

Magnetic phase diagram of a five-orbital Hubbard model in the real-space Hartree-Fock approximation varying the electronic density

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Using the real-space Hartree-Fock approximation, the magnetic phase diagram of a five-orbital Hubbard model for the iron-based superconductors is studied varying the electronic density n in the range from five to seven electrons per transition metal atom. The Hubbard interaction U is also varied, at a fixed Hund coupling $J/U = 0.25$. Several qualitative trends and a variety of competing magnetic states are observed. At $n = 5$, a robust G-type antiferromagnetic insulator is found, in agreement with experimental results for BaMn_2As_2 . As n increases away from 5, magnetic states with an increasing number of nearest-neighbors ferromagnetic links become energetically stable. This includes the well-known C-type antiferromagnetic state at $n = 6$, the E-phase known to exist in FeTe, and also a variety of novel states not found yet experimentally, some of them involving blocks of ferromagnetically oriented spins. Regions of phase separation, as in Mn oxides, have also been detected. Comparison to previous theoretical investigations indicate that these qualitative trends may be generic characteristics of phase diagrams of multi-orbital Hubbard models.

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I. INTRODUCTION

The study of iron-based high critical temperature superconductors continues attracting the attention of the condensed matter community [1]. Early theoretical investigations suggested a relatively simple picture of the magnetic and superconducting properties as arising from weak-coupling Fermi surface nesting effects. However, recent experimental and theoretical studies have unveiled a variety of compounds and chemical compositions that display a more complex physics where intermediate-range electronic repulsion effects cannot be neglected [2]. In particular, there are materials with no Fermi surface nesting that nevertheless become superconducting, and there are compounds with a very large magnetic moment in the ground state that do not fit into the weak-coupling picture [3]. Moreover, at room temperature clear indications of local magnetic moments exist [4], incompatible with weak-coupling scenarios where the formation of moments and the long-range order develop simultaneously upon cooling.

For these reasons, a more serious consideration of the effects of the Hubbard on-site repulsion U and on-site Hund coupling J is needed. While this task is in principle difficult due to the scarcity of unbiased many-body techniques that can handle a multiorbital Hubbard model, the use of mean-field approximations can at least unveil qualitative tendencies in phase diagrams and the characteristics of the dominant states. In fact, the Hartree and Hartree-Fock approximations have been recently successfully used by our group [5,6] and others [7,8] to study the dominant states in the presence of the $\sqrt{5} \times \sqrt{5}$ distribution of iron vacancies that exists in some selenides [9] and also for the case of two-leg ladder geometries [10]. In all these cases, the phase diagrams involve several different magnetic states and for this reason phase competition is anticipated to occur.

Also in more recent times, a novel avenue of research motivated by the iron-based superconductors has been expanding. It consists of replacing entirely Fe by another $3d$ transition element such as Mn or Co. The average electronic population

of these elements in the new compounds is different from that of iron, but the crystal structures are similar. Thus, as a first approximation this chemical substitution effectively amounts to exploring the effects of varying substantially the electronic density away from the original density of the iron-based materials. For example, in the case of the 100% replacement of Fe by Mn, the compound BaMn_2As_2 was found to develop a G-type antiferromagnetic (AFM) state with staggered spin order, a Néel temperature of 625 K, and a magnetic moment of $3.88\mu_B/\text{Mn}$ at low temperatures [11]. The G-type AFM order is very robust, as recent investigations of $\text{Ba}_{1-x}\text{K}_x\text{Mn}_2\text{As}_2$ have unveiled [12]. This state emerges naturally from the population $n = 5$ at each Mn atom, namely one electron per $3d$ orbital. In the other limit of full Co substitution for Fe, such as for the case of SrCo_2As_2 , the material has a complex Fermi surface and there are tendencies to magnetic order in the form of spin fluctuations in the C-type channel [13], although *ab initio* calculations suggest that a ferromagnetic instability can also occur (for a list of recent references see Ref. [13]). Note that ferromagnetic tendencies have been reported for LaCoOX ($X = \text{P,As}$) as well [14].

These interesting recent studies motivated the model Hamiltonian investigations reported here, where the electronic density per transition metal atom n is allowed to vary over a wide range, centered at the $n = 6$ value corresponding to pnictides and selenides where the ground state is a C-type antiferromagnet. In previous efforts, the G-type AFM state at $n = 5$ was already reported [15,16]. Other investigations assigned a crucial role to the $n = 5$ G-type AFM state to understand the physics of the $n = 6$ limit [17]. In some studies the superconducting state of pnictides was visualized as emerging from the $n = 5$ G-type insulator [18] as opposed to being induced from the C-type antiferromagnetic metal of $n = 6$. All these previous efforts provided additional motivation for our studies. Thus, drastically altering the electronic concentration far away from $n = 6$ may lead to interesting perspectives to understand the pnictide and selenide superconductors.

The main result of this publication is the phase diagram of a five-orbital Hubbard model in the real-space Hartree-Fock approximation, varying U at fixed J/U and, more importantly, the electronic density from $n = 5$ to 7. Three main tendencies have been identified. (i) There are multiple magnetic states competing for space in the phase diagram. This is indicative of a complex landscape of free energies. The results are compatible with several states already unveiled experimentally for different compounds [1,3], and with other recent mean-field studies as well [15,16], but there are phases in the present theoretical phase diagram that are novel and worth searching for experimentally. (ii) The general tendency in the evolution of the magnetic states with increasing n is to evolve from the G-AFM state at $n = 5$ to states with more ferromagnetic links as $n = 7$ is approached, particularly at robust J/U . (iii) There are regions in the phase diagram that present the phenomenon of phase separation. This phenomenon was widely discussed before in manganites [19–22] and in cuprates [23], but it was only recently that this effect has been mentioned in the context of the iron-based superconductors; their consequences are still unclear. Our present conclusions are compatible with theoretical results by other groups that also reported phase separation tendencies [15,24,25], and also with previous investigations by our group that revealed the presence of stripes in some models [6].

The organization of the results is the following. In Sec. II, the model and details of the calculations are explained. In Sec. III, the main results and phase diagram are presented. Sections IV and V include the results addressing the density-of-states and phase separation tendencies, respectively. Finally, conclusions are presented in Sec. VI.

II. MODEL

In this effort a five-orbital Hubbard model will be used, with emphasis on the magnetic states that are obtained by varying couplings and the electronic density n . Superconducting tendencies will not be investigated in the present study. The model used is exclusively based on electrons that are located in the Fe $3d$ orbitals, widely believed to be the most relevant orbitals at the Fermi surface for the pnictides and selenides. Moreover, recent angle-resolved photoemission studies of BaCo_2As_2 compared to BaFe_2As_2 suggested that a nearly rigid shift of the Fermi level accounts for the complete substitution of Co for Fe [26], thus further motivating our use of a single model with varying chemical potential to study a variety of materials.

The model includes a tight-binding term defined as

$$H_{\text{TB}} = \sum_{\langle i,j \rangle} \sum_{\alpha,\beta,\sigma} t_{ij}^{\alpha\beta} (c_{i,\alpha,\sigma}^\dagger c_{j,\beta,\sigma} + \text{H.c.}), \quad (1)$$

where $c_{i,\alpha,\sigma}^\dagger$ creates an electron with spin σ at the orbital α of the transition metal site \mathbf{i} (a square lattice is used) and $t_{ij}^{\alpha\beta}$ refers to the tunneling amplitude of an electron hopping from orbital α at site \mathbf{i} to orbital β at site \mathbf{j} . The Coulombic interacting portion of the five-orbital Hubbard Hamiltonian is standard

and given by

$$\begin{aligned} H_{\text{int}} = & U \sum_{i,\alpha} n_{i,\alpha,\uparrow} n_{i,\alpha,\downarrow} + (U' - J/2) \sum_{i,\alpha < \beta} n_{i,\alpha} n_{i,\beta} \\ & - 2J \sum_{i,\alpha < \beta} \mathbf{S}_{i,\alpha} \cdot \mathbf{S}_{i,\beta} \\ & + J \sum_{i,\alpha < \beta} (d_{i,\alpha,\uparrow}^\dagger d_{i,\alpha,\downarrow}^\dagger d_{i,\beta,\downarrow} d_{i,\beta,\uparrow} + \text{H.c.}), \quad (2) \end{aligned}$$

where α, β denote the five $3d$ orbitals with a label convention defined in Table III below, $\mathbf{S}_{i,\alpha}$ ($n_{i,\alpha}$) is the spin (electronic density) of orbital α at site \mathbf{i} , and the relation $U' = U - 2J$ between the Kanamori parameters has been used. The first two terms give the energy cost of having two electrons located in the same orbital or in different orbitals, both at the same site, respectively. The third term is the Hund's coupling that favors the ferromagnetic (FM) alignment of the spins in different orbitals at the same lattice site. The "pair-hopping" is the fourth term and its coupling is equal to J by symmetry.

With regards to the tight-binding parameters, the set of hoppings used in the present effort is taken from Ref. [27], which provides a Fermi surface that compares well with experiments and band structure calculations for the pnictides. The actual hoppings employed here are provided in Table III of the Appendix. The approximate bandwidth W of the tight-binding hopping term is 4.7 eV, and the ratio U/W should be used to judge whether the phases of interest are or not, e.g., in the strong-coupling regime where $U/W \sim 1$. A ratio $U/W \sim 0.5$ is more typical for the location of the experimentally relevant phases based on previous Hartree-Fock investigations [2,6], signaling an intermediate-coupling regime. However, note that the quantum fluctuations not considered in mean-field studies will tend to increase the critical values of U/W .

It is important to remark that a different set of tight-binding parameters was provided in Ref. [28] (see their Tables VII and VIII for nearest- and next-nearest neighbors Fe-Fe hopping amplitudes), and in other publications as well. In the approach of the authors of Ref. [28] the Fe-Fe hoppings are deduced in the strong-coupling limit from a more fundamental Hubbard model involving both the Fe and As atoms. Alternatively, in Ref. [27] the Fe-Fe hoppings were simply chosen to reproduce accurately the band structure calculation results at the Fermi surface. Both are valid approaches, and our choice of one set over the other is merely practical (in previous publications by our group the set found in Ref. [27] had already been used; repeating the same set of hoppings allowed us a better comparison and cross-checks of previous and new results). However, note that the overall conclusions of our study (such as the transition from G-type AFM to stronger FM tendencies varying the electronic density from 5.0 to 7.0) are sufficiently generic that they are likely to be valid even if another set of hopping amplitudes are used, although certainly the details and actual critical couplings will change from set to set.

To study the ground-state properties of the multi-orbital Hubbard model, the Hartree-Fock (HF) approximation will be applied to the Coulombic interaction. The HF Hamiltonian is solved by minimizing the energy via a numerical real-space self-consistent iterative process that was widely discussed in previous efforts [6,9,10]. All the HF expectation values are

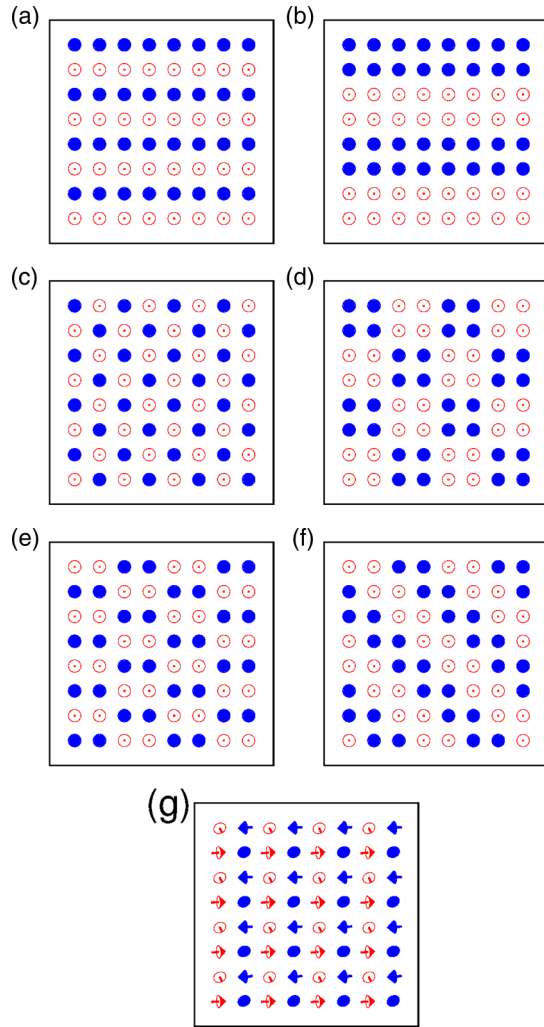


FIG. 1. (Color online) Magnetic states observed in the phase diagram of the five-orbital Hubbard model used in this study, treated in the Hartree-Fock (HF) approximation. These magnetic states are named as follows: (a) C, (b) DC, (c) G, (d) Block, (e) GC, (f) E, and (g) Flux.

initially assumed independent from site to site, which allows the system to select spontaneously the state that minimizes the HF energy, reducing the bias into the calculations. In the self-consistent iterative process, initially all the HF expectation values are set to random numbers, physically corresponding to random initial states. The iterative process converges to states that resemble uniformly ordered states, albeit still with some deviations that are difficult to remove in the (slow) iterative process. Inspired by the results obtained with random starts, then fully ordered starting configurations are also used as starting points for comparison. At the end, the ground states are selected by comparing the final energies after convergence. In Fig. 1 the set of relevant states that appeared spontaneously in the real-space energy minimization used in the present effort can be found. All the numerical results are obtained using a real-space 8×8 square lattice with periodic boundary conditions. The criteria of convergence is set so that the changes of the individual HF expectation values are less than 10^{-4} . Under these criteria, the typical number of iterations is

from 500 to 1000 if random initial states are used, and from 50 to 200 if the starting configurations correspond to ordered states as those in Fig. 1.

III. MAIN RESULTS

A. Phase diagram

The effort described in this publication was computationally intense since there were two parameters to change (U and n ; J/U was fixed to 0.25, a value considered realistic from previous investigations [6]) and the real-space HF process is typically characterized by a slow convergence in the iterative process. The main result of this study is summarized in the HF phase diagram of the five-orbital Hubbard model, varying the on-site coupling U and electronic density n , shown in Fig. 2.

Let us now describe in detail the results. Starting at $n = 5$, i.e., five electrons for the five $3d$ transition metal orbitals, the state has a strong tendency to form a G-type AFM state. This is to be expected given the electronic population, and this result is in excellent agreement with experiments [11] for BaMn_2As_2 and with previous theoretical efforts [15,17,18]. The robustness of the G-AFM state suggests that using other hoppings' amplitudes, such as those more quantitatively adequate to describe BaMn_2As_2 , will likely lead to similar conclusions.

The G-AFM state has individual spins that are antiferromagnetically coupled to their four neighbors. As n increases,

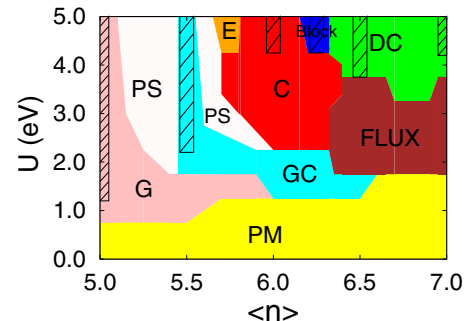


FIG. 2. (Color online) Phase diagram of the five-orbital Hubbard model varying the on-site same-orbital repulsion U and the electronic density n (number of electrons per transition metal site). The Hund coupling was fixed to $J/U = 0.25$. The notation for the many states was explained in Fig. 1. Light pink areas correspond to “phase separation” (PS) regions where the energy vs. n curves have a negative curvature (as described later in the paper). In practice, at least a vestige of magnetic order is typically found in the numerical process even for very small values of U . However, previous experience indicates that this is likely a “paramagnetic” (PM) state since it is smoothly connected to the $U = 0$ limit. Thus, in practice the PM state is defined as the state where the order parameter m , of any kind, is smaller than a cutoff chosen as 4% of the saturated value for the same state at other densities or couplings. Since the order parameters often raise steeply at the critical U that separates the PM from magnetic states, then selecting other cutoffs give similar results. Note also that the banded regions at electronic densities 5.0, 5.5, 6.0, 6.5, and 7.0, they signal an insulating state based on the presence of a gap in the density of states (for details see Sec. IV).

growing tendencies toward developing more ferromagnetic links are observed. In fact, the novel “GC” state (see Fig. 1) is stabilized next when increasing n away from 5, and this state has three AFM links and one FM link. This state can be considered as a combination of the G-AFM and C-AFM states, thus the notation GC. Its dominant wave vector is $(\pi/2, \pi)$, and the state breaks rotational invariance between the two axes x and y , as the C-AFM state does, but also has a staggered order as the G-AFM state does, although involving 2×1 blocks. Thus, with hindsight it is not surprising to find this GC state stabilized in between the G and C states. A somewhat surprising result is that the area of stability of the GC state also includes a region of weak U coupling at $n = 6$ where it is widely believed that the C-type AFM state should dominate. This C-AFM state indeed is stable in increasing U but not at very weak coupling. Considering that recent Monte Carlo computational studies including lattice distortions and using three orbitals in the context of a spin-fermion model do favor the C-AFM state [29,30], then probably the absence of lattice degrees of freedom in the present effort may lead to a spurious larger region of stability of the GC state that includes portions of the $n = 6$ axis. Thus, it should be noted that the region of true stability of the GC-AFM state may be smaller than the HF approximation suggests, particularly after lattice effects and quantum fluctuations are incorporated. In general, only qualitative trends are expected to be robust in the present study but not detailed quantitative aspects. The prediction arising from this effort is that it would not be surprising to find the GC state stabilized in materials where the relevant electronic density is approximately $n = 5.5$.

As already mentioned, centered at $n = 6$ and for intermediate and large U the C-AFM state is stabilized, in agreement with many experiments and several other theoretical studies [1–3]. Since this state has been widely discussed before in many contexts, there is no need to repeat those discussions and the focus here now shifts to values of n larger than 6. In this regime, several exotic states are stabilized in the HF approximation. One of these novel states is the “Flux” state, shown in Fig. 1(g). Note that this state is not collinear. A similar state has been discussed before in the context of two-orbital Hubbard models [31], and in small regions of the phase diagram of a five-orbital Hubbard model defined on two-leg ladders [10]. To our knowledge this Flux state has not appeared in previous studies when using two-dimensional geometries and five-orbital models, and it has not been observed experimentally yet.

Another exotic and novel state stabilized at n larger than 6 is the double-C, “DC”, state shown in Fig. 1(b). The notation double C is in reference to the doubled period in one direction with respect to the well-known C state. This DC state has a spin structure factor peaked at $(0, \pi/2)$ or $(\pi/2, 0)$ depending on the lattice instabilities that may appear in a real system. This DC state is representative of the previously mentioned growing ferromagnetic tendencies with increasing n since each spin has three (one) ferromagnetically (antiferromagnetically) aligned neighbors. It is conceivable that with further increasing n and/or U and J , a fully ferromagnetic state can be stabilized, as already observed in previous HF approximation studies in other contexts such as ladders and with iron vacancies [9,10]. Note also that from

our results near $n = 7$ (Fig. 2) there are no indications that the C-type AFM state can become stable at such large electronic densities, at least at the level of ground states. Thus, the recent inelastic neutron scattering results [13] for SrCo_2As_2 reporting C-type fluctuations remain paradoxical, and deserve further studies.

In addition to the dominant G, GC, C, Flux, and DC states, there are two small regions where two exotic states, the E and Block states, are stabilized. These states need a robust U to become stable (i.e., $U/W \sim 1$ is needed for their stability) and they have been mentioned in other contexts before. For instance, the Block-AFM state is made of 2×2 FM blocks that are coupled antiferromagnetically. This state was proposed to be the ground state of KFe_2Se_2 in previous theoretical investigations [32]. A similar “Block” structure has been unveiled experimentally and theoretically in materials with iron vacancies [3,9] and also in selenides with two-leg ladder geometries [10]. These Block states have individual spins with two antiferromagnetic links and two ferromagnetic links, thus their location next to the C-AFM state is reasonable since they share this same property. This line of reasoning is mainly of relevance for discussions involving localized spins, as they occur at robust U . It is gratifying that the Block-AFM appears spontaneously in our calculations without the need for introducing lattice distortions.

The other exotic state stabilized in a small region at robust U/W is the “E” state shown in Fig. 1(f). This state has a peak in the spin structure factor located at $(\pi/2, \pi/2)$, which is compatible with experimental neutron scattering results [33] for FeTe. Historically, the E phase was reported initially in investigations of manganites [34]. The existence of the E phase is also compatible with more recent theoretical studies that used the spin-fermion model, involving a mixture of localized and itinerant degrees of freedom with two active orbitals [35]. The E state was also reported by another group in previous investigations of a five-orbital Hubbard model, using momentum-space mean-field and Heisenberg techniques and a different set of hopping amplitudes [15]. Note that in the previous publication Ref. [15] the E state was actually called the DS state. Here, the historical notation that started with the manganites is used and the state is called E. Note also that recent investigations suggest ferro-orbital order and a bond-order wave in $\text{Fe}_{1.09}\text{Te}$ in the regime of the E phase [36], implying that the region where the E state is here reported to be stable should deserve further study.

In summary, the four states G, C, E, and Block have been observed before in different materials of the family of iron-based superconductors and in other theoretical studies. The possible stability of the three states GC, Flux, and DC, are original predictions of the present study. Note that the mean-field approximation used here tends to exaggerate the presence of magnetic order. While the predictions are expected to be reasonable at special density fractions such as $n = 5.0, 5.5, 6.0, \dots$, the phase diagram unveiled here at intermediate values of n is at best indicative of qualitative tendencies that may exist, perhaps only in the form of short-range correlations. Also note that superconducting states have not been proposed in this mean-field study, so the focus is only on magnetic order (and its concomitant orbital order, as described below).

TABLE I. Magnetic moments of the seven competing states at selected couplings and densities. The details are as follows: C state ($U = 3.0, n = 6.0$); Flux state ($U = 3.0, n = 6.5$); G state ($U = 3.0, n = 5.0$); GC state ($U = 3.0, n = 5.5$); E state ($U = 5.0, n = 5.75$); Block state ($U = 5.0, n = 6.25$); DC state ($U = 5.0, n = 6.75$). The * indicates phases where the magnetic moment is not the same at each site. Typically, there are four sites that repeat themselves in most of the cases, but sometimes the periodicity involves two sites or eight sites. The numbers used for these states in the present table are their average values.

	xz	yz	x^2-y^2	xy	z^2	Total
C	0.9235	0.5426	0.5678	0.9499	0.7451	3.7289
Flux*	0.6094	0.6735	0.4812	0.8372	0.5693	3.1692
G	0.9475	0.9475	0.9242	0.9609	0.9682	4.7481
GC	0.9362	0.7853	0.7027	0.9540	0.8625	4.2407
E*	0.8589	0.8602	0.6063	0.9843	0.8702	4.1799
Block	0.8296	0.8296	0.6559	0.9573	0.3944	3.6667
DC	0.7632	0.6043	0.5470	0.9102	0.3611	3.1858

B. Magnetic order parameters

In Table I, characteristic magnetic moments of the seven phases found in Fig. 2 are provided at representative couplings and densities. The values shown tend to indicate a robust magnetic moment. However, in the phases that are in contact with the weak-coupling PM state in the phase diagram (i.e., the G, GC, and Flux states), there is a region of rapid change in the value of the magnetic moment when magnetism develops, as shown in Figs. 3 and 4. Thus, values of the magnetic moments weaker than those in Table I are also possible for some of the phases.

In Fig. 3, the order parameter at $n = 6$ is explicitly shown, varying U . While the C-AFM state that is stabilized at intermediate and large U is to be expected, the presence of the GC-AFM state in the weak-coupling regime is a surprise, as already discussed. In view of the many approximations involved in arriving to this state, it would be premature to claim that the GC state should be stable in portions of the phase diagram corresponding to the Fe-based compounds, but its presence in the phase diagram can be considered as indicative of a competition between many magnetic states. In practice, other degrees of freedom, such as the lattice, are probably

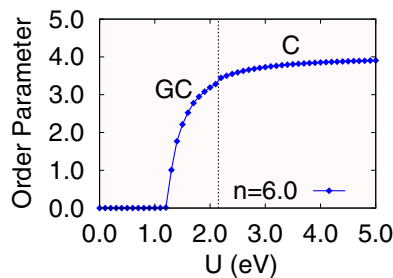


FIG. 3. (Color online) Hartree-Fock order parameters (Bohr magneton units) vs. U at density $n = 6.0$ and $J/U = 0.25$. The magnetic states GC and C have been presented in Fig. 1. The bandwidth W is 4.7 eV.

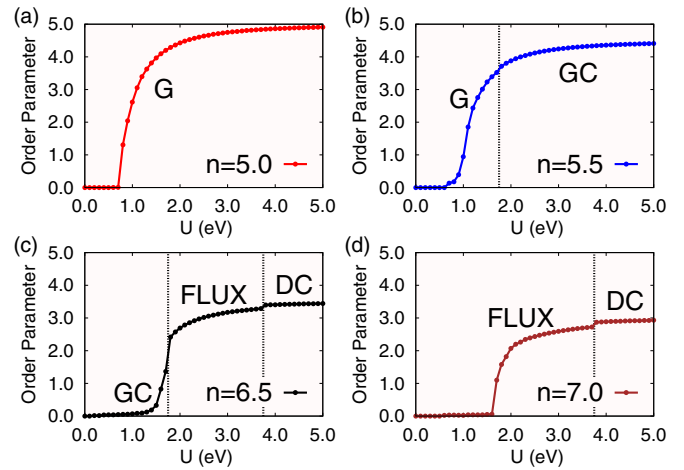


FIG. 4. (Color online) Hartree-Fock order parameters (Bohr magneton units) vs. U at $J/U = 0.25$ and several electronic densities: (a) $n = 5.0$; (b) $n = 5.5$; (c) $n = 6.5$; (d) $n = 7.0$. All the states indicated are shown explicitly in Fig. 1.

crucial in deciding which state is the most stable in an actual compound.

Similar results were obtained at other electronic densities, as shown in Fig. 4. At $n = 5$, the G-AFM state is clearly dominant, with an order parameter (in units of the Bohr magneton) that tends to the maximum value 5 as U grows. At the other electronic densities shown, there is always phase competition between two or three states, and this phase competition may preclude the order parameters from reaching their maximum value, at least in the range studied. The transitions between different magnetic states are of first order but the jumps in the order parameters tend to be rather small and in some cases the curves look almost continuous.

C. Orbital composition

The orbital compositions of the seven states unveiled in the phase diagram of Fig. 2 are given in Table II. From the perspective of these occupations, the G-AFM state has clear indications of being an insulator since all the five orbitals are approximately equally populated with one electron per orbital. On the other hand, most of the orbitals of the other six states have a population substantially different from one, potentially giving rise to a metallic state (perhaps with coexisting itinerant and localized degrees of freedom). However, the Block-AFM state should be insulating due to the peculiar spin geometry of the state that renders difficult for electrons to transition from block to block while keeping the same spin orientation.

IV. DENSITY OF STATES

To investigate the metallic versus insulating characteristics of the states in the phase diagram, the density of states have been analyzed. Results are shown in Fig. 5. The situation for the G-AFM state is clear: the state is an insulator with a robust gap. The Block-AFM state involving spin blocks is also insulating, as discussed above. This can be understood since in the Block

TABLE II. Orbital compositions of the seven competing states at selected couplings and densities. The details are as follows: C state ($U = 3.0, n = 6.0$); Flux state ($U = 3.0, n = 6.5$); G state ($U = 3.0, n = 5.0$); GC state ($U = 3.0, n = 5.5$); E state ($U = 5.0, n = 5.75$); Block state ($U = 5.0, n = 6.25$); DC state ($U = 5.0, n = 6.75$). Similarly as in Table I, the * indicate phases where the orbital population is not the same at each site. Typically, there are four sites that repeat themselves in most of the cases, but sometimes the periodicity involves two sites or eight sites. The numbers used for these states in the present table are their average values.

	xz	yz	x^2-y^2	xy	z^2	Total
C	1.0048	1.3911	1.3659	1.0099	1.2281	6.0
Flux*	1.3083	1.2435	1.4462	1.1108	1.3912	6.5
G	0.9998	0.9998	1.0029	0.9965	1.0009	5.0
GC	1.0017	1.1606	1.2269	1.0025	1.1083	5.5
E*	1.1249	1.1236	1.3758	1.0046	1.1212	5.75
Block	1.1509	1.1509	1.3244	1.0297	1.5940	6.25
DC	1.2183	1.3796	1.4397	1.0807	1.6317	6.75

state there are no paths from one extreme to the other of the crystal with spins displaying the same spin orientation.

The C-AFM state is metallic, in agreement with previous calculations [6], and the DC state is also metallic, at least at the electronic densities and couplings used in the figure. This is reasonable since C and DC only differ in the periodicity along the y direction (strictly speaking, for the 8×8 cluster

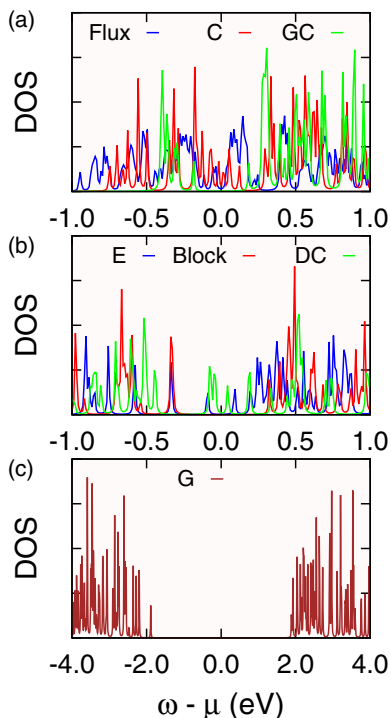


FIG. 5. (Color online) Density of states (DOS) at representative values of couplings and densities, corresponding to the seven magnetic states in the phase diagram of Fig. 2. (a) Flux state ($U = 3.0, n = 6.5$); C state ($U = 3.0, n = 6.0$); GC state ($U = 3.0, n = 5.5$); (b) E state ($U = 5.0, n = 5.75$); Block state ($U = 5.0, n = 6.25$); DC state ($U = 5.0, n = 6.75$); (c) G state ($U = 3.0, n = 5.0$).

there is a tiny gap in the density of states (DOS) for the DC state in Fig. 5 but this may be caused by finite-size effects). The E phase also displays a small gap, but it is difficult to say whether it will become insulating or metallic in the bulk limit. Finally, the Flux state appears to be clearly metallic, while the GC-AFM state is insulating. The latter has this property because it is formed by isolated 2×1 spin blocks, qualitatively similar to the characteristics that led to the insulating nature of the Block-AFM state made of isolated 2×2 spin blocks.

In Fig. 2, the insulating regions have been indicated. As expected, special electronic densities such as $n = 5.0, 5.5, 6.0, 6.5$, and 7.0 display an insulating state at values of U smaller than for other intermediate densities. The insulating states are shown in the region of parameters displayed in Fig. 2. The metal versus insulator character of the state was decided based on the density of states, and its weight at the Fermi level. In most cases, before the actual metal-insulator transition there is a region with a pseudogap on the metallic side, with low (or very low) weight at the Fermi energy. For electronic densities other than the five indicated above, eventually for sufficiently large U (not shown in the figure) an insulating state (or a pseudogap state with very small weight at the Fermi energy) is found.

V. PHASE SEPARATION

The phase diagram shown in Fig. 2 contains regions of phase separation (PS). The conclusion that there are unstable regions with these characteristics in the phase diagram was based on the study of the curvature of the $E(n)$ versus n curves, where $E(n)$ is the ground-state energy at the electronic density n . Phase separation in multiorbital systems occurs in other contexts, such as in double exchange models for manganites [19–22], thus it is not unexpected to find the same phenomenon in the five-orbital Hubbard model as well. To visualize the presence of regions with negative curvature in the $E(n)$ versus n curves it is better to introduce $\Delta E(n) = E(n) - E_0(n)$, where $E_0(n)$ is a straight line that joins the energies at the boundary densities of the PS region. Therefore, $\Delta E(n)$ should be positive if $E(n)$ versus n has a negative curvature. Some representative results are shown in Fig. 6, where indeed it is clear that PS exist in the regimes of parameter space corresponding to those curves.

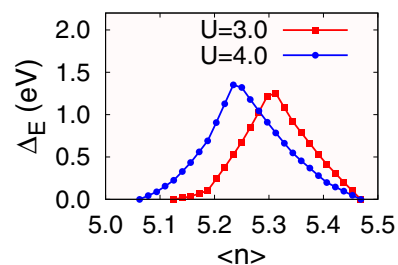


FIG. 6. (Color online) Plots of $\Delta E(n)$ vs. n showing the existence of negative curvature, namely phase separation. The results were obtained for $U = 4.0$ and $U = 3.0, J/U = 0.25$, and in the range of densities indicated. Here $\Delta E(n) = E(n) - E_0(n)$, where $E(n)$ is the actual ground-state energy at electronic density n and $E_0(n)$ is a straight line that joins the energies of the two densities at the boundaries of the PS regions.

The two regions in which the PS state separates are in principle macroscopic in size. However, previous experience with Mn oxides [21] suggest that once other interactions are included, particularly the long-range portion of the electronic Coulombic repulsion, the PS regions become unstable. This macroscopic separation is replaced by complex states that are mixtures, at the nanometer length scale, of the two phases at the boundaries of the PS portions of the phase diagram. In this regime, nonlinear responses to external fields could be expected [21].

Note that phase separation was also observed in previous studies of multi-orbital Hubbard models, employing related momentum-space mean-field and Heisenberg mean-field techniques and a different set of hopping amplitudes [15]. In particular, the PS regions found in Ref. [15] also involved the G and C states as in our results, although in our case the GC state (not included in the study found in Ref. [15]) also plays an important role. Although the agreement is not quantitative, the similarities of both studies suggest that PS must be considered when phase diagrams of multi-orbital Hubbard models are constructed. As mentioned before, the presence of PS was also reported in recent related calculations that employed a mean-field approximation to a model with weakly coupled electrons having an electron- and a hole-band with imperfect nesting [24,25]. The qualitative agreement with these previous results suggest once again that the PS tendency may be generic and should be considered into future studies, and even in the interpretation of some experiments.

To complete the comparison of our present results to the existing literature, note that in Ref. [15] charge order tendencies were observed in the DS state. With this previous report as a motivation, exhaustive searches for charge-ordered states were carried out here, in the density window from $n = 5.5$ to $n = 6.5$. Indeed charge modulations in a checkerboard pattern were observed in some of our studies, particularly when starting the runs using a charge-modulated initial state as guidance. However, these states end up having a higher energy than the other states reported in our study. This should not be considered a critique of Ref. [15] since their model and technique are not identical to ours, but it provides further support to our main conclusion: there are a variety of interesting states competing in the phase

diagram of multi-orbital Hubbard models, particularly at intermediate/large U .

VI. CONCLUSION

The phase diagram of a five-orbital Hubbard model has been presented in this publication, working at a fixed Hund coupling $J/U = 0.25$, varying the Hubbard repulsion U and the electronic density n in the range from 5 to 7, and employing the real-space Hartree-Fock approximation as the many-body technique. While our results cannot be considered quantitatively accurate due to the intrinsic deficiencies of mean-field approximations, qualitative trends appear reasonable and moreover they are in good agreement with other independent theoretical investigations. These trends include the presence of many competing magnetic states (superconducting states were not studied here), suggesting a rich free-energy landscape with several local minima. Perhaps not surprisingly based on previous studies on colossal magnetoresistive Mn oxides, this rich landscape may lead to regions of phase separation where complex states involving a nanometer-scale mixture of the competing phases could be stabilized. In addition, there is a clear tendency to evolve from fully antiferromagnetic states at $n = 5$ to states with an increasing number of ferromagnetic links as n grows.

Several of the states that spontaneously appeared in our phase diagram are known to exist in experiments, either for layered materials or in other geometries such as with regularly spaced Fe vacancies or in two-leg ladders. These states are the G-, E-, and C-type antiferromagnets, and also the 2×2 Block state. In addition, three novel states have been found in our study: the GC, Flux, and DC states. Experimental efforts should be devoted to the search for these states in actual compounds. The similarity of our results with the conclusions of other theoretical efforts give us confidence that the trends studied here are robust and the characteristics of multi-orbital Hubbard models in general, in the range of densities from five to seven electrons per transition metal atom.

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TABLE III. Hopping amplitudes for the tight-binding portion of the five-orbital Hubbard model used in this study. Here m and n label the Fe $3d$ orbitals as follows: $1 = xz$, $2 = yz$, $3 = x^2 - y^2$, $4 = xy$, $5 = 3z^2 - r^2$, and i labels the hopping directions. ϵ_{mn} in the last column is the on-site energy. The explicit form of the tight-binding Hamiltonian can be found in Ref. [27]. The overall energy unit is electron volts.

t_i^{mn}	$i = x$	$i = y$	$i = xy$	$i = xx$	$i = xxy$	$i = xyy$	$i = xxyy$	ϵ_{mn}
$mn = 11$	-0.14	-0.4	0.28	0.02	-0.035	0.005	0.035	0.13
$mn = 33$	0.35		-0.105	-0.02				-0.22
$mn = 44$	0.23		0.15	-0.03	-0.03		-0.03	0.3
$mn = 55$	-0.1			-0.04	0.02		-0.01	-0.211
$mn = 12$			0.05		-0.015		0.035	
$mn = 13$	-0.354		0.099		0.021			
$mn = 14$	0.339		0.014		0.028			
$mn = 15$	-0.198		-0.085				-0.014	
$mn = 34$					-0.01			
$mn = 35$	-0.3				-0.02			
$mn = 45$			-0.15				0.01	

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APPENDIX

For completeness, the hopping amplitudes used in this study are given in Table III.

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