Phase diagram of a generalized Hubbard model applied to orbital 
order in manganites

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Abstract

The magnetic phase diagram of a two-dimensional generalized Hubbard model proposed for manganites is studied within Hartree-Fock approximation. In this model the hopping matrix includes anisotropic diagonal hopping matrix elements as well as off-diagonal elements. The antiferromagnetic (AF), ferromagnetic (F), canted (C) and paramagnetic (P) states are included in the analysis as possible phases. It is found that away from half-filling only the canted and F states may exist and AF and P states which are possible for the usual Hubbard model do not appear. This is because the F order has already developed for on-site repulsion $U = 0$ due to the hopping matrix of the generalized model. When applied for manganites the orbital degree is described by a pseudospin. Thus our “magnetic” phase diagram obtained physically describes how orbital order changes with $U$ and with doping for manganites. Part of our results are consistent with other numerical calculations and some experiments.
The three-dimensional (3D) cubic manganites R$_{1-x}$A$_x$MnO$_3$ (R is a rare earth element such as La or Nd, A is a divalent alkali such as Sr or Ca) and the layered ones La$_{n-2x}$Sr$_{1+n-x}$Mn$_n$O$_{3n+1}$ ($n = 1, 2$) have attracted intensive interest due to their rich material properties \[1\]. Most prominently they show a colossal magnetoresistance which may be qualitatively understood on the basis of double exchange (DE) model or the more general ferromagnetic Kondo lattice model. However, many recent experimental findings such as the doping dependence of charge, orbital, spin ordered phases \[2\] suggest that additional physical mechanisms beyond the DE model should be involved. The possible ingredients are: $e_g$ orbital degeneracy \[3–5\], electron correlation \[6\] as well as electron-lattice interaction \[7\], e.g., by Jahn-Teller coupling \[8\]. Though there exist some works to study the complex interplay of spin, orbital and lattice degrees of freedom \[9–11\], it is still very helpful to clarify the role of each individual mechanism separately with the assumption that other degrees of freedom are frozen out. Actually, experiments showed that the spins in many 3D manganites R$_{1-x}$A$_x$MnO$_3$ are ferromagnetically ordered or A-type antiferromagnetically ordered (ferromagnetic layers coupled antiferromagnetically) in a large region of the doped phases, and A-type antiferromagnetic ordered in the undoped phase \[12,2\]. This means that a perfect spin-polarized two-dimensional (2D) plane is always retained over large region of doping. Therefore, the spin degree of freedom may be discarded and the following effective 2D Hamiltonian with only orbital degree of freedom is proposed \[13,14\]:

$$
\mathcal{H} = -\sum_{<ij> \sigma \sigma'} t_{ij}^{\sigma \sigma'} c_{i \sigma}^\dagger c_{j \sigma'} + U \sum_i (n_i \uparrow - 1/2)(n_i \downarrow - 1/2),
$$

(1)

where $<ij>$ indicates summation over nearest-neighbor sites, $t_{ij}^{\sigma \sigma'}$ denotes the hopping integral and $U$ is the effective inter-orbital Coulomb interaction. The two orbitals $|x^2 - y^2\rangle$ and $|3z^2 - r^2\rangle$ have been assumed as pseudospin $\uparrow$ and $\downarrow$, respectively. The hopping matrix is explicitly given by $t_{ij}^{\uparrow \uparrow} = t_1 = 3t/4$, $t_{ij}^{\uparrow \downarrow} = t_2 = t/4$, $t_{ij}^{\downarrow \uparrow} = t_1^{\dagger} = -(+)t_3 = -(+)\sqrt{3}t/4$ along the $x(y)$-direction \[15\]. The most important feature here is the orbital dependence of the integral $t_{ij}^{\sigma \sigma'}$, which distinguishes the present model from the usual Hubbard model where we have $t_{ij}^{\sigma \sigma'} = t\delta_{\sigma \sigma'}$. 

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Although the above 2D model ignores some important effects of three dimensionality as we discuss in the later, it may still contain important physics for 3D cubic manganites. For this the above model or its strong coupling version, the so-called orbital $t$-$J$ model has been used to study the unusual optical conductivity observed in doped LaMnO$_3$ \cite{14, 16}. At the same time it should be also noted that the above model may be of direct relevance to layered manganites, which consist of stacking of single or double MnO$_2$ layers. Thus a full understanding of the properties of the above model is necessary. While its optical conductivity was studied by others, we discuss a different aspect here. It is natural to ask in which properties the present model deviates from the usual Hubbard model. For example, as a basic problem, what are the differences between their magnetic (it actually means “orbital” for the real manganites) phase diagrams? This will be the main topic addressed in this work. Though the orbital ordering for manganites based on the current model has been numerically studied at some points \cite{13, 16}, the full phase diagram has not been discussed. So the purpose of this paper is twofold: On one hand we want to know how its magnetic phase diagram is modified by the generalized hopping matrix, in analogy to the recent investigation of the influence of next-nearest-neighbor hopping \cite{17} on the phase diagram. On the other hand, as a real model for manganites, our “orbital” phase diagram obtained below is certainly useful for the nontrivial question of how the orbital order is changed upon doping.

In the following we use the Hartree-Fock (HF) approximation to study the magnetic phases of the Hamiltonian (1). Although the HF approximation may overestimate the appearance of the ordered states due to neglect of quantum fluctuations, this simple approximation may still give many useful information. So it should be kept in mind that the quantitative aspects of the results given here should not be taken literally but that these results provide a basis for further more elaborated theoretical studies. In this respect the so-called slave-boson mean field theory is an improved method, but requires much more numerical efforts \cite{18}. Besides the usual ferromagnetic (F), antiferromagnetic (AF) ordered and paramagnetic (P) states considered here the canted ordered (C) state is also taken into
account as a possible phase. Although it has rarely been considered in previous studies of the Hubbard model, we include it here motivated by the fact that experiments on LaMnO$_3$ [19] have confirmed the type of $|3x^2 - r^2\rangle/|3y^2 - r^2\rangle$ orbital ordering which corresponds to a canted spin order in the pseudo-spin representation [20], as illustrated in Fig. 4. Other complicated spin ordered states which have been studied for the usual Hubbard model such as spiral phase [21] etc. will not be considered.
FIG. 1. Pseudospin representation of staggered \(|3x^2 - r^2|/|3y^2 - r^2|\) orbital ordering in \(xy\) plane under the basis: \(|x^2 - y^2\rangle \uparrow\) and \(|3z^2 - r^2\rangle \downarrow\).

In HF approximation the Hamiltonian (1) can be rewritten as [22] (irrelevant constants are ignored):

\[
\mathcal{H}_{\text{HF}} = -\sum_{<ij>} \sum_{\sigma\sigma'} t_{ij}^{\sigma\sigma'} c_i^{\sigma} c_j^{\sigma'} - \frac{2}{3} U \sum_i \langle 2\vec{S}_i \cdot \langle \vec{S}_i \rangle - \langle \vec{S}_i \rangle \cdot \langle \vec{S}_i \rangle \rangle,
\]

where \(\vec{S}_i = \frac{1}{2} \sum_{\sigma\sigma'} c_i^{\sigma} \sigma_{\sigma'} c_i^{\sigma'}\) and \(\sigma\) are Pauli matrices. We restrict to solutions with uniform electron density and canted order of the magnetic moments characterized by

\[
\langle \vec{S}_i \rangle = \begin{cases} 
  m(\sin \theta, 0, \cos \theta) & \text{if } i \in A, \\
  m(-\sin \theta, 0, \cos \theta) & \text{if } i \in B.
\end{cases}
\]

Here we have assumed a bipartite lattice with sublattices A and B. For later discussion it is indispensable to understand the nature of all possible ordered states characterized by the parameter \(\theta\) (with \(m\) describing the size of the order parameter), as well as their corresponding orbital ordering [24].

1. \(\theta = 0\) (\(\pi\)): F order with spin \(\uparrow\) (\(\downarrow\)) or homogenous \(|x^2 - y^2\rangle \uparrow\) (\(|3z^2 - r^2\rangle \downarrow\)) orbital ordering.

2. \(\theta = \pi/2\): AF order or staggered \((|x^2 - y^2\rangle + |3z^2 - r^2\rangle) /(|x^2 - y^2\rangle - |3z^2 - r^2\rangle)\) orbital ordering.

3. other \(\theta\) values: canted-F or AF order. For example, \(\theta = \pi/3\) (\(2\pi/3\)) corresponds to staggered \(|3x^2 - r^2\rangle /|3y^2 - r^2\rangle\) \(|y^2 - z^2\rangle /|x^2 - z^2\rangle\) orbital ordering.

In addition we note that due to broken SU(2) symmetry by the hopping matrix in Eqs. (1,2) the direction of spin polarization in the ordered states is no longer rotationally invariant,
contrary to the case for the usual Hubbard model. For example, the F phases with spin $\uparrow$ and $\downarrow$ are not equivalent now. We also remark that the spins are lying within the plane in the AF ordered state described by Eq. (3).

With new fermion operators $a$ and $b$ corresponding to sublattice A and B, respectively, we may write the Hamiltonian (2) in the momentum space as $\mathcal{H}_{\text{HF}} = 2NUm^2/3 + (a_{k\uparrow}^\dagger b_{k\uparrow}^\dagger a_{k\downarrow}^\dagger b_{k\downarrow}^\dagger)\mathcal{H}^M(a_{k\uparrow} b_{k\uparrow} a_{k\downarrow} b_{k\downarrow})^T$ with $\mathcal{H}^M$ denoting a $4 \times 4$ Hermitian matrix. Here $N$ is the total number of lattice sites and the reduced Brillouin zone is $|k_x| + |k_y| \leq \pi$ or $-\pi/2 < k_1, k_2 \leq \pi/2 (k_{x,y} = \pm k_1 + k_2)$. In principle $\mathcal{H}^M$ leads to four energy bands $\varepsilon_k^\alpha (\alpha = 1, 2, 3, 4)$. The ground state energy is given by $E_{\text{GS}} = \sum_{k,\alpha} \varepsilon_k^\alpha + 2NUm^2/3$, where the first contribution depends on the band filling $n = N_e/N$ where $N_e$ is the total electron number. Next we calculate numerically the values $m, \theta$ by minimizing the $E_{\text{GS}}$ for given repulsion $U$ and band filling $n$ or doping $\delta (= 1 - n)$. For this purpose we have used a mesh of $10^2 \times 10^2 k$ points in the Brillouin zone. In the following discussion of results $t$ is set as energy unit.

With values of $m, \theta$ obtained from the minimization of $E_{\text{GS}}$ we may plot the magnetic phase diagrams in the plane $(\delta, U)$, as shown by Figs. 4 and 5. Although there are a lot of studies for the usual Hubbard model (i.e., $t_1 = t_2 = 1, t_3 = 0$) [15], we give its phase diagram again in Fig. 2 since the canted ordered state is added here. We also want to compare it with the result for the current generalized Hubbard model whose phase diagram is displayed in Fig. 3 (solid line). In the present model, the hopping matrix involves anisotropic diagonal elements and off-diagonal ones. To see more clearly how the phase diagram is influenced by them, we plot it for a simplified model with a hopping matrix which only includes anisotropic diagonal elements (i.e., $t_1 = 3/4, t_2 = 1/4, t_3 = 0$); it is denoted by a dashed line in Fig. 3.
FIG. 2. Magnetic phase diagram for the usual Hubbard model with inclusion of ferromagnetic (F), antiferromagnetic (AF), canted (C) ordered and paramagnetic (P) states.

FIG. 3. Magnetic phase diagrams. The solid (dashed) line are for the generalized Hubbard model with $t_1 = 3/4, t_2 = 1/4, t_3 = \sqrt{3}/4$ ($t_1 = 3/4, t_2 = 1/4, t_3 = 0$) respectively. F(P) denote the stable phase at $U=\delta=0$ for both cases.

From Figs. 2 and 3, a number of differences can be seen. Firstly, the phases for the usual Hubbard model include AF, F, P states as well as a narrow region with a canted phase. It appears in a crossover region from AF to F phase, which is understandable. The phase diagram is then qualitatively modified by introduction of anisotropic diagonal elements where only the canted and F ordered phases exist and the original AF and P phases are excluded away from half-filling (i.e., $\delta > 0$). Furthermore when the off-diagonal elements are introduced the phase diagram is mainly quantitatively modified, i.e., the stability region of
the F ordered phase is enlarged. We point out that the F phase in Fig. 3 always means that spins align in the up direction (↑) due to a larger hopping matrix element $t_{ij}^{↑↑}$ (i.e., $t_1 > t_2$).

The above results may be understood if we consider the property of the kinetic term alone, i.e., assume that $U = 0$. Then the Hamiltonian (1) may be exactly diagonalized with two bands:

$$\epsilon_k^\pm = -(t_1 + t_2)(\cos k_x + \cos k_y) \pm \sqrt{(t_1 - t_2)^2(\cos k_x + \cos k_y)^2 + 4t_3^2(-\cos k_x + \cos k_y)^2}.$$

From $\epsilon_k^\pm$ the z-axis magnetization $M_z = \langle c_{i↑}^\dagger c_{i↑} - c_{i↓}^\dagger c_{i↓} \rangle / 2$ may be calculated, as shown in Fig. 4 where the curves $M_z/n$ vs $\delta$ are given. For the usual Hubbard model $M_z$ is always zero, corresponding to P state for the abscissa in Fig. 2. However, a finite magnetization (with spin ↑) is always exhibited for the present model as shown by the solid line in Fig. 4; also for the simplified model (zero off-diagonal hopping) shown by the dashed line, except at the point $\delta = 0$. Moreover, the $M_z$ value for the current model is always bigger than that for the simplified one, which means that the F order of the former is stronger. Because of the underlying F order already in the $U = 0$ case only the canted (with nonzero F component involved) and F ordered phases may exist in finite $U$ region away from half-filling. It is also easily understood why the F phase region is enlarged after inclusion of the off-diagonal hopping matrix elements.

\[\text{FIG. 4. The z-axis magnetization for the generalized Hubbard model (solid line: } t_3 = \sqrt{3}/4, \text{ dashed line: } t_3 = 0 \text{) for on-site repulsion } U = 0.\]
We consider the case of half-filling (i.e., $\delta = 0$). It has been shown that the usual Hubbard model has an AF ground state for any finite $U$, corresponding to the ordinate in the phase diagram of Fig. 2. We speculate that this conclusion might also be true for our present generalized Hubbard model. Although the present ground state is F ordered at $U = 0$ as given in Fig. 4, it is found to have AF order for $U > 1.2$. This was concluded from a calculation employing a mesh of $10^3 \times 10^3$ $k$ points. Whether or not there exists a crossover between F and AF for finite $U$ is not yet certain.

Our “magnetic” phases obtained from Hamiltonian (1) actually correspond to the orbital orderings relevant for the manganites as mentioned before, therefore we now discuss them in detail. To see clearly how the orbital order changes with doping $\delta$ we have plotted in Fig. 5 the relation of parameter $\theta$ with $\delta$ for fixed $U$. It is found $\theta$ decreases monotonically from $\pi/2$ to 0 with increase of $\delta$ indicating the process $\text{AF} \rightarrow \text{C} \rightarrow \text{F}$ order for the pseudospins as shown in Fig. 3. Let us take $U = 10$ as an example in the following. (The real value for it in manganites is about $4 \sim 10$).

In the undoped case, $\theta = \pi/2$ means a staggered $\langle |x^2 - y^2\rangle + |3z^2 - r^2\rangle \rangle / (|x^2 - y^2\rangle - |3z^2 - r^2\rangle)$ orbital ordering, which is consistent with the result by Motome and Imada from quantum Monte Carlo calculation [13], but slightly different from the experimentally observed $|3x^2 - r^2\rangle / |3y^2 - r^2\rangle$ [19]. This may be due to some other physical mechanism, e.g., a Jahn-Teller effect which is present in real materials but not included here [13]. On the other hand, it is found that the $|3x^2 - r^2\rangle / |3y^2 - r^2\rangle$ type orbital ordering may be also exhibited from our pure orbital model at very small doping $\delta \simeq 0.06$. With increase of doping the orbital order changes continuously until at some critical value $\delta_\text{c} \simeq 0.12$ which is still small it becomes $|x^2 - y^2\rangle$ type. This behaviour for small $\delta_\text{c}$ has also been noted by Horsch et al. based on the orbital $t$-$J$ model (i.e., large $U$ version of ours) with the exact diagonalization method [16]. Interestingly it is also seen that the value $\delta_\text{c}$ is not a monotonic function of $U$, which reaches a maximum $\sim 0.2$ at about $U = 5$. Recently Akimoto et al. found an A-type antiferromagnetic metallic ground state for La$_{1-x}$Sr$_x$MnO$_3$ at doping $x > 0.5$, and they proposed that $|x^2 - y^2\rangle$ orbitals should be occupied in this state [23]. This is consistent with our result derived from the planar model.
In addition, we also noticed the experimental findings that many cubic manganites are 3D ferromagnets in the intermediate doping regime nearby $\delta = 0.3$ [12,12], where the hopping along the $z$-axis is allowed by the DE mechanism. Thus it is instructive to discuss the effect of three dimensionality neglected in our model in this doping region, see also Ref. [14]. For a 3D model, the hopping along the $z$-axis is orbitally highly anisotropic; only the hopping between two $|3z^2 - r^2\rangle$ orbitals is permitted. So the 2D ferro-orbital order with $|x^2 - y^2\rangle$ type polarization, as found above, may be suppressed in order to gain the kinetic energy along the $z$-axis. Such a depolarization may be simulated by introducing a negative chemical potential $\mu$ on the $|3z^2 - r^2\rangle$ orbital [14]. It is found that, with reasonable $\mu$ valid for 3D manganites the disordered orbital liquid state may appear at some doping nearby $\delta = 0.3$.

This orbital liquid was first discussed by Ishihara et al. [24], which may be enhanced by the quantum fluctuations beyond HF approximation [25]. On the other hand, for the layered manganites with single or double layers of MnO$_2$ where the inter-layer or bilayer hopping (or correspondingly $\mu$) is assumed very small, the orbital liquid state may be excluded and our ferro-orbital ordered state is still expected to exist in the doping region mentioned above.

![Image](image_url)

**FIG. 5.** The variation of parameter $\theta$ (in units of $\pi$) characterizing the orbital ordering with doping $\delta$ for fixed $U$ for the generalized Hubbard model [1].

In the above discussion we have shown the possible orbital ordering as function of doping $\delta$ and repulsion $U$. The results are partly consistent with previous numerical calculations, and also with some experimental results on manganites although only orbital degree of free-
dom is retained in the present model. For a full understanding of various phases observed in manganites experimentally, one needs to consider the spin and orbital orderings simultaneously \[10,11\], as well as include lattice degree of freedom in some cases \[13\]. However, our orbitally ordered structures obtained above are very instructive to understand the role of orbital degree of freedom itself, i.e., how the interplay of the orbital kinetics (with attention to its peculiar matrix character) and orbital correlation induces the orbital ordering.

Moreover, they may be also possibly observed under some conditions, e.g., at large external magnetic fields.

In summary, within HF approximation we have studied the magnetic phase diagram of a generalized Hubbard model proposed for manganites where the hopping matrix includes anisotropic diagonal elements and off-diagonal elements. The AF, F, canted ordered and P states are considered as possible phases. It is found that in the doped case only the canted and F states may exist, while the AF and P phases of the usual Hubbard model are not favored. This is because the F order has already been established at \( U = 0 \) due to the peculiar hopping matrix. When applied for manganites, the spin index of this model actually represents the orbital degree of freedom. Thus our obtained magnetic phase diagram is able to describe how the orbital order changes upon doping.

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**Note Added in Proof:** Recently the scenario for phase separation has been extensively studied for various models in the manganites \[26\]. Such a tendency of separation into orbitally ferro- and antiferro- ordered regions may also exist in our case of the canted phase in Fig. 3. This problem deserves further detailed investigation.
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