Effects of Electron Correlation, Orbital Degeneracy and Jahn-Teller Coupling in Perovskite Manganites

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Roles of Coulomb interaction, orbital degeneracy and Jahn-Teller coupling in double-exchange models are examined for Mn perovskite oxides. We study the undoped Mott insulator as well as metal-insulator transitions by hole doping, and especially strong incoherence of ferromagnetic metal. We derive models where all the spins are fully polarized in two-dimensional planes as in the experimental indications, and investigate their ground-state properties by quantum Monte Carlo method. At half filling where the number of $e_g$ electron is one per site on average, the Coulomb interaction opens a Mott gap and induces a staggered orbital ordering. The opening of the Mott gap is, however, substantially slower than the mean-field results if the Jahn-Teller coupling is absent. The synergy between the strong correlation and the Jahn-Teller coupling largely enhances the Mott gap amplitude and reproduces realistic amplitudes and stabilization energy of the Jahn-Teller distortion. Upon doping, the orbital ordering stabilized by the Coulomb interaction is destroyed immediately. Toward the metal-insulator transition, the short-ranged orbital correlation is critically enhanced in metals, which should be related to strong incoherence of charge dynamics observed in experiments. Our model, moreover, exhibits a uniform ordering of $d_{x^2-y^2}$ orbital in a wide region of doping in agreement with experimental indications.

KEYWORDS: perovskite manganites, double exchange model, Coulomb interaction, orbital degeneracy, Jahn-Teller coupling, Mott gap, orbital ordering, Jahn-Teller distortion, metal-insulator transition, ferromagnetic metal, incoherent charge dynamics, quantum Monte Carlo method

‘Simple’ double-exchange (DE) models, that is, models with a single non-interacting conduction band ferromagnetically coupled with localized spins, have been intensively studied to understand physical properties of Mn perovskite oxides, especially colossal magnetoresistance. These models have successfully explained several experimental aspects at least qualitatively: for instance, ferromagnetic metals in a hole-doped region with a transition to a paramagnetic state by raising temperature, and a large negative magnetoresistance near the transition. All these properties are due to the so-called double-exchange mechanism; doped holes tend to gain kinetic energy by aligning localized spins in parallel.

However, many open problems still remain. In particular, we focus here the following: (i) All the materials are the Mott insulator with a charge gap of order of eV at half filling (one $e_g$ electron per Mn site on average), where two-dimensional (2D) anisotropy realizes in spin and orbital orderings and a cooperative Jahn-Teller (JT) distortion. (ii) Upon doping of holes, a metal-insulator (MI) transition occurs from the anisotropic Mott insulator to an isotropic ferromagnetic metal through disordered ferromagnetic insulator. (iii) In the ferromagnetic metallic state, charge dynamics shows strong incoherence with tiny Drude weight even at low temperatures while the linear specific-heat coefficient $\gamma$ remains small. All these problems suggest importance of elements neglected in the simplified models: Coulomb interaction, orbital degrees of freedom, JT coupling and so on.

In several recent studies, effects of these factors previously neglected were also explored; mean-field approximation,\textsuperscript{1-5} exact diagonalization of small clusters,\textsuperscript{6-10} Gutzwiller technique,\textsuperscript{11-13} slave-fermion theory,\textsuperscript{14-15} dynamical mean-field theory,\textsuperscript{16} and perturbation theory.\textsuperscript{17-19} Nevertheless it is still controversial which of the electron correlation, orbital degeneracy or the JT coupling is the driving mechanism of experimental properties, particularly strongly incoherent charge dynamics, and what are realistic parameters of theoretical models. These need to fully consider quantum fluctuations.

In this work, we investigate DE models including Coulomb interaction, orbital degeneracy of conduction bands and JT coupling. Especially, we discuss quantum fluctuation effects of on-site Coulomb interaction on half-filled states as well as on MI transitions by hole doping in the ground state. In order to obtain unbiased results under strong quantum fluctuation, we use here quantum Monte Carlo (QMC) technique. Our results at half filling show that a strong Coulomb interaction is required to understand undoped manganites quantitatively. Experimentally-observed JT distortions are reproduced as a consequence of the synergy between the strong correlation and the JT coupling. Nature of the MI transition is investigated in detail; we show that this transition is a continuous one with a critical enhancement of orbital correlations which may be relevant to incoherent charge dynamics. A uniform orbital ordering observed in doped materials\textsuperscript{20-22} is also repro...
duced in our model.

The model we study here consists of three terms as

\[ H = H_{el} + H_{el-ph} + H_{ph}. \]

(1)

The first term is derived in a particular limit of DE models with on-site Coulomb interaction as well as with twofold degeneracy of \( e_g \) orbitals. The original form of \( H_{el} \) is given by \( H_{DE} = H_t + H_{int} + H_K \), where \( H_t = \sum_{ij} t_{ij} \epsilon_{\nu} c^\dagger_i \epsilon_{\nu} c_j \) is the hopping term, here \( \epsilon_{\nu} c^\dagger_i \epsilon_{\nu} c_j \) annihilates (creates) a \( \sigma \)-spin \( e_g \) electron at site \( i \), \( -1 \leq \nu \leq 1 \); \( H_{int} \) contains on-site interactions within the doubly-degenerate \( e_g \) orbitals; and \( H_K = K \sum_i S_i^x S_i^y \) denotes the Hund’s rule coupling between \( e_g \) electrons and \( t_{2g} \) localized spins. Following previous studies, we consider the limit of \( K|S^2| \gg t_{ij}^2 \). In this limit, \( S_i^x S_i^y \) aligns parallel to \( S_i^z \) in each site, therefore \( t_{ij}^2 \) is renormalized by a relative angle of \( t_{2g} \) spins in sites \( i \) and \( j \). Moreover, we assume perfect polarization of spins in the ground state based on the following arguments. At finite hole doping, it is known that \( H_{DE} \) shows a metallic ground state with perfect polarization of spins, which corresponds well to many doped manganites \([4, 5]\). At half filling, these materials commonly become a A-type antiferromagnetic insulator which consists of ferromagnetic layers stacking antiferromagnetically. These show that the 2D structure of perfectly-polarized ferromagnetic layers stacking antiferromagnetically persists in both sides of MI transition caused by hole doping. Therefore, within a 2D plane at low temperature, spin degrees of freedom may be dropped. Then the Hamiltonian in the plane reads

\[ H_{el} = \sum_{ij, \nu \nu'} \tilde{t}_{ij}^\nu \epsilon_{\nu}^i c^\dagger_{\nu} c_{\nu j} + \tilde{U} \sum_i (n_i - 1)(n_i - 1/2), \]

(2)

where \( n_{\nu} = c^\dagger_{\nu} c_{\nu} \) is a number operator. The transfer matrices are renormalized independently of sites because of the perfect polarization; and the interaction \( \tilde{U} \) is not a bare interorbital Coulomb repulsion \( U_{12} \) but \( U_{12} - J_{12} \), where \( J_{12} \) is the Hund’s rule coupling between orbitals \( \nu \) and 1 and 2. Here hopping integrals between nearest-neighbor sites in the 2D plane are explicitly given as \( \tilde{t}_{11} = -3t_0/4 \), \( \tilde{t}_{22} = -t_0/4 \), \( \tilde{t}_{12} = \tilde{t}_{21} = -(+)\sqrt{3}t_0/4 \) in the \( x(y) \rangle \) direction for \( d_{3z^2-r^2} (\nu = 1) \) and \( d_{5z^2-r^2} (\nu = 2) \) orbitals, where \( t_0 \) is defined later. This model can be viewed as a generalization of ‘ordinary’ Hubbard models where \( t_{ij}^\nu \propto \delta_{ij, \nu} \). In the following, we consider the above 2D model partly because of its numerical feasibility. Although it ignores some of important effects due to three-dimensionality, it may contain at least nontrivial important physics of the MI transition by hole doping where the 2D anisotropy was suggested to be relevant. Moreover, this model is useful to discuss an orbital ordering at half filling since it also has 2D structure as the spin ordering. We also note that our model may have some relevance to layered Mn compounds \([6, 7]\) which consists of stacking of single or double MnO\(_2\) layers with rather small crystal-field splitting of \( d_{3z^2-r^2} \) and \( d_{5z^2-r^2} \).

The rest terms in eq. (2) denote the JT coupling in a classical treatment \([8, 9]\). These should be appropriate when lattice distortion has a long-ranged order. In perovskite manganites, a cooperative JT distortion which also has 2D anisotropy as spin and orbital ordering appears at half filling \([8, 9]\). Because of the symmetry of wave functions, we consider only two phonon modes.\([10, 11]\) Then we obtain the forms as

\[ H_{el-ph} = \sum_i g_i \cdot I_i, \quad H_{ph} = k \sum_i u_i^2, \]

(3)

where \( g \) and \( I \) are two-component vectors defined as \( g_i = -2gu_i (\cos 2\theta_i, \sin 2\theta_i) \) and \( I_i = (T_i^x, T_i^z); \) \( g \) and \( k \) are the electron-phonon coupling and the spring constant. Here \( u_i \) denotes displacement of oxygens surrounding the \( i \)-th Mn site and \( \theta_i \) determines the coupling angle. \( T_i^\mu (\mu = x, y, z) \) is called the pseudo-spin operator which denotes two degrees of freedom of orbitals as \( T_i^\mu = \frac{1}{2} \sum_{\nu \nu'} \sigma_{\nu \nu'} c^\dagger_{\nu i} c_{\nu i} \), where \( \sigma \) is the Pauli matrix.

When the oxygen between the \( i \) and \( j \)-th Mn sites moves by \( u_i \), the hopping integral between Mn sites changes since originally it consists of a product of overlap integrals between Mn and O sites. Note that in both phonon modes, oxygens shift only along the direction of Mn-O-Mn bonds. A displacement of \( u_i \) modifies the Mn-O hoppings by a factor of \( (1 \pm u_i)^{1/2} \). Therefore we define a unit of the Mn-Mn hopping integrals in eq. (2) as \( t_0 = t_0 (1 + u_i)^{1/2} (1 - u_i)^{1/2} \).

In the following, we discuss ground state properties of the model eq. (1) in two dimensions by the projection QMC method \([12, 13]\). Computational details including the negative sign problem will be described elsewhere. We take energy and length units as \( t_0 \) and the lattice constant, respectively. From experiments and band calculations, \( t_0 \) is considered to be around 0.5 eV and \( U \) is estimated at several eV \([14, 15]\). In the present study, we change \( U/t_0 \) as a parameter and discuss its realistic value based on our results. The spring constant \( k \) is roughly estimated by the frequency of an oxygen bond stretching phonon at order of 10 or 100 eV \([16]\). The electron-phonon coupling \( g \) is not easy to determine experimentally, however, it may be several eV \([17, 18]\). We set here \( k = 100 \) and \( g = 10 \). The parameters \( u_i \) and \( \theta_i \) are determined by a mean-field scheme for simplicity; we fix \( \theta_i \) at experimental values as mentioned below and determine a uniform solution \( u_i = u \) to minimize total energy obtained from the QMC calculations.

First, we discuss results at half filling \((\sum_{\nu \nu} n_{\nu \nu} = N_S)\). Fig. 1 shows the \( \tilde{U} \) dependence of charge gap and staggered moment of orbital polarization in the absence of the JT coupling. For the comparison, QMC results for ‘ordinary’ 2D Hubbard models are also plotted with the mean-field results. Here, the charge gap is calculated from shifts of chemical potential upon doping. In our models, the charge gap opens considerably slower than the case of ‘ordinary’ Hubbard models, which leads to a remarkable deviation from the mean-field results, presumably because of their characteristic nesting property \([19]\). In order to reproduce the realistic charge-gap amplitude within the electronic model eq. (2), we need a much stronger interaction. Fig. 1 (b) shows that the interaction \( \tilde{U} \) induces the staggered long-ranged orbital ordering of \( T^x \) component, that is, \( (|d_{3z^2-r^2}⟩ + |d_{5z^2-r^2}⟩)/(|d_{3z^2-r^2}⟩ - |d_{5z^2-r^2}⟩) \) type, whose
pattern is slightly different from the experimentally-observed one, |d_{3z^2-r^2}|/|d_{3y^2-r^2}|. This discrepancy has also been pointed out in previous studies by the mean-field approximations. The moment grows rapidly as the values of $\tilde{U}$ probably as a consequence of its uniaxial anisotropy. Our results show that the Coulomb interaction $\tilde{U}$ by itself leads to a Mott insulating state with a staggered orbital ordering, although its ordering pattern does not show complete agreement with experiments.

If we take the JT coupling into account, importance of electron correlation becomes clearer. Fig. 2 shows ground state energy per site as function of oxygen displacement $u$. Here we assume $\theta_1 = (-1)^{\pi/2+r_1^2/\pi}/6$, following the JT pattern observed in experiments. The total energy is substantially lowered and minimized at a finite $u$; the stabilization energy $E_{JT} \simeq 0.13$ at $u \simeq 0.04$ for $\tilde{U} = 4$. At the same time, the orbital-ordering structure changes to the experimentally-observed one, namely $|d_{3z^2-r^2}|/|d_{3y^2-r^2}|$. In addition, the charge gap amplitudes become considerably larger than those without the JT coupling; for instance, at $\tilde{U} = 4$, $\Delta_e \geq 1$ ($\sim 1.1$ for hole doping and 1.7 for electron doping). These stabilization energy and charge gap grow with increasing $\tilde{U}$ or $g/k$. This indicates suppression of quantum fluctuations as a cooperative and combined effect of $\tilde{U}$ and $g/k$. Experimentally, $u$ is about 0.04 and $E_{JT}$ is below or around 0.1 eV in the light of the structural transition temperature (for instance, ~800K for LaMnO$_3$). It is quite surprising that in spite of neglecting the three-dimensionality, our present results show quantitative agreement with these experimental results; although more tuning of $\tilde{U}$ or $g/k$ (probably larger $\tilde{U}$) is required to obtain more realistic value of the Mott gap. We should stress that in the absence of $\tilde{U}$, the JT distortion is far insufficient in reproducing these results. Synergetic effects of the strong correlation and the JT coupling play a crucial role to reproduce the realistic JT distortion, orbital order configurations and the Mott gap amplitude.

Doped holes lead to an MI transition from this Mott insulating state. We focus effects of Coulomb interaction on this transition. The ferromagnetic insulator presumably with the JT distortion adjacent to the Mott insulator is beyond the scope of this paper because the JT coupling was not studied in detail in doped cases. Our data of doping concentration dependence of chemical potential indicate that there is no phase separation. In Fig. 3, we plot the inverse of peak values of the orbital correlation function $T^\mu(Q)$ as function of doping concentration at $\tilde{U} = 4$. The gray line is the linear fit to the data at $N_S = \infty$.}

### Fig. 1
QMC results (circles) without JT coupling for (a) the charge gap and (b) the staggered orbital polarization. The data are shown in the limit of $N_S \to \infty$, which are obtained by size extrapolations from $N_S = 4 \times 4$ to $10 \times 10$. Squares are QMC results for ‘ordinary’ Hubbard models. The gray (dotted) curve shows the mean-field results for our model (for the ‘ordinary’ Hubbard model).

### Fig. 2
Ground state energy per site at half filling as function of the oxygen distortion $u$. We take $\tilde{U} = 4$, $g = 10$ and $k = 100$. The curve is a polynomial fit to the data at $N_S = \infty$.

### Fig. 3
Inverse plot of peak values of the orbital correlation function as function of doping concentration at $\tilde{U} = 4$. The gray line is the linear fit to the data at $0 < \delta < 0.15$. Doped holes lead to an MI transition from this Mott insulating state.
over, for small $\delta$, they are scaled as $T^z(Q)^{-1} \sim \delta$. These indicate that the staggered orbital polarization stabilized by $\hat{U}$ is destroyed simultaneously with the MI transition at $\delta = 0$. In ‘ordinary’ Hubbard models, the similar scaling of spin correlations and an anomalous scaling of compressibility were found. These suggest a novel universality class of the MI transition where residual entropy of spin degrees of freedom may induce strong incoherence of a metal near the critical point. In our model, although we have not explicitly studied the compressibility anomaly yet, the critical behavior of orbital correlations and its implication of large entropy may well be the origin of a strong incoherence observed in experiments.

In doped cases, our model exhibits a uniform ordering of $d_{x^2-y^2}$ orbital which has been suggested in recent experiments. Our results show that a positive peak of $T^z(k = 0)$ grows as $\delta$ and has a maximum around $\delta = 0.5$. This ordering presumably comes from an optimization of the kinetic energy in the 2D planes, since it is observed even in the non-interacting 2D model. We note that this ordering is substantially enhanced by $\hat{U}$.

To summarize, we have investigated ground states of double-exchange models with on-site Coulomb interaction, twofold degeneracy of conduction bands and JT coupling using the QMC method under the condition of perfect-polarization of spins in 2D planes. Experimental results of undoped manganites, especially the JT distortion, are quantitatively reproduced with realistic parameters. Importance of the synergy between the strong electron correlation and the JT coupling is clarified. Upon doping, our models show a continuous metal-insulator transition with a critical enhancement of staggered orbital correlations. We have speculated its relation to strong incoherence of charge dynamics in ferromagnetic metals observed in experiments. In addition, our models exhibit a uniform ordering of $d_{x^2-y^2}$ orbital in doped cases, which agrees with experimental indications.

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