh (Fig. 2). The Technetium compounds are special among those: they are located very close to the metal-insulator transition. We are not aware of transport measurements on these compounds, but a recent study [28] indeed reports antiferromagnetism with a very large Néel temperature $T_N \simeq 1000$ K for $SrTcO_3$. Simple model considerations do suggest that the vicinity of the Mott critical coupling leads to largest values of T_N. As a test of our classification, we predict that Sr_2TcO_4 is an insulator or a very strongly correlated metal.

The Mo-, Ru- ,and Rh- based compounds are metallic. For tetragonal 214's an orbital average of the measured values yields $Z^{-1} = m^*/m \sim 2$ for Sr_2MoO_4 ($4t_{2g}^2$) [29], ~ 4 for Sr_2RuO_4 ($4t_{2g}^4$) [1] and ~ 2 for Sr_2RhO_4 ($4t_{2g}^5$) [30]. These variations are explained by a closer examination of the electronic structure of these materials. For example, values for Sr_2MoO_4 and Sr_2RuO_4 differ because the t_{2g} density of states is not particle-hole symmetric: the ruthenate has the Fermi level close to a van Hove singularity and therefore a smaller effective bandwidth [7]. On the other hand, relatively large correlations found in rhodates occur due to the bandwidth narrowing and the orbital polarization induced by rotations of the octahedra. In the regime of weak to moderate correlations with 2 electrons (Fig. 1), Z has a steep dependence on U/D: this explains that $SrMoO_3$ has an unusually large metallic conductivity among oxides [31]. $4d$ materials can be driven also to the extreme bad-metal regime by rotation-induced narrowing of the bandwidths achieved by Ca substitution. An example is $Sr_{1-x}Ca_xRuO_3$, which at $x = 1$ has $m^*/m > 5$ and remains incoherent down to lowest temperatures measured [32].

There is thus a class of Hund's correlated materials which are strongly correlated but driven by J rather than the proximity to a Mott insulator. In this respect, we note that the importance of the Hund's rule coupling has also been emphasized for the iron-based superconductors [2,5,6]. With 6 electrons in 5 active orbitals, the bad-metal behavior observed for these materials can be attributed to the conflicting action of the Hund's rule coupling. This puts pnictides on the map of Hund's correlated material along with $SrCrO_3$ and $SrRuO_3$ but also raises important questions. What is the nature of such materials above the coherence scale and how do they differ from materials

close to the Mott transition? How are the instabilities to magnetism and superconductivity affected?

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