Investigation of the charge-orbital ordering mechanism in single-layered Pr$_{0.5}$Ca$_{1.5}$MnO$_4$

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Abstract. Motivated by the experimental study of half-doped single-layered Pr$_{0.5}$Ca$_{1.5}$MnO$_4$ showing charge, orbital, and spin orderings [1], we propose a model to theoretically study the system to explain such ordering phenomena. The ground state electron configuration reveals that the charges form a checkerboard pattern with alternating Mn$^{3+}$/Mn$^{4+}$ sites, while the orbitals are aligned in zigzag chains [1, 2]. We calculate the ground state energy of this system to find the most preferable configuration by comparing three types of configurations (charge-unordered, charge-ordered, and charge-orbital-ordered states). The calculations are based on a tight-binding model representing effective electron hoppings among Mn ions in MnO$_2$-plane. We take into account the horizontally- and vertically-oriented orbital and spin degrees of freedom at Mn sites. We assume that the hopping integral values depend on the relative orientation between the corresponding orbitals of adjacent Mn ions. The interaction terms we incorporate into our effective Hamiltonian include inter-orbital, intra-orbital Hubbard repulsions, and Jahn-Teller distortion [2]. We absorb the exchange interaction between spins into local self-energy that we calculate within dynamical mean field algorithm [2]. Within our model we show a circumstance in which the charge-orbital ordered configuration has the lowest energy, consistent with the ground state ordering revealed by the experimental data.

1. Introduction

The emergence of various properties in manganites has become hot research topics in the area of condensed-matter physics since the last few decades [3, 4]. The manganites present a very rich phase diagram involving charge, orbital and spin orderings. Compounds of Pr-Ca-Mn-O are among those of manganites that can exhibit charge and orbital ordering phenomena [5]. In 2D system, single-layered Pr$_{1-x}$Ca$_{1+x}$MnO$_4$ shows the domination of insulator anti-ferromagnetic phase along the hole doping range [5, 6]. The most interesting phenomenon in this system is the formation of charge-orbital ordering (CO/OO). The system below charge-orbital ordering temperature $T_{CO/OO}$ shows that Mn$^{3+}$/Mn$^{4+}$ are arranged alternately as a checkerboard pattern and $e_g$ orbitals are arranged in zigzag chain. Meanwhile, the spins of Mn ions, formed by their $t_{2g}$ electrons, are ferromagnetically coupled along zigzag chain and anti-ferromagnetically coupled between adjacent zigzag chains [1]. Such an ordering pattern is referred to as the CE type order as depicted in Figure 1. The appearance of such an ordering contributes to transport, optical and magnetic properties of the system. Therefore, in hope of being able to exploit the system for applications, we need more understanding about the mechanism of this fascinating phenomenon.
In this paper, we present our theoretical study on single-layered half-doped Pr$_{0.5}$Ca$_{1.5}$MnO$_4$ to investigate the mechanism governing its ground-state charge and orbital configurations. Recent experimental study has revealed that this system shows charge-orbital ordering at temperature below $T_{CO/OO} \sim 325$ K and forms insulating phase [1]. We propose a model incorporating relevant interactions and seek the circumstances leading to the lowest energy with such configuration. We hypothesize that the charge-orbital ordering arises as a result of the interplay between various interactions involving hopping integral values that depend on relative orientations between $e_g$ orbitals of adjacent Mn ions.

**Figure 1.** CE type and AF ordering scheme on MnO$_2$-plane.

**Figure 2.** Unit super-cell of our model for MnO$_2$-plane.

### 2. Model

We construct our model to accommodate the charge-orbital ordering phenomena as follows. As we would like to consider only the dynamics of electrons in Mn orbital, we do not incorporate the presence of Pr, Ca and O ions explicitly in our model. In addition, we also neglect coupling between layers assuming that it is very weak compared to the hopping electrons on the same layer. Furthermore, to accommodate the formation of charge ordering and orbital ordering, we construct a unit super-cell with an area of $4a \times 4a$ as shown in Fig 2. Each unit super-cell consists of 16 atomic sites ($s$) where each atomic site has 2 $e_g$ orbitals ($A,B$) with 2 possible space orientations ($\alpha,\beta$) and 2 spin orientations ($\uparrow,\downarrow$). Hence, we use $16 \times 2 \times 2 \times 2 = 128$ basis states out of Mn $e_g$ orbitals in the unit super-cell to construct our Hilbert space, with each basis state denoted as $|\text{Mn}_{d\alpha}^{s\gamma\sigma}\rangle$. This basis set is used to form our model Hamiltonian as below

$$
H = \frac{1}{N} \sum_{\mathbf{k}} \eta_{\mathbf{k}}^\dagger H_0(\mathbf{k})\eta_{\mathbf{k}} + \sum_{\mathbf{i},\mathbf{s},\gamma,\sigma,\sigma'} U_{\alpha} n_{\mathbf{i}\gamma\sigma}^\alpha n_{\mathbf{i}\gamma\sigma'}^\alpha + \sum_{\mathbf{i},\mathbf{s},\gamma,\sigma} U_{\alpha} n_{\mathbf{i}\gamma\uparrow}^\alpha n_{\mathbf{i}\gamma\downarrow}^\alpha + \sum_{\mathbf{i},\mathbf{s},\sigma} J_{S_{\mathbf{i}\gamma},\sigma} + \sum_{\mathbf{i},\mathbf{s},\gamma,\sigma} J_{S_{\mathbf{i}\gamma},\sigma} \left( n_{\mathbf{i}\gamma\sigma}^\alpha - n_{\mathbf{i}\gamma\sigma}^\alpha \right)
$$

The first term of Eq. 1 is the kinetic part, where the matrix $[H_0(\mathbf{k})]$ is a $128 \times 128$ matrix containing the on-site and hopping energies as functions of the wavevector $\mathbf{k}$ in the Brillouin zone (BZ), and $\eta_{\mathbf{k}}^\dagger$ ($\eta_{\mathbf{k}}$) is a row (column) vector containing the corresponding creation (annihilation) operators. The second term represents the inter-orbital Coulomb repulsion that we shall treat at mean-field level. The third term represents intra-orbital Coulomb repulsion between spin up and down electrons in the same orbital. In this case, we set $U_{\alpha}$ to be infinitely large to avoid double occupancy on each Mn orbitals. The fourth and fifth terms represent two modes of vibrations related to electron-phonon Jahn-Teller interaction, with $u_i$ and $v_i$ being the corresponding local lattice displacements, and $g$ the electron-phonon coupling. In our approximation, we ignore the
dynamics of the Jahn-Teller displacement, rather we take the equilibrium values of \( u_i \) and \( v_i \) defined as \( u_0 \) and \( v_0 \) [2]. We can derive \( u_0 \) and \( v_0 \) from the equation: 
\[
\frac{\partial}{\partial \mu} \left( \frac{k}{2} u^2 + g_0 \langle n_{i \gamma} \rangle \right)_{\mu=\mu_0} = 0.
\]
Then, with \( u_0 \) and \( v_0 \) as new parameters, the constants in the fourth and fifth terms can be reexpressed, respectively, as 
\[
g_0 u_0 \equiv U_{JT} \langle n_{i \alpha \sigma} \rangle \quad \text{and} \quad g_0 v_0 \equiv V_{JT}.
\]

The last term represents the magnetic interaction between spin of itinerant electron and total spin of the localized \((t_{2g})\) electrons of Mn, which we shall treat within dynamical mean field algorithm.

Our specific goal is to compare the total energy of three different ordering configurations: charge-unordered, charge-ordered, and charge-orbital-ordered. The description of the three ordering configurations is the following. Consider that there are \( 8 \) itinerant electrons per unit super-cell such that the electron filling satisfies \( \sum_{n\gamma\sigma} \langle n_{n\gamma\sigma}^{i} \rangle = 8 \). In charge-unordered state, electrons have same probability to occupy each site, so that each occupation takes a value \( \langle n_{n\gamma\sigma}^{i} \rangle = \frac{8}{128} = \frac{1}{16} \). In charge-ordered state, electrons choose to occupy one of two neighboring sites. So if site \( s \) is occupied by an electron, the nearest site \( s' \) will be empty. There are \( 64 \) combinations of \( s, \alpha, \gamma \) and \( \sigma \), so that \( \langle n_{n\gamma\sigma}^{i} \rangle = \frac{8}{64} = \frac{1}{8} \). The occupation of charge-orbital-ordered state is similar to charge-ordered state but the electron only occupies one of two \( e_g \) orbitals at a site. There are \( 32 \) combinations of \( s, \gamma \) and \( \sigma \) so that \( \langle n_{n\gamma\sigma}^{i} \rangle = \frac{8}{32} = \frac{1}{4} \).

3. Result and Discussion
At the same atomic site, there are three Coulomb repulsive interactions we may consider to be distinct: 1) Coulomb repulsion between electrons in different \( e_g \) orbitals A and B, regardless of space \((x,y)\) and spin orientation; 2) Coulomb repulsion between electrons in the same \( e_g \) orbital A or B, but at different space-orientation states \((x \text{ and } y)\), regardless of the spin orientations; and 3) Coulomb repulsion between electrons in the same \( e_g \) orbital A or B at the same space-orientation state \((x \text{ or } y)\), with different spin orientations. We want to calculate the total energy of each of the above three ordering configurations at \( T = 0 \) for two different possible scenarios. Since we are interested only in the ground-state properties, i.e. \( T = 0 \), for all calculations we freeze the Mn-spin configuration according the zigzag CE-type configuration as depicted in Fig. 1. Note that, unless we make a specific statement about the values of certain parameters we use in this paper, we use all the parameters given in Ref. [2].

3.1. Scenario 1
We assume the strength of the Coulomb repulsion 1) and 2) above to be of finite value \( U \), while 3) is taken to be infinity. Figures 3 and 4 show how the total energy of each of the three ordering configurations vary with \( U \), assuming the hopping parameters being the same and different for different space-configuration states, respectively. Regardless of whether the hopping parameters are the same or different, we see that the energy of charge-unordered configuration increases and becomes the highest among the three configurations. Meanwhile, the energy of charge-ordered and charge-orbital-ordered configurations decrease as \( U \) increases. But the charge-orbital-ordered energy is found to be much higher than that of charge-ordered. This is an unexpected result as the experimental study at low temperatures [1] indicates that the ground-state phase of the system is charge-orbital ordered.

3.2. Scenario 2
Now, we assume the strength of the Coulomb repulsion 1) to be of finite value \( U \), while both 2) and 3) are taken to be infinity. In Figure 5 and 6, we can see the total energy of the different ordering configurations. Again, regardless of whether the hopping parameters are the same or different, the energy of all the three ordering configurations increase as \( U \) increases. More importantly, as \( U > 1 \) eV charge-unordered phase has the highest energy indicative of being unfavorable phase at \( T = 0 \). The formation of charge-ordered or charge-orbital-ordered phase is also followed with the transition from metallic to insulating-like phase (not shown).
Still with scenario 2, Figs. 7 and 8 show us the effect of Jahn-Teller parameter ($U_{JT}$) on the splitting energy between charge-ordered and charge-orbital-ordered states as $U_{JT}$ increases, while $U = 4$ eV is set fixed.

If we inspect further through Fig. 9, there is a significant difference in energy of the charge-orbital-ordered phase between the case with the same hopping parameters and that with different parameters. The dependence of the hopping parameter values on the relative orbital orientation decreases further the charge-orbital-ordered energy of the system.

4. Conclusion
We have developed a model to describe the mechanism of charge-orbital ordering in the ground state of single-layered Pr$_{0.5}$Ca$_{1.5}$MnO$_4$ by comparing the total electronic energy among three different possible charge configurations. We test two scenarios to see which Coulomb repulsion should be considered much larger than others. We find that the scenario 2 (as detailed above) is more suitable for the system being studied, for which it can show that the charge-orbital-ordered phase is lowest in energy compared to the charge-unordered and the charge-ordered phases.
addition, the model with the choice of scenario 2, demonstrates that the charge-ordered and the charge-orbital-ordered phases can be lower in energy compared to the charge-unordered phase only for $U$ above some threshold value, confirming the important role of the $U$ parameter for the formation of charge-ordered and charge-orbital-ordered phases [2, 7]. Moreover, we have also demonstrated that at some finite $U$ value (e.g. $U = 4$ eV) the Jahn-Teller effect and the dependence of the hopping parameters on the relative orbital orientation increase the energy difference between charge-ordered state and charge-orbital-ordered phases.

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