

Mott transitions with partially-filled correlated orbitals.

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We investigate the metal-insulator Mott transition in a generalized version of the periodic Anderson model, in which a band of itinerant electrons is hybridized with a narrow and strongly correlated band. Using dynamical mean-field theory, we show that the precondition for a Mott transition is an integer total filling of the two bands, while for an integer constant occupation of the correlated band the system remains a correlated metal at arbitrary large interaction strength. We picture the transition at a non-integer filling of the correlated orbital as the Mott localization of the singlet states between itinerant and strongly interacting electrons, having occupation of one per lattice site. We show that the Mott transition is of the first-order and we characterize the nature of the resulting insulating state with respect to relevant physical parameters, such as the charge-transfer energy.

Introduction. – Mott localization induced by strong repulsive interaction is intrinsically a physics of commensuration. A paradigmatic example is the Mott-Hubbard transition in the Hubbard model which, in the absence of symmetry breaking, only takes place if the number of correlated electrons equals the number of lattice sites for a single-orbital model [1–4], or an integer multiple of it in the multi-orbital case [5–8]. A metal-insulator transition (MIT) occurs as the local repulsion reaches a critical value of the order of the bandwidth, when it becomes energetically convenient for the interacting electrons to localize at any lattice site. The energy gain associated to the electronic motion becomes smaller than the cost associated to charge fluctuations. Hence, the commensurability of the electron density $n = N_{el}/N_{sites}$ naturally emerges as a necessary condition to obtain a Mott insulator. Intuitively this commensuration implies the absence of spare sites where an electron can hop without paying extra electrostatic energy.

This idealized picture becomes less clear for more realistic systems, in which the correlated electrons in valence orbitals hybridize with nearly uncorrelated ligand orbitals. This is the case of many different transition-metal oxides (TMO) or the Iron pnictides/chalcogenides [9–12], where the transition-metal d -orbitals are intertwined with p -orbitals of the oxygen or pnictogen/chalcogen atoms. Investigations of these systems have suggested that a crucial control parameter to determine the degree of correlation is the filling of the correlated d orbitals [13–19], which however does not generally correspond to an integer total number of electrons per site. Moreover, simplified models for these systems display seemingly contradictory results, where the hybridization between a correlated electronic band and a wide band of non-interacting electrons can either forbid [20] or allow [21–24] the Mott transition in different physical regimes.

This rich spectrum of results leaves many questions open about the very presence of the Mott transition in

systems of this kind, and about the nature of the carriers which localize, i.e., if the ligand p orbitals play a role, or they are mainly spectators of the d -electron localization.

In this work we provide an answer to some of these questions. We study the conditions under which a Mott transition takes place, and what are its properties in a simple, yet generic, model which captures the essential ingredients of the collective behavior of strongly correlated d -electrons hybridized with a band of non-correlated electrons. We solve the model using dynamical mean-field theory (DMFT) [25, 26], a powerful and reliable non-perturbative method which has been widely used to address the Mott-Hubbard transition in a variety of models and realistic systems [8]. Our key result is to show that a zero temperature Mott transition exists only for an integer total density per site, i.e. that the necessary condition is an integer total number of electrons including also those occupying uncorrelated ligand orbitals. We show that this transition corresponds to the localization of singlets of mixed character between the two bands with density of one per lattice site. Finally, we characterize the nature of the correlated insulating state with respect to experimentally relevant parameters of the system. We show that the mentioned past literature connects in this perspective and fits well in the Zaanen-Sawatzky-Allen diagram [27].

Model. – The starting point of our analysis is a generalized version of the periodic Anderson model [22, 23, 28–33]. The model Hamiltonian reads:

$$\mathcal{H} = \sum_{\mathbf{k}\sigma} \psi_{\mathbf{k}\sigma}^{\dagger} \hat{h}(\mathbf{k}) \psi_{\mathbf{k}\sigma} + U \sum_i d_{i\uparrow}^{\dagger} d_{i\uparrow} d_{i\downarrow}^{\dagger} d_{i\downarrow} \quad (1)$$

where:

$$\hat{h}(\mathbf{k}) = \begin{pmatrix} \epsilon_p + \epsilon_{\mathbf{k}} & \gamma(\mathbf{k}) \\ \gamma^*(\mathbf{k}) & \epsilon_d + \alpha\epsilon_{\mathbf{k}} \end{pmatrix}.$$

For the sake of definiteness we consider a two-dimensional system on a square lattice. The spinor $\psi_{\mathbf{k}\sigma} =$

$(p_{\mathbf{k}\sigma} \ d_{\mathbf{k}\sigma})^T$ collects the operators $p_{\mathbf{k}\sigma}$, $d_{\mathbf{k}\sigma}$ respectively annihilating electrons with spin $\sigma = \{\uparrow, \downarrow\}$ in the wide band with dispersion $\varepsilon_{\mathbf{k}} = -2t_{pp}[\cos(k_x) + \cos(k_y)]$ centered at ε_p , and in the narrow correlated band of dispersion $\alpha\varepsilon_{\mathbf{k}}$ ($\alpha \in [0, 1]$) centered at ε_d . The two orbitals hybridize with an amplitude $\gamma(\mathbf{k}) = v_0 - 4t_{pd} \sin(k_x) \sin(k_y)$. The second term in (1) describes the local repulsion experienced by the d -electrons. In the following we set the energy unit to the conduction electrons half-bandwidth $D = 4t_{pp} = 1$ and we introduce the charge-transfer energy $\Delta = \varepsilon_d - \varepsilon_p$. We focus on the case $\Delta \geq 0$ as similar results holds for the $\Delta < 0$ case. Without loss of generality we fix the zero of the energy to $\varepsilon_d = 0$ and adjust the total density $\langle n \rangle = \langle n_p \rangle + \langle n_d \rangle$ (where $n_p = \sum_{\sigma} p_{i\alpha\sigma}^{\dagger} p_{i\alpha\sigma}$ and $n_d = \sum_{\sigma} d_{i\alpha\sigma}^{\dagger} d_{i\alpha\sigma}$ are the local number operators) by tuning the chemical potential μ . We consider the zero temperature regime $T = 0$.

We solve the model (1) using Dynamical Mean-Field Theory (DMFT) [25, 33]. We limit ourselves to paramagnetic solutions in which magnetic ordering is neglected, in order to reveal the pure Mott physics. The lattice problem is mapped onto a quantum impurity problem describing a single d -orbital coupled to an effective electronic bath [34]. The auxiliary impurity problem is described in terms of the local *Weiss Field* (WF) $\mathcal{G}_0^{-1}(i\omega_n)$. A self-consistency condition relates the WF to the local properties of the lattice problem: $\mathcal{G}_0^{-1} = G_d^{-1} + \Sigma$, where Σ is the self-energy function and G_d is the d -component of the local interacting Green's functions, i.e.

$$\begin{aligned} G_d(i\omega_n) &= \sum_{\mathbf{k}} \frac{\zeta_p - \varepsilon_{\mathbf{k}}}{D_{\mathbf{k}}(i\omega_n)} \\ G_p(i\omega_n) &= \sum_{\mathbf{k}} \frac{\zeta_d - \alpha\varepsilon_{\mathbf{k}}}{D_{\mathbf{k}}(i\omega_n)} \\ D_{\mathbf{k}}(i\omega_n) &= (\zeta_p - \varepsilon_{\mathbf{k}})(\zeta_d - \alpha\varepsilon_{\mathbf{k}}) - |\gamma(\mathbf{k})|^2 \end{aligned} \quad (2)$$

with $\zeta_p = i\omega_n + \mu - \varepsilon_p$ and $\zeta_d = i\omega_n + \mu - \varepsilon_d - \Sigma(i\omega_n)$.

The DMFT equations are closed by computing the impurity self-energy $\Sigma(i\omega_n)$ from the numerical solution of the auxiliary impurity problem [25]. In this work we use the exact diagonalization method, in which the effective bath is discretized into a number N_b of levels [35]. The resulting Hamiltonian problem is solved using the Lanczos algorithm to obtain both the lower part of the spectrum and the Green's function [36, 37]. The results of this work have been obtained with $N_b = 9$ and their robustness with respect to N_b has been tested in selected cases.

Mott transition. – In the symmetric case ($\Delta = 0$, $\langle n_p \rangle = \langle n_d \rangle = 1$) the model describes a Kondo insulator for a large enough value of the local hybridization: $v_0 > \sqrt{\alpha}D$ [20] for any interaction strength U . At smaller v_0 a metal is obtained instead with two bands of mixed p - d character due to hybridization. In the absence of hybridization the two bands with different orbital character decouple

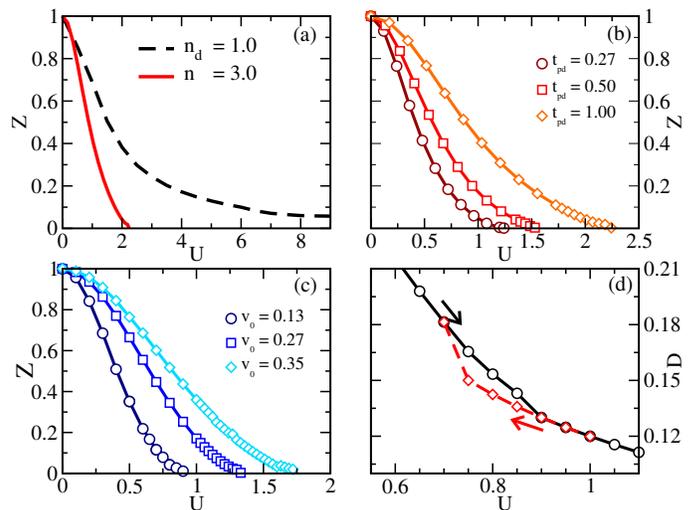


Figure 1. (Color online) Renormalization constant Z and double occupancy $\langle d \rangle$ of the correlated band for $\Delta = 1.0$ and $\alpha = 0.27$. (a) Z as a function of the interaction U , for either $n_d = 1.0$ (dashed line) or $\langle n \rangle = 3.0$ (solid line). The other model parameter are $v_0 = 1.0$ and $t_{pd} = 0.0$. (b)-(c) Z as a function of U for $v_0 = 0.0$ and increasing t_{pd} (b) or $t_{pd} = 0.0$ and increasing v_0 (c). (d) Hysteresis cycle of the double occupancy $\langle d \rangle$ near the Mott transition for $t_{pd} = 0.0$ and $v_0 = 0.13$.

and the d -band describes a half-filled Hubbard system. The latter is known to undergo a zero temperature Mott transition at a critical interaction strength $U = U_{c2}^{\text{HM}}$ of the order of the three times the d -band half-bandwidth αD . However, such Mott transition does not survive the presence of any small hybridization [20].

Since no Mott transition can occur in the presence of hybridization in the symmetric model, we move to the mixed-valence regime ($\Delta > 0$, $\langle n_d \rangle \neq \langle n_p \rangle$), where the orbital occupations of the two orbitals are different.

To pinpoint a Mott transition, we compute the quasi-particle residue $Z = [1 - \partial\Sigma/\partial\omega]^{-1}$ as a function of the interaction strength U (black dashed line). The reduction to zero of this quantity would signal a MIT. We first consider the case of integer filling for the correlated orbitals only. In Fig.1(a) we present results where we actually fix $\langle n_d \rangle = 1$, which implies that the total density is different from an integer number and the p bands are partially filled. However, as our calculations show, Z remains finite up to huge values of the interaction, $U \gtrsim 10D$. In this regime the partially filled p bands provide a delocalization channel for the correlated electrons, ultimately preventing charge localization.

A Mott transition can however be realized in a different regime for any value of the hybridization, as we shall show in the following. On rather general grounds, a sufficiently large hybridization drives the formation of local singlets via the dynamical binding of two electrons on different orbitals [32, 38] (see also Fig.2). Thus, a MIT can be realized upon localization of such compos-

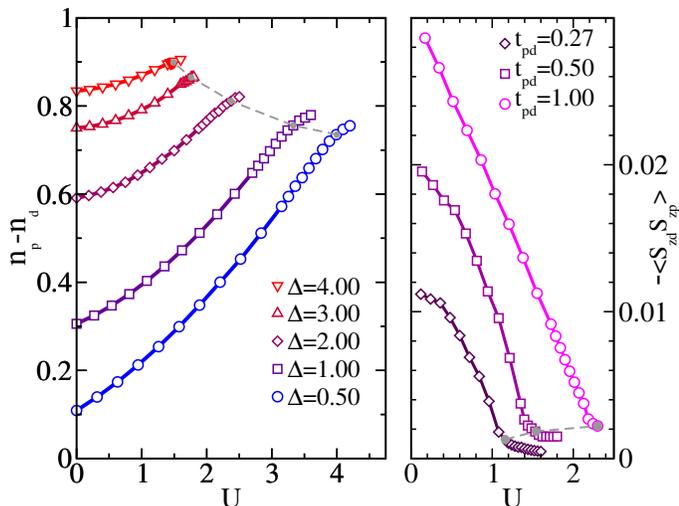


Figure 2. (Color online) *Left panel:* Orbital polarization $\langle n_p \rangle - \langle n_d \rangle$ as a function of the U . Data are for increasing Δ and $v_0 = 1.0$, $t_{pd} = 0.18$, $\alpha = 0.27$. *Right panel:* Inter-orbital spin-spin correlation $\langle s_{zd} s_{zp} \rangle$ as a function of U . Model parameters are as in Fig.1(b). Grey dotted lines mark the Mott transition points.

ite fermionic states for large enough interaction, provided their occupation is one per lattice site. We now show that this is realized for a total density $\langle n \rangle = \langle n_d \rangle + \langle n_p \rangle = 3$. In Fig.1(a) we report the behavior of Z for this occupation. Our results show that Z approaches zero at a critical value of the correlation $U = U_{c2}$. The existence of a Mott transition in this regime turns out to be generic with respect to the amplitude and the character of the hybridization, as shown in Fig.1(b)-(c), where we compare results for local and non-local hybridizations. In both cases we observe the existence of a metal to Mott insulator transition at a critical interaction increasing with the hybridization amplitude. Similarly to the single-band Hubbard model, we find a coexistence of metallic and insulating solutions. This is demonstrated by our results in Fig.1(d), reporting a small hysteresis cycle of the double occupation $\langle d \rangle = \langle n_{d\uparrow} n_{d\downarrow} \rangle$ at the d -orbital.

To better understand the mechanism behind the MIT at $\langle n \rangle = \langle n_d \rangle + \langle n_p \rangle = 3$ and the absence of a transition for $\langle n_d \rangle = 1$, we follow the evolution of the orbital occupations $\langle n_p \rangle$ and $\langle n_d \rangle$. Our results are summarized in the left panel of Fig. 2, which reports the orbital polarization $\langle n_p \rangle - \langle n_d \rangle$ as a function of the correlation U . In the integer-valence regime, where a pure- d picture would apply, $\langle n_p \rangle = 2$ and $\langle n_d \rangle = 1$. As shown by our calculations, the system remains in its intermediate-valence regime up and throughout to the transition, i.e. the Mott transition occurs with a non-integer value of the individual occupations of the orbitals. Increasing the interaction strength U enhances the orbital polarization, by transferring charge from the correlated orbital to the uncorrelated orbitals. For a fixed value of U , the or-

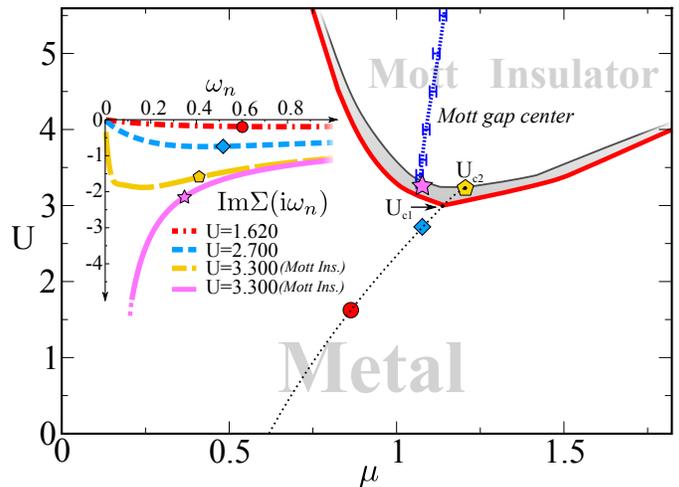


Figure 3. (Color online) Phase-diagram in the U - μ plane. Data are for $v_0 = 1.0$, $t_{pd} = 0.18$, $\alpha = 0.27$ and $\Delta = 1.0$. The (red) solid line is the boundary of the Mott region. The shaded (gray) area indicates the coexistence regions of metallic and insulating solution. The (black) dotted line indicates the $\langle n \rangle = 3$ path, ending at $U = U_{c2}$. The symbols mark the points corresponding to $\text{Im}\Sigma(i\omega_n)$ curves in the inset. The (blue) dashed line and points indicate center of symmetry for the Mott gap (see main text).

bital polarization naturally increases as a function of the charge-transfer energy Δ . This effect translates the fact that orbital mixing is larger when the two orbitals are brought near one another in energy, and decreases rapidly with increasing energy separation. Indeed, the integer-valence regime can only be reached asymptotically in the $\Delta \rightarrow \infty$ limit [32].

In the right panel of Fig.2, we report the evolution of inter-orbital spin-spin correlation $\langle s_{zd} s_{zp} \rangle$. This quantity describes the binding of the magnetic moments between the d - and p -electrons, which defines the formation of the local singlets. Our results show that the inter-orbital spin-spin correlation remains finite across the MIT, exhibiting the persistence of the local singlets in the Mott state. The decreasing behavior of $\langle s_{zd} s_{zp} \rangle$ as a function of U results from the renormalization of the hybridization amplitude, which ultimately leads to a loosening of the magnetic binding.

Mott gap opening. – In order to investigate the opening of the Mott gap in the intermediate-valence regime, we mapped out the U - μ phase diagram, reported in Fig.3. The condition $\langle n \rangle = 3$ determines a line in the metallic part of the diagram intercepting the “V”-shaped Mott insulating region at $U = U_{c1}$. The metallic solution however disappears inside the insulating region at the critical $U = U_{c2} > U_{c1}$ point. The opening of the Mott gap is associated to the presence of a pole in the self-energy on the real-axis $\text{Im}\Sigma(\omega + i\eta)$ close to $(\omega = 0)$. When the pole is not exactly at zero frequency, the large value of the real part of the self-energy prevents quasiparticle excitations

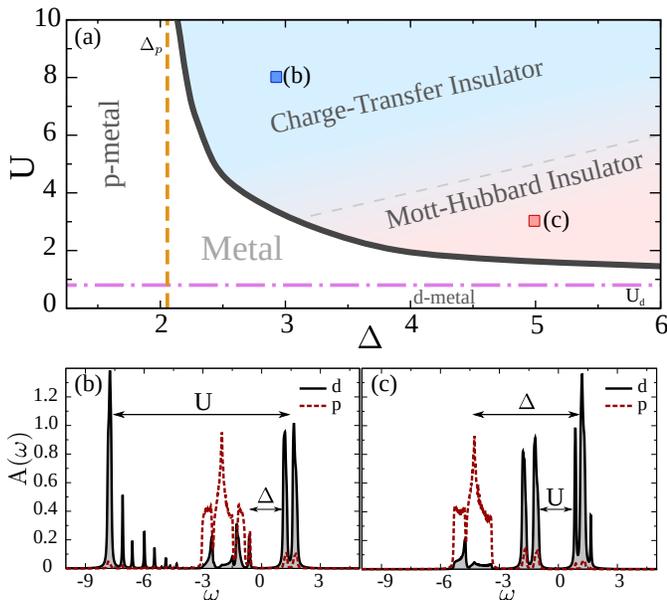


Figure 4. (Color online) (a) Phase-diagram in the U - Δ plane, for $\alpha = 0.27$, $v_0 = 1.0$ and $t_{pd} = 0.18$. The (black) solid line delimitates the insulating region, separated from the metallic solution by a first order transition. The insulating region is divided in two parts: the Charge-Transfer (b) and the Mott-Hubbard (c) for (see main text). The lower panels show the spectral densities $A_\alpha(\omega) = -\text{Im}G_\alpha(\omega)/\pi$, $\alpha = d, p$, for the two points (b),(c) in the diagram. The vertical line at $\Delta = \Delta_p = 2.1$ is the boundary of the p -metal regime, while the horizontal line at $U = U_d = 1.3$ delimitates the d -metal (see main text).

inside the gap. Correspondingly (due to the Kramers-Krönig relations) the imaginary part is found to go to zero at $\omega = 0$, i.e. $\text{Im}\Sigma(i\omega_n)$ vanishes on the *Matsubara* axis with a very large linear slope (see inset of Fig.3). The set of points in the diagram where $\text{Im}\Sigma(i\omega_n)$ instead diverges, i.e. when the pole of the self-energy is at $\omega = 0$, determine the center of symmetry of the Mott gap (see dotted line in Fig.3).

Phase-diagram. – Finally, we studied the dependence of the Mott transition with respect to the charge-transfer energy Δ . Our findings are reported in Fig.4(a), showing the phase-diagram in the U - Δ plane, which closely follows the Zaanen-Sawatzky-Allen diagram [27]. We identify two distinct regimes: A charge-transfer insulator (CTI) for $U \gtrsim \Delta$ and a Mott-Hubbard insulator (MHI) for $U \lesssim \Delta$. The different nature of these two insulating solutions is underlined by the spectral functions $A_{p/d}(\omega) = -\text{Im}G_{p/d}(\omega)/\pi$, presented in the bottom panels of the figure. For the CTI (see Fig.4(b)) the smallest gap is of order Δ and corresponds to the excitations from the wide central band, with prevalently p -character, to the upper Hubbard band. Conversely, in the MHI (see Fig.4(c)) the smallest gap is set by the energy separation of the two Hubbard band of order U . A small coexistence region of metallic and insulating solutions is found. The

boundary line for the Mott transition is proportional to $1/\Delta$. For large Δ the boundary line approaches the critical value of a Hubbard system for the correlated band only, i.e. $U_d = \alpha U_{c2}^{\text{HM}}$ (d -metal). This corresponds to the suppression of the indirect delocalization of the correlated electrons of the order of $\sum_{\mathbf{k}} |\gamma(\mathbf{k})|^2/\Delta$. In the limit of large interaction U a MIT is obtained by closing the charge-transfer gap. For any finite hybridization, there exist a critical charge-transfer energy Δ_p below which the conduction band crosses the Fermi level. As follows from the structure of the Eqs. 2, the critical value Δ_p is ultimately determined by the equation: $D_{\mathbf{k}}(0) = 0$, i.e. $\varepsilon_{\mathbf{k}} + \varepsilon_p - \mu = \frac{\gamma(\mathbf{k})}{\alpha \varepsilon_{\mathbf{k}} + \text{Re}\Sigma(0) - \mu}$. which corresponds to having a Green's functions pole at the Fermi level, for any value of the interaction (p -metal). The solution of this equation is possible for any $\text{Re}\Sigma(0)$ as long as the bare p -band crosses the Fermi level. The absence of this band at the Fermi level is thus a necessary condition for the Mott transition. Since for any fixed hybridization the charge-transfer energy tunes monotonically the density of correlated electrons $\langle n_d \rangle$, this motivates the arising of a non-integer threshold level of $\langle n_d \rangle$ for the Mott transition at large U , as reported in [16] and illustrated by the dashed line in Fig.2a. This value depends on the other parameters (most notably the hybridization) and is non-universal. Our conclusion is thus that the integer criterion for the total density plus the requirement that the bare p -band does not cross the Fermi level rationalizes the seemingly diverging results of the literature cited in the introduction, under the general perspective of the Zaanen-Sawatzky-Allen diagram [27].

Conclusions. – We investigated a paradigmatic model of strongly correlated electrons hybridized with a non-interacting ligand band. We demonstrated that a $T = 0$ Mott transition occurs for any non-vanishing hybridization amplitude in the mixed-valence regime. This transition corresponds to the Mott localization of singlet states formed by the binding between correlated and conduction band electrons. We point out that a necessary condition for the Mott transition is to have an odd total integer filling $\langle n \rangle = 3$, corresponding to a singlet density of one per site but to a non-integer filling of the correlated orbitals. Finally, we identify the first-order nature of the transition and discuss the mechanism for the gap opening as well as its dependence on the charge-transfer energy, pointing out that MIT only occurs if the bare p -band does not cross the Fermi level. These results are relevant to understand the physics of d -orbital materials, such as TMO. The extension of this study to the more realistic case of multi-orbital systems, which better capture the physics of t_{2g} and e_g orbitals and their different hybridization with ligand atoms in TMO, is an interesting future direction of research.

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