Electronic correlations and competing orders in multiorbital dimers: A cluster DMFT study

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We investigate the violation of the first Hund's rule in 4*d* and 5*d* transition-metal oxides that form solids of dimers. Bonding states within these dimers reduce the magnetization of such materials. We parametrize the dimer formation with realistic hopping parameters and find not only regimes where the system behaves like a Fermi liquid or as a Peierls insulator, but also strongly correlated regions due to Hund's coupling and its competition with the dimer formation. The electronic structure is investigated using the cluster dynamical mean-field theory for a dimer in the two-plane Bethe lattice with two orbitals per site and 3/8 filling, which is three electrons per dimer. It reveals dimer-antiferromagnetic order of a high-spin (double-exchange) state and a low-spin (molecular-orbital) state. At the crossover region, we observe the suppression of long-range magnetic order, fluctuation enhancement, and renormalization of electron masses. At certain interaction strengths, the system becomes an incoherent antiferromagnetic metal with well-defined local moments.

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I. INTRODUCTION

A standard paradigm of strongly correlated materials involves competition between on-site Coulomb repulsion (U), which tends to localize electrons on particular sites, and band effects (characterized, e.g., by the width of a corresponding band, W), making them delocalized [1,2]. In effect, there can be a transition from a homogeneous metallic to a homogeneous insulating state. In real materials, this picture can be enriched by an unusual band topology [3-5], namely spinorbit coupling [4,6], which is an interplay between different degrees of freedom, such as orbital, charge, spin, etc. [7–9]. However, there can be another option-a system may prefer an inhomogeneous scenario forming metallic clusters within an insulating media (molecules-in-solids conception [10]). The simplest example of such clusters is a dimer. If U is not very large, the wave function is essentially a molecular orbital with an electron delocalized over both sites. But there are also materials with other types of clusters: trimers [11,12], tetramers [13], and even heptamers [14]. The electrons can easily propagate within these clusters, but hoppings between them are suppressed.

There are two main problems in this regard. First of all, there is no general theory, which explains why some of the systems remain homogeneous while others form (spontaneous) clusters. We knew for a long time that such transitions can be induced by Peierls and spin-Peierls effects [15,16], or, more generally, by a charge-density-wave (CDW) instability due to nesting of the Fermi surface [9,17], but a complete understanding of how strong electronic correlations, spin-orbit coupling, and exchange coupling affect this transition is still lacking. Moreover, calculations for real materials show that there is no nesting in many systems, whose properties were supposed to be explained by the formation of a CDW, or that there is nesting at a wrong wave vector [18].

Another problem is a theoretical description of such inhomogeneous systems. While the homogeneous situation with a Mott-Hubbard transition was extensively investigated over the years, the physical properties of clusterized materials remain mostly unexplored. Up to now, most of the efforts were concentrated on a study of the so-called two-plane Hubbard model (known also as the dimer Hubbard model), which is the Hubbard model on the Bethe lattice composed of dimers; see also Sec. II. Most of the attention has been paid to the situation with one orbital per site in a dimer and half-filling [19–22]. This model allows us to describe the transition from a band to a Mott insulator and is particularly relevant for such materials as VO_2 , V_2O_3 , and Ti_2O_3 [23–26]. The two-orbital case has been considered for the one-dimensional chain using the dynamical mean-field theory (DMFT) [27,28]. The orbital-selective behavior has been found for different electron fillings and has been shown to strongly affect the magnetic properties of a system, since some of the electrons occupying bonding orbitals may form spin-singlets. In effect, only part of the electrons contribute to the total magnetic moment. This violates Hund's rules and may dramatically change exchange coupling between neighboring dimers [28]. However, the onedimensional lattice is not a natural choice for the DMFT because of the small number of nearest neighbors.

Hund's coupling stems from the Coulomb interaction. It represents the intra-atomic exchange, and it has a strong influence on the electronic correlations and therefore also on the Mott transition [29–32]. It can shift the critical interaction value of the Mott transition and also diminish or promote the coherence of Fermi liquids. This depends strongly on the filling [33], i.e., for half-filling the effective Coulomb interaction is increased, and for all other fillings it is decreased. Therefore, Hund's coupling can suppress the Mott transition, but not the correlations. Thus there can be strongly correlated materials that are not close to a Mott transition, but they still

exhibit enhanced electron masses, local moments, and orbital selectivity [34].

In the present paper, the simplest model of multiorbital (two orbitals) dimers on the two-plane Bethe lattice with an odd number of electrons (three) is considered. The parameters of the model are chosen to be close to those specific parameters in real materials based on the late transition-metal ions. We not only find the transition between states with different total spin (S = 1/2 to 3/2) as a function of the hopping in the dimer, but we also observe the suppression of the long-range magnetic ordering by the temperature in the crossover region near this transition. Moreover, surprisingly such a transition can be induced by the hopping in the Bethe lattice. We discuss the electronic and magnetic properties of the considered twoplane Bethe lattice model, and we identify regimes where the system behaves like a Fermi liquid, a Peierls insulator, and a correlated metal. These results not only advance our knowledge of the properties of the two-plane Bethe lattice model, but they can also be useful for the description of dimerized materials, which are presently under close examination.

II. MODEL AND METHOD

While the two-plane Hubbard model seems to be a rather natural choice in the case of VO₂ with a single electron in the 3*d* shell, for a realistic description of materials with a larger number of *d* electrons one needs to take into account the orbital degeneracy and possible crystal-field splitting. The latter can be due to (i) a nearest-neighbor ligand's environment (below, for the sake of simplicity, we will consider the octahedral case) and (ii) bonding with other transition-metal ions.

The dimerization occurs when two transition-metal ions are able to come close enough to each other to lower the total energy due to the formation of bonding orbitals. This is possible when ligand octahedra share their edges or faces, whereas a common corner geometry prevents dimerization because of a negatively charged ligand sitting in between two transition metals. Edge-sharing structures can be achieved, e.g., in delafossites, spinels, 213 honeycomb iridates (which are very popular at present), and ruthenates. Face-sharing is more common in one-dimensional materials such as 6Hperovskites, ZrI₃, etc., but there are also three-dimensional corundum-like structures.

It is rather important that in addition to a trivial splitting of the *d* orbitals onto lower-lying t_{2g} and higher-lying e_g manifolds, there is always an additional splitting in these geometries due to neighboring transition-metal ions. The last can be effectively integrated out. In the edge-sharing octahedra, the t_{2g} orbitals turn out to be split into xy and yz/zx orbitals. The xy orbitals of neighboring metals point to each other. This results in a strong bonding-antibonding splitting, while the xz/yz orbitals may still be considered as site-localized [10]. This is especially important for the 4*d* and 5*d* transition-metal ions, since their wave functions are more spatially extended, and the corresponding bonding-antibonding splitting is much larger than for the 3*d* transition-metal ions. A similar situation occurs for face-sharing octahedra, where the a_{1g} orbitals form a bonding orbital and the e_g^p orbitals remain localized [35,36].



FIG. 1. Left: The two Bethe lattices with hopping t_b are interconnected by dimers of two atomic orbitals (c, d) and two sites (0,1). The Bethe lattice coordination is finite, i.e., z = 3, for illustrative purposes. The sites can form bonding (B) and antibonding (A)molecular orbitals. The bipartite Bethe lattice can be divided into sublattices $(\Lambda, \bar{\Lambda})$. Right: Two possible ground-state configurations in the case of N = 3 electrons: the molecular-orbital (MO) and the double-exchange (DE) states. Their competition is defined by Hund's exchange coupling J, screened intra- (U) and interorbital (U') Coulomb repulsion, and the dimer hoppings t_1^c and t_1^d .

Thus, in order to describe dimerized transition-metal compounds with more than one electron, one needs at least two different sets of atomic orbitals, which differ by the value of the hopping parameters. Due to computational limitations, we will restrict ourselves to the minimal model with two orbitals per site. We label the orbital forming the molecular orbital as *c* and the localized one as *d* (see Fig. 1). Corresponding intradimer hopping parameters are t_{\perp}^c and t_{\perp}^d . A dimer is considered to be a vertex of the Bethe lattice with infinite coordination. For the sake of simplicity, we assume that hoppings along the Bethe lattice, t_b , are the same for both orbitals. Spatial correlations beyond the dimer do not exist because of the infinite coordination.

The Hamiltonian of the model above is

$$\hat{H} = -t_b \sum_{\langle \lambda, \lambda' \rangle \sigma} \sum_{\alpha i} \hat{c}^{\dagger}_{\lambda \sigma \alpha i} \hat{c}_{\lambda' \sigma \alpha i} + \sum_{\lambda} \hat{H}^{\text{dimer}}_{\lambda}, \qquad (1)$$

where i denotes a nearest-neighbor dimer, σ is a spin, $i = \{0, 1\}$ runs over sites within a dimer, and $\alpha = \{c, d\}$ is an orbital index of the t_{2g} orbitals. Therefore, the first term describes a hopping of the electron between dimers with the amplitude t_b , and the second term is responsible for the "local" (intradimer) interaction and can be written as

$$\hat{H}_{\lambda}^{\text{dimer}} = \sum_{\sigma i \alpha} t_{\perp}^{\alpha} \hat{c}_{\lambda \sigma \alpha i}^{\dagger} \hat{c}_{\lambda \sigma \alpha \bar{i}} + U \sum_{i \alpha} \hat{n}_{\lambda \uparrow \alpha i} \hat{n}_{\lambda \downarrow \alpha i} + U' \sum_{\sigma i} \hat{n}_{\lambda \sigma c i} \hat{n}_{\lambda \bar{\sigma} d i} + (U' - J) \sum_{\sigma i} \hat{n}_{\lambda \sigma c i} \hat{n}_{\lambda \sigma d i} - J \sum_{i} (\hat{c}_{\lambda \downarrow c i}^{\dagger} \hat{c}_{\lambda \uparrow d i}^{\dagger} \hat{c}_{\lambda \downarrow d i} \hat{c}_{\lambda \uparrow c i} + \hat{c}_{\lambda \uparrow d i}^{\dagger} \hat{c}_{\lambda \downarrow d i}^{\dagger} \hat{c}_{\lambda \uparrow c i} \hat{c}_{\lambda \downarrow c i} + \text{H.c.}).$$
(2)

The orbital differentiation (the first term) is caused by the intradimer hopping parameters, t_{\perp}^{α} , and we do not introduce crystal-field splittings (*c*-*d*). The intradimer hopping can also be written in matrix notation,

$$t_{\rm loc} = \begin{pmatrix} -t_{\perp}^c & 0\\ 0 & -t_{\perp}^d \end{pmatrix} \otimes \sigma_x, \tag{3}$$

where the Pauli matrix σ_x creates the off-diagonal entries of the site space. The local electron-electron interaction at each site [the last terms in Eq. (2)] is modeled via the Kanamori parametrization [37], where U, U' are intra-/ interorbital Coulomb repulsions, and J is Hund's exchange coupling. We choose the interorbital Coulomb interaction by cubic symmetry as U' = U - 2J.

The model is solved at finite temperatures exactly using the cluster dynamical mean-field theory (CDMFT) [38–41] with a continuous-time quantum Monte Carlo impurity solver [the continuous-time hybridization expansion solver (CTHYB)] [42–45]. The solver as well as the CDMFT code have been written using the TRIQS library [46].

The dimer's degrees of freedom of our auxiliary impurity model contain two spins, two orbitals, and two sites. The Bethe lattice can be divided onto two equivalent sublattices Λ and $\bar{\Lambda}$; see Fig. 1. The CDMFT self-consistency equation describes a particle of Λ fluctuating through its environment $\bar{\Lambda}$. Since we are interested in a solution of a broken spinsymmetry, we apply the antiferromagnetic condition for the construction of the Weiss field,

$$\mathcal{G}_{\sigma}^{-1}(i\omega_n) = (i\omega_n + \mu)\mathbb{1} - t_{\text{loc}} - t_b^2 G_{-\sigma}(i\omega_n), \qquad (4)$$

where 1 is a unit matrix, $\mathcal{G}(i\omega_n)$ is the Weiss field, and $G(i\omega_n)$ is the local Green's function; the latter two are both matrices in spin, orbital, and site space. Note that the antiferromagnetic order described by Eq. (4) exists between the dimers (dimer antiferromagnetism) and not within them. To find CDMFT solutions of broken spin symmetry, we add a small external magnetic field to the Hamiltonian, which is switched off after a few CDMFT iterations. It is worth mentioning that there are also other interesting solutions, which allow for the coexistence of insulating behavior and ferromagnetism [47], but a study of this part of the phase diagram is beyond the scope of the present paper. We also use a diagonal basis of the site space in the block structure of the Green's function (see below), and thereby solutions of broken site symmetry within dimers are excluded, i.e., charge ordering within the dimers was forbidden by construction.

The local Green's function, which is needed to calculate the chemical potential μ in the CDMFT self-consistency, can be found using the following equation:

$$G_{\sigma}^{-1}(i\omega_n) = (i\omega_n + \mu)\mathbb{1} - t_{\text{loc}} - t_b^2 G_{-\sigma}(i\omega_n) - \Sigma_{\sigma}(i\omega_n).$$
(5)

This implicit equation has to be solved iteratively, which begins by setting it equal to the impurity Green's function of the last CDMFT cycle $G(i\omega_n) = g(i\omega_n)$, which is also the self-consistency condition for the CDMFT. The self-energy is calculated via the Dyson equation from the impurity quantities $\Sigma(i\omega_n) = \mathcal{G}^{-1}(i\omega_n) - g^{-1}(i\omega_n)$, and initially it is set to zero.

To make the quantum Monte Carlo impurity solver more efficient, we use a standard unitary transformation on the site space $j \in \{0, 1\}$:

$$\hat{\tilde{c}}_{\sigma\alpha i} = \sum_{i} R_{ij} \hat{c}_{\sigma\alpha j}, \quad R = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 & 1\\ 1 & -1 \end{pmatrix}, \quad (6)$$

transforming to the bonding (*B*)/antibonding (*A*) basis, labeled by $i \in \{A, B\}$, with corresponding creation/annihilation operators labeled by a tilde. This transformation diagonalizes the local Green's function in site space and thereby also in all single-particle orbitals.

To sum up, even taking into account all constraints and simplifications, there are still five parameters in our model $(U, J, t_{\perp}^c, t_{\perp}^d, t_b)$. To reduce this number further, we will restrict ourselves by typical values met in real materials. We choose two groups of compounds with the general formulas Ba₃MeTM₂O₉ [48–52] and Re₅TM₂O₁₂ [53–55], where Re is a rare-earth ion, TM is a transition-metal ion, and Me is a rare-earth, alkali-, or transition-metal ion. There are dimers formed by two TMO₆ octahedra in these two classes of systems (sharing their faces in Ba₃MeTM₂O₉ and edges in Re₅TM₂O₁₂).

Typically, TM ions are 4d metals such as Ru, Re, Mo, and Os for which Hund's exchange $J \sim 0.7$ eV and Hubbard $U \sim 4.5 \text{ eV}$ (i.e., $U' \sim 3 \text{ eV}$) [10]. Therefore, we will fix the screened Coulomb interaction and Hund's exchange to the values above. The hopping of the more localized orbital is set to $t_{\perp}^d = 0.2$ eV. The hopping parameters, t_{\perp}^c and t_b , will be varied in what follows. Based on density-functional theory calculations, we also suggest typical values of the hopping parameters in these materials: t_{\perp}^{c} changes from 0.7 to 1.4 eV, while $t_{\perp}^d \sim 0.2$ eV and $t_b \sim 0.2$ eV. One should also note that the electron filling per dimer will be fixed to the value of N = 3, i.e., 3/2 electrons per site. This is the simplest nontrivial case with odd-number electrons in the two-orbital model (a situation with five electrons, i.e., three holes, is the same in the presence of particle-hole symmetry; one- or seven-electron filling, i.e., one hole, is trivial). Such a filling is not only interesting from the model point of view, but it also reflects the situation realized in many different transitionmetal oxides with dimerized crystal structure, such as, e.g., Ho₅Mo₂O₁₂ [56], V₄O₇ [57,58], Nb₂O₂F₃ [59], and many others. Additionally, we remind the reader that the antiferromagnetic (AFM) and paramagnetic (PM) self-consistency conditions will be used throughout this study.

A. Atomic limit at T = 0

We start with a treatment of our model in the atomic limit, where the hopping in the Bethe planes is suppressed, i.e., $t_b = 0$. There are two possible ground states for the isolated dimer with N = 3 electrons and two different orbitals c and d. The first state, with one electron residing bonding c and two other electrons occupying d orbitals with the same spin, will be referred to as the double-exchange (DE) configuration, since it maximizes the total spin of the dimer. Another configuration, called the molecular-orbital (MO) state, is a state with a completely filled bonding c orbital and the remaining electron distributed over localized d orbitals (the charge ordering is forbidden by construction; see Sec. II).



FIG. 2. Spectrum *E* depending on the dimer-hopping t_{\perp}^c in the atomic limit of an isolated dimer (T = 0). States are characterized by $\langle S_{\dim}^2 \rangle$. The ground-state energy E_0 per t_{\perp}^c is subtracted from all energies.

Neglecting quantum fluctuations, one can approximate these states by their largest contribution to the wave function:

$$|\mathrm{MO}\rangle \approx \hat{c}^{\dagger}_{\uparrow dB} \hat{\tilde{c}}^{\dagger}_{\uparrow cB} \hat{\tilde{c}}^{\dagger}_{\downarrow cB} |0\rangle, \quad |\mathrm{DE}\rangle \approx \hat{c}^{\dagger}_{\uparrow d0} \hat{c}^{\dagger}_{\uparrow d1} \hat{\tilde{c}}^{\dagger}_{\uparrow cB} |0\rangle, \tag{7}$$

as illustrated in Fig. 1, which provides an understanding of the spin quantum numbers of the ground state. However, since we use a large U, the ionic and homopolar terms in the MO wave function will have somewhat different weights, and therefore a variational approach [28] would be more reasonable to estimate transition energies. In the case of T =0, we can use the exact diagonalization for a Hilbert space of 256 states. The results are shown in Fig. 2. At a critical $1.05 < \tilde{t}_{\perp}^c < 1.1$ eV, we observe a ground-state crossover from a spin-quadruplet ($\langle S_{dim}^2 \rangle = 3.75$), which we identify as the DE state, to a spin-doublet ($\langle S_{dim}^2 \rangle = 0.75$), i.e., the MO state. In the considered range of $t^c \perp (0.7-1.4 \text{ eV})$, the spectrum contains only these two states within energies up to ~0.1 eV.

B. Noninteracting regime

To identify the effects of the interaction below, we first present the electronic structure in the noninteracting regime in Fig. 3. It is reminiscent of the simplified sketch shown in the right part of Fig. 1. The density of states in this limit is a superposition of four semicirculars with the individual bandwidth $W = 4t_b$. The bands, corresponding to the *c*(*d*) orbitals, are centered at energies of $\pm t_{\perp}^c (\pm t_{\perp}^d)$ in a site representation (see the upper panel of Fig. 3). A site equivalence leads to an overlay of the densities of state (DOSs) from different sites. Because in our consideration $t_{\perp}^c > t_{\perp}^d$, the *c* bands are always farther away from the Fermi level than the *d* bands. One should note that the Fermi level is not at the middle of the *d* band since we are not at half-filling (which would be for N = 4).

The transformation of the noninteracting model to the bonding-antibonding (BA) representation simplifies drastically an examination of the DOS (see the lower panel of Fig. 3). For example, in the site representation, the band of



FIG. 3. The density of states in the noninteracting limit (i.e., U = J = 0) as a function of intradimer hopping of the *c*-electrons t_{\perp}^{c} and excitation energy ω . Hopping within the Bethe plane is chosen to be $t_{b} = t_{\perp}^{d} = 0.2$ eV.

c character at site 0 or 1 was located at $-t_{\perp}^{c}$ and $+t_{\perp}^{c}$, while after BA transformation there are two bands (instead of two sites) of pure *c* bonding character at $-t_{\perp}^{c}$ and *c* antibonding character at $+t_{\perp}^{c}$. Thus, in ascending order, one has four bands of pure character: *c* bonding (*c*, *B*), *d* bonding (*d*, *B*), *d* antibonding (*d*, *A*), and *c* antibonding (*c*, *A*). The bonding and antibonding states are separated by $2t_{\perp}^{c} - 4t_{b} (2t_{\perp}^{d} - 4t_{b})$. If $t_{\perp}^{c} > t_{\perp}^{d} + 4t_{b}$, there is a gap between *c* (anti)bonding and *d* (anti)bonding states. Additionally, if $t_{\perp}^{d} > 2t_{b}$, there is a small gap between bonding and antibonding states of *d* character. The formation of these bands can be considered as a local crystal-field effect with the $t_{\perp}^{c} (t_{\perp}^{d})$ playing the role of crystalfield splitting.

Crystal fields are known to compete with Hund's coupling. This leads to a number of very important phenomena, such as, e.g., spin-state transitions [9,29]. Whereas intra-atomic Hund's exchange tends to the uniform orbital occupancy (strictly speaking, this can be achieved only at half-filling), the crystal field promotes orbital polarization when some of the orbitals are less occupied than others [60]. However, the interpretation of the BA splitting as an effective crystal field



FIG. 4. The magnetic moment of the dimer $\langle S_{dim}^z \rangle$ as a function of temperature *T* and intradimer hopping of the *c*-orbitals t_{\perp}^c for $t_{\perp}^d = t_b = 0.2$ eV. For certain temperatures, the double-exchange state (DE) and the molecular-orbital state (MO) are separated by a quantum critical region (QC). The red and green dashed lines mark the positions of local minima of the spin and orbital correlations, respectively.

also needs to take into account that the coefficients of the interaction terms also change under the BA transformation. In the next section, we discuss the phase diagram of the two-plane Bethe lattice for an intermediate situation when both intradimer hoppings and interaction (given by U and J) strength are not small.

III. PHASE DIAGRAM

Previous studies of the two-plane Bethe lattice have focused on the single-orbital case. It was found to hold not only the Mott and band insulators, but also a correlated mixed state with coherent and incoherent peaks in the local density of states. Competition between intra- and interplane exchange interactions was shown to affect the formation of the local moments [19,22,26]. We will demonstrate that substantial orbital differentiation due to different interplane hoppings, $t_{\perp}^{d} \gg t_{\perp}^{d}$, results not only in a spin-state-like transition, but also in a strong suppression of a long-range magnetic order in the critical region.

Throughout this section, we discuss the results for fixed $t_b = 0.2$ eV. Figure 4 shows the phase diagram of our model obtained by the CDMFT described in Sec. II. There are three main regions. At low temperature and for small t_{\perp}^c we find the DE state with a total spin $S_{\text{dim}}^z = \pm 3/2$ (red part of the phase diagram). All dimers are antiferromagnetically ordered, so that $\langle S_{\text{dim}}^z \rangle \sim 3/2$. This DE state transforms into the MO state with the total spin $S_{\text{dim}}^z = \pm 1/2$ upon increasing intradimer hopping t_{\perp}^c (the light blue part of the phase diagram). This can be considered as a spin-state transition for the cluster. The critical \tilde{t}_{\perp}^c is close to the value obtained in the atomic limit (see Sec. II A). At low temperatures, dimers in the MO phase are antiferromagnetically ordered and $\langle S_{\text{dim}}^z \rangle \sim 1/2$.

Increasing the temperature, we get to the last region with paramagnetic dimers (this phase can again be divided according to $\langle S_{\rm dim}^2 \rangle$ in the DE or MO parts). Interestingly, however, the temperature dependence of $\langle S_{\rm dim}^z \rangle$ is very different in





FIG. 5. The magnetic moment of the dimer $\langle S_{\text{dim}}^z \rangle$ as a function of intradimer hopping of the *c*-orbitals t_{\perp}^c for $t_{\perp}^d = t_b = 0.2 \text{ eV}$ and temperatures *T*.

different parts of the phase diagram. We see that the paramagnetic phase appears at much lower temperatures in the critical region of $t_{\perp}^c \sim 1.05$ eV. The DE and MO states have different quantum numbers (different total spins), and thus in the limit of isolated dimers ($t_b = 0$) the transition between them must be discontinuous at T = 0. Obviously, no longrange magnetic order is possible in this situation. However, fluctuations can result in a crossover. In this crossover region, the system becomes frustrated and the paramagnetic phase is promoted by the competition of the DE and MO states forming a hybrid state (HYB) with properties that are distinct from both.

In Fig. 5 we present a selection of data of Fig. 4 in order to resolve more detailed properties of the DE/MO transition. In particular, it shows that the order parameter $\langle S_{\dim}^z \rangle$ is smooth along the transition, and since furthermore no coexistence of the two phases is found, it suggests that the lattice exhibits a phase transition of second order at \tilde{t}_{\perp}^c corresponding to the ground-state crossover of the isolated dimer. The integrated occupancies

$$N_{\sigma} = \sum_{\alpha \in \{c,d\}} \sum_{i \in \{B,A\}} \tilde{n}_{\sigma\alpha i}, \quad \sigma \in \{\uparrow,\downarrow\},$$

$$N_{\alpha} = \sum_{\sigma \in \{\uparrow,\downarrow\}} \sum_{i \in \{B,A\}} \tilde{n}_{\sigma\alpha i}, \quad \alpha \in \{c,d\},$$

$$N_{i} = \sum_{\sigma \in \{\uparrow,\downarrow\}} \sum_{i \in \{B,A\}} n_{\sigma\alpha i}, \quad i \in \{B,A\},$$
(8)

 $N_i = \sum_{\sigma \in \{\uparrow,\downarrow\}} \sum_{\alpha \in \{c,d\}} n_{\sigma\alpha i}, \quad t \in \{B, A\},\$ are shown in Fig. 6 (top), confirming our illustration of the DE and MO states (Fig. 1). For low temperatures, fluctuations are suppressed by AFM order and the integrated occupancy has a sharper crossover. In fact the crossover region, in close proximity to its boundaries, shows local minima of the spin and orbital correlations $\langle SN, SN \rangle = \langle N, N \rangle = \langle N, N \rangle$ with r =

bital correlations $\langle \delta N_x \delta N_{\bar{x}} \rangle = \langle N_x N_{\bar{x}} \rangle - \langle N_x \rangle \langle N_{\bar{x}} \rangle$ with $x = \uparrow, \downarrow$ and x = d, c, respectively. The physical reasoning behind this is that the fluctuations are always very strong in the vicinity of phase transitions. The temperature dependences of the $\langle \delta N_x \delta N_{\bar{x}} \rangle$ minima are shown in Fig. 4 by dashed lines.

The phase diagram shows that both originate from the DE/MO ground-state crossover, but their temperature



FIG. 6. Occupations (top) and correlations (bottom) of the single-particle orbitals across the t_{\perp}^c driven DE/MO transition at T = 0.02 eV (left) and T = 0.01 eV (right). N_x is the integrated occupancy. Dashed lines mark the t_{\perp}^c of the correlation's respective local minimum for the spin (red) and orbital (green) correlations.

dependence is very different. The spin correlation minimum is very close to the critical temperature of the DE state for all t_{\perp}^c . The decoupling of spins is much stronger than that of the orbitals, which is rather independent of the temperature. The comparison of the correlations at different temperatures (Fig. 6, left and right) shows that also the magnitude of spin fluctuations of the DE state depends strongly on the temperature whereas the orbital fluctuations do not. The orbital fluctuations are less temperature-dependent because of a rather large U' that suppresses them. In contrast, the main impact of the relatively small J is on the spin fluctuations, and therefore they set in at lower temperatures. A prominent feature of the ground-state crossover is also the inversion of the orbital polarization, which agrees with our estimated critical value of \tilde{t}_1^c in Sec. II A.

To estimate the evolution of quasiparticles, we use the description of renormalized quasiparticle bands [26]. The quasiparticle residue

$$Z^{-1} = 1 - \frac{\partial \operatorname{Re}\Sigma(\omega)}{\partial\omega}\Big|_{\omega=0} \tag{9}$$

renormalizes the noninteracting bandwidth $W = 4t_b$ to

$$W_{\tilde{\epsilon}} = ZW,\tag{10}$$

and thereby the imaginary part of the self-energy $\Sigma(i\omega_n)$ on the Matsubara axis encodes the coherence of the quasiparticles. Additionally, the real part of the self-energy shifts the energies of the quasiparticles,

$$\tilde{\epsilon} = Z[\tilde{t}_{\text{loc}} - \mu + \text{Re}\Sigma(\omega = 0)].$$
(11)

One can see in Fig. 7 that far from the critical region ($t_{\perp}^c \ll 1.05 \text{ eV}$ or $t_{\perp}^c \gg 1.05 \text{ eV}$) both *c* and *d* states are (mostly) shifted from the Fermi level (by strong bond-antibonding splitting and by correlation effects). In contrast, three bands appear in the vicinity of the Fermi level close to critical t_{\perp}^c , which favors frustration effects.

In Fig. 4, we use the notion of a quantum critical (QC) region for the low-temperature ($T \sim 0.02 \text{ eV}$) paramagnetic phase. It is critical in the sense that the scattering rates of all



FIG. 7. Renormalized quasiparticle bands of the majority (left) and the minority (right) spin at T = 0.02 eV. Bonding (b) and antibonding (a) combinations of the atomic *c* and *d* orbitals. The renormalized bandwidths are represented by the colored regions.

quasiparticles in proximity to the Fermi level diverge, i.e., the quasiparticle residue and renormalized bandwidth go to zero. The mechanism behind the formation of the paramagnetic insulator for $1 < t_{\perp}^c \leq 1.1 \text{ eV}$ is the divergence of self-energies in several orbitals. This is distinct from interaction-induced effective field splittings encoded in the real part of the self-energies, and it is reminiscent of the Mott insulator. The QC region is bounded from below. At low temperatures, this criticality is avoided by the quasiparticles as they leave the Fermi level.

It is interesting that different molecular spin-states (such as our DE and MO) have been observed experimentally in dimerized materials mentioned in Sec. II with the general formula $Ba_3MeTM_2O_9$ depending of the choice of Me [48–50,52]. Moreover, some of these materials are characterized by a puzzling suppression of the long-range magnetic order and even a possible realization of the quantum spin-liquid phase due to frustrations [61–63].

IV. LATTICE EFFECT

The Bethe hopping parameter t_b controls the embedding of the correlated dimer into the lattice. The limits of $t_b = 0$ and $t_b \rightarrow \infty$ correspond to isolated dimers and disconnected Bethe lattices, respectively. The situation of $t_b \ll t_{\perp}^c$ corresponds to not yet disconnected dimers, but "uncorrelated" ones with the charge concentrated on the bonds rather than sites. This state corresponds to the uncorrelated Peierls insulator. Apart from that, t_b controls the strength of quantum fluctuations of the bath, because it scales the hybridization for the corresponding Anderson impurity model that CDMFT maps to.

In this section, we pick three values of $t_{\perp}^c = 0.7$, 1.05, and 1.4 eV as representatives of the DE, HYB, and MO states, respectively, at the temperature of T = 0.01 eV, and we vary the Bethe-hopping t_b for each of them. The first part focuses on spin-polarized solutions and the second on paramagnetic ones.



FIG. 8. Top: Dimer magnetization $\langle S_{dim}^z \rangle$ as a function of the Bethe hopping t_b for the dimer hoppings $t_{\perp}^c = 0.7$ eV (DE), 1.05 eV (HYB), and 1.4 eV (MO) at T = 0.01 eV. At the crossover, the spin-freezing (SF) phenomenon exists at certain t_b . Filled and empty markers present insulating and metallic states, respectively. Metallicity is determined by analytical continuation using the maximumentropy method. Bottom: Squared total spin of the dimer $\langle S_{dim}^2 \rangle$ as a function of the Bethe hopping t_b for the dimer hoppings $t_{\perp}^c = 0.7$, 1.05, and 1.4 eV at T = 0.01 eV.

A. Dimer antiferromagnetism

The upper panel of Fig. 8 shows the dimer magnetization $\langle S^z_{\rm dim} \rangle$ (for the sake of simplicity, we omit the g factor) at T = 0.01 eV as a function of the Bethe hopping parameter t_b in three regimes: the antiferromagnetically ordered DE $(t_{\perp}^{c} = 0.7 \text{ eV})$ state, the crossover region $(t_{\perp}^{c} = 1.05 \text{ eV})$, and the antiferromagnetically ordered MO ($t_{\perp}^{c} = 1.4 \text{ eV}$) phase. One may see from this figure that there is no net magnetization in the limit of very small t_b (< 0.1 eV), which corresponds to nearly isolated dimers as for $t_b = 0.1$ eV the single-particle gap of the *d*-orbital opens up. In the region of intermediate t_b , both the DE and MO solutions have nearly maximal $\langle S_{dim}^z \rangle$, 3/2 and 1/2, respectively. It is interesting that the t_b range of the nonzero magnetization is smallest for $t_{\perp}^{c} = 1.05$ eV corresponding to the HYB state of the crossover region. Here, the fluctuations between the dimers are enhanced by the competing MO and DE states and suppress long-range magnetic order.

It is useful to compare the upper and lower panels of Fig. 8, where the square of the total spin, $\langle S_{\rm dim}^2 \rangle$, is plotted for the same values of t_{\perp}^c . While $\langle S_{\rm dim}^z \rangle$ measures ordered spin, $\langle S_{\rm dim}^2 \rangle$ simply tells us what is the total spin of a configuration. The squares of the total spin [= S(S + 1)] for the DE and MO states in the atomic limit and at T = 0 are 3.75 and 0.75. Comparing Fig. 8 (top) and Fig. 8 (bottom), we first make sure that two transitions for the MO solution at $t_b = 0.1$ eV and 0.4 are due to a transition to the paramagnetic state, and the total spin per dimer is still well defined even for $t_b < 0.1$ eV and $t_b > 0.4$ eV. $\langle S_{\rm dim}^2 \rangle$ for both the MO and DE solutions depend on t_b only weakly. Thus, the formation of spin order is not due to local moment formation, but rather to suppression of the fluctuations.

Second, we see from Fig. 8 that an increase of t_b suppresses the DE state and increases the MO contribution in the crossover region (i.e., for $t_1^c = 1.05 \text{ eV}$). Using corresponding

values of $\langle S_{\rm dim}^2 \rangle$ for these two states, one may estimate their contributions to the wave function for arbitrary t_b . If for $t_b = 0.1$ eV there is roughly a 50/50 ratio between the weights of the DE and MO states, then for $t_b = 0.35$ we have ~90% of the MO and only 10% of the DE state. This can be rationalized by treating it with a correction to the total energy of both states due to hopping within the Bethe lattice, i.e., t_b , using the perturbation theory.

We assume that the intradimer hopping t_{\perp}^{c} , Hubbard U, and Hund's exchange J are leading parameters. Then the second-order correction to the total energy due to t_b would be $\sim -t_h^2/\delta\varepsilon$, where $\delta\varepsilon$ is the energy difference between excited and ground states. Clearly, the excited energy for the MO state will be much smaller than for the DE configuration, since the transfer of the d electrons between two antiferromagnetically coupled dimers in the MO state does not cost Hund's exchange energy [there are two electrons with opposite spin projections on the bonding c orbitals in the MO state, and when transferring d electrons between dimers we keep the number of electrons (per site) with the same spin]. Neglecting spin-flip and pair-hopping terms for the sake of simplicity, we get $\delta \varepsilon_{\rm MO} \sim U/2$. The transfer of the c electrons in the MO configuration is rather unfavorable, since it is possible only to antibonding orbitals. In contrast, one may transfer the celectrons in the DE state, which gives $\delta \varepsilon_{\text{DE}} \sim U/2 + J$, while an electron hopping via d orbitals results in $\delta \varepsilon_{\rm DE} \sim U +$ J/2—both much larger than the energy of the excited state in the MO configuration. This explains the gradual increase of the MO weight and the decrease of $\langle S_{dim}^2 \rangle$ in the crossover region with increasing t_b .

Third, there is a rather nontrivial evolution of both $\langle S_{dim}^z \rangle$ and $\langle S_{dim}^2 \rangle$ with t_b for $t_{\perp}^c = 0.7$ eV (i.e., nominally for the DE solution). In particular, for large t_b (≥ 0.4 eV) we observe the coexistence of two regimes: a conventional insulating DE solution with long-range magnetic ordering and $\langle S_{dim}^z \rangle = 3/2$, and a metallic and paramagnetic solution with suppressed $\langle S_{dim}^2 \rangle \approx 2$. The value of $\langle S_{dim}^2 \rangle$ for the second solution is close to what one may expect for the spin triplet.

Figure 9 shows the local density of states in the crossover region with an increase of t_b . One can see that for $t_b =$



FIG. 9. The dimer density of states for different Bethe hoppings t_b at T = 0.01 and $t_{\perp}^c = 1.05$ obtained via the stochastic optimization method [64,65]. Inset: the corresponding dimer magnetizations $\langle S_{dim}^z \rangle$.



FIG. 10. Imaginary part of the self-energy (solid) on Matsubara frequencies together with a power-law low-frequency fit (dotted) for different t_b , $t_{\perp}^c = 1.05$ eV and T = 0.01 eV. The fitted power is shown in the inset.

0.4 eV our system is in a metallic state, characterized by a large quasiparticle peak. Reducing t_b , we arrive at the broken spin-symmetry situation, where the peak becomes less coherent (the width at half-maximum height decreases), and then eventually we observe the formation of a pseudogap for $t_b = 0.33$ eV, which corresponds to a sudden increase in the magnetization. The maximum of $\langle S_{dim}^z \rangle$ is exceeded at $t_b \approx 0.24$ eV, where the pseudogap transforms to a real gap. A further decrease of t_b results in a transition to the paramagnetic state, which is accompanied by a modification of the spectral function. In particular, for $t_b = 0.24$ eV there is a sharp edge for electron excitations, while for $t_b = 0.1$ eV we have a sharp edge for hole excitations.

In Fig. 10 we focus on the incoherent metal with local moments of $0.33 < t_b < 0.4$ eV, and we identify the underlying mechanism of spin-freezing, which has been found in a previous single-site DMFT multiorbital study [66-68] and is a property of Hund's metals. It is a non-Fermi-liquid described by the constant spin-spin correlation function at long times and a strong enhancement of the local susceptibility [69]. It has been pointed out that the ground-state degeneracy seems to be an important component of spin-freezing. We can confirm that as our model shows the feature only in proximity to the ground-state crossover. The self-energy of that phase is non-Fermi-liquid-like, but still the system is metallic in the freezing process. Since electrons scatter at the frozen moments, the self-energy shows power-law behavior $\Sigma(i\omega_n \rightarrow$ 0) = $(i\omega_n)^{\alpha}$ with $\alpha < 1$ and can be fit with a quantum critical crossover function,

$$-\mathrm{Im}\Sigma(\omega_n)/t = C + A(\omega_n/t)^{\alpha}.$$
 (12)

A minimal exponent of $\alpha = 0.5$ was found at the critical point in the original study [66]. At the magnetization jump, i.e., $t_b =$ 0.34 eV, we also find a drop in α leading to a value $\alpha \approx 0.5$. The crossover region we found is very similar to that of studies that investigated a high-spin/low-spin transition driven by a crystal field [70]. In that context, one can also expect to find an instability toward spin-orbital ordering, i.e., an excitonic insulator [71]. The latter is suppressed as we do not consider interorbital hybridization in our numerical calculations.



FIG. 11. Partial DOSes in BA representation as a function of intradimer hopping, t_{\perp}^c , and Bethe hopping, t_b , parameters (rows and columns, respectively). The fixed parameters are: U = 4.5 eV, J = 0.7 eV, $t_{\perp}^d = 0.2 \text{ eV}$, T = 0.01 eV and paramagnetism is enforced. Obtained by the Maximum Entropy method.

B. Spectral properties

Even though a paramagnetic solution may only be metastable, one can enforce it to enhance scattering processes and thereby also amplify the electronic correlations. Thus, the paramagnetic solution is a tool to investigate ordering mechanisms and quasiparticles, whose diverging scattering rates eventually lead to a symmetry-broken solution.

Figure 11 presents partial DOSs in the BA representation for various values of the intradimer hopping of the *c* electrons, t_{\perp}^{c} , and the Bethe hopping, t_{b} , which controls the bandwidth of noninteracting states. The most comprehensible is the MO state with $t_{\perp}^{c} = 1.4 \text{ eV}$ and $t_{b} = 0.1 \text{ eV}$ (the lower-right part of Fig. 11). At these values of parameters, the bonding and antibonding c orbitals are almost completely occupied $(n_{(c,B)} = 1.78)$ and empty $(n_{(c,A)} = 0.2)$, respectively, and can be integrated out. Therefore, one deals with a single electron in the double-band model with crystal-field splitting defined by $2t_{\perp}^d = 0.4$ eV [72]. Such a large value of the crystal-field splitting in comparison to the bandwidth, $W = 4t_b = 0.4 \text{ eV}$, results in a further lifting of the degeneracy, and finally one has a conventional Mott-Hubbard single-band insulator, which occurs for the (d, B) orbital. By increasing t_b (from bottom to top, right column of Fig. 11), this insulating state is determined to be a single-band metal at $t_b = 0.2$ eV and a three-band metal at $t_b = 0.4$ eV. The latter happens due to such factors as the bandwidth increase of (c, B) and (d, A)states and its touching of the Fermi level (see the lower panel of Fig. 12). One should note that the (c, A) state remains empty at all values of the Bethe hopping. This picture of the insulator-to-metal transition is confirmed by the renormalized quasiparticle bands, $(\tilde{\epsilon}, W_{\tilde{\epsilon}})$, and the quasiparticle residue



FIG. 12. Quasiparticle residues Z and renormalized quasiparticle bands ($\tilde{\epsilon}$, $W_{\tilde{\epsilon}}$) as a function of the Bethe hopping t_b . The renormalized quasiparticle bands vanish if $Z \approx 0$. The shaded area depicts insulating phases determined by analytical continuation (maximum entropy method). Paramagnetism is enforced, T = 0.01.

Z, shown in Fig. 12 (lower panel). The energetic order of the bands is determined by t_{loc} , i.e., bonding orbitals are lower than antibonding orbitals, and the *c* orbital is lower than the *d* orbital. At small values of t_b , all renormalized bands except (*d*, *B*) are placed far from the Fermi level. The corresponding quasiparticle residue, $Z_{(d,B)}$, is close to zero. At $t_b > 0.2 \text{ eV}$, $Z_{(d,B)}$ is increased and the system becomes a correlated metal.

The spectral function of the DE state (lower-left part of Fig. 11) is also consistent with the atomic picture. The (d, B) and (d, A) states are occupied with one electron per spin orbital, $n_{(d,B)} = n_{(d,A)} = 1$, which is equivalent to a singleelectron occupation of site-centered orbitals. The remaining electron is on the (c, B) state (the antibonding part is completely empty). The Coulomb interaction leads to a gap opening for these states in different ways. Although the QP bands for all these orbitals are away from the Fermi level (see the upper panel of Fig. 12), the quasiparticle residues behave differently for (c, B) and (d, B), (d, A) states. $Z_{(c,B)}$ goes to zero at small values of t_b , while for larger t_b they have finite values. This results in the orbital selective Mott transition at increased values of $t_b = 0.3$ eV. A further increase of t_b closes the gap in the (c, B) spectral function. One should note that the overall quasiparticle residues of the DE solution are smaller than its MO counterparts, indicating stronger electronic correlations in this regime.

The hybrid state, $t_{\perp}^{c} = 1.05$ eV, has an even stronger quasiparticle renormalization than the DE state for all orbitals. The (c, B), (d, B), and (d, A) quasiparticle residues go to zero approximately at $t_{b} = 0.25$ eV. This is related to the quantum critical region, which we have discussed in the context of Fig. 4. It results in the metal-to-insulator transition and gap opening in the corresponding spectral functions; see Fig. 11.

It is interesting to note that a critical value of the Bethe hopping, t_b^* , decreases with the increase of the intradimer hopping parameter t_{\perp}^c . In the MO case, there is only one active electron, which leads to an increased value of the critical Coulomb interaction for the multiband model [31], which also corresponds to a decreased value of t_b . With the decrease of the intradimer hopping, t_{\perp}^c , all of the electrons have to be regarded for a description of the model. Therefore, the effective number of electrons is increased, which results in a decreased value of the Coulomb interaction parameter, or an increased value of the critical Bethe lattice hopping, t_b .

V. CONCLUSIONS

The electronic and magnetic properties of multiorbital dimers in solids have been studied using a cluster extension of the DMFT. We used the model consisting of two orbitals per site constituting a dimer with specific filling of 3/8 electrons per site (three per dimer). The parameter range of the model was motivated by the density-functional calculations for two large classes of materials with the general formula Ba₃MeTM₂O₉ (face sharing of TMO₆ octahedra) and $Re_5TM_2O_{12}$ (edge sharing of TMO_6 octahedra). We argue that already such a minimal model can be used to describe various physical phenomena observed in real materials with dimerized crystal structure. For example, the ratio of hopping parameters of strongly overlapping orbitals (t_{\perp}^{c}) and Hund's rule exchange (J_H) may strongly affect the value of the observed magnetic moments. These effects were indeed observed in $Ba_3MeTM_2O_9$ (through modification of the hopping parameters by lattice distortions induced by different Me ions) [52,73].

In our simplistic two-orbital model, \tilde{t}_{\perp}^c defines a critical hopping parameter, which separates the regions where the high-spin, S = 3/2, or low-spin, S = 1/2, states are realized. Close to this critical parameter, the lattice of such dimers is in a strongly correlated state, where the long-range antiferromagnetic order is substantially suppressed. This fact can be important in connection with recent findings on the formation of the spin liquid state in Ba₃ZnRu₂O₉ [61,63] and Ba₃ZnIr₂O₉ [74]. This correlated state exhibits electrons with strongly renormalized masses in both orbitals (*c* and *d*) and separates orbital decoupling from spin decoupling. Both decouplings originate from the dimer–ground-state crossover of \tilde{t}_{\perp}^c . Furthermore, the long-range spin order is more sensitive to temperature fluctuations than orbital order, and that renders the MO state more stable against temperature fluctuations. Correlation effects could be induced by the change of the electron's itineracy within the Bethe planes (t_b) as it promotes quantum fluctuations from the lattice on the dimers. We explain the larger stability of the AFM order in the MO configuration with the exchange energy $t_b^2/(U/2)$ of the *d* electrons as opposed to the exchange energy of the DE state, i.e., $t_b^2/(U/2 + J)$ for the *c* electrons. The competition of the DE and MO states causes the formation of a new hybrid state, which exhibits qualitatively new features, e.g., an incoherent metallic spin-polarized state with a non-Fermi-liquid selfenergy corresponding to the spin-freezing phenomenon.

We used the cluster DMFT to study the correlationenhanced enforced paramagnetic calculations that unveiled the orbital selectiveness of the DE state—typical for Hund's physics. The MO state shows correlation features, but the metal-to-insulator transition is of Peierls-type instead. Finally, the hybrid state has a metal-insulator transition involving the renormalization of all d and the bonding c states around PHYSICAL REVIEW B 99, 045115 (2019)

the same value of the Bethe lattice hopping, emphasizing the large impact of competing interactions on the electronic correlations.

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