Effects of Orbital Degeneracy and Electron Correlation on Charge Dynamics in Perovskite Manganese Oxides

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Taking the orbital degeneracy of $e_g$ conduction bands and the Coulomb interaction into account in a double-exchange model, we investigate charge dynamics of perovskite Mn oxides by the Lanczos diagonalization method. In the metallic phase near the Mott insulator, it is found that the optical conductivity for a spin-polarized two-dimensional system exhibits a weight transfer to a broad and incoherent structure within the lower-Hubbard band together with a suppressed Drude weight. It reproduces qualitative feature of the experimental results. As an orbital effect, we find that an anomalous charge correlation at quarter filling suppresses the coherent charge dynamics and signals precursor to the charge ordering.

KEYWORDS: perovskite manganites, double-exchange model, Coulomb interaction, orbital degeneracy, metal-insulator transition, ferromagnetic metal, optical conductivity, Drude weight, incoherent charge dynamics, charge ordering, exact diagonalization, strongly correlated electron system

Although properties of perovskite manganese oxides $R_{1-x}A_x$MnO$_3$ ($R$=rare earth, $A$=Ca, Sr, Ba or Pb) showing colossal magnetoresistance are to some extent reproduced by a double-exchange (DE) model composed of non-interacting (NI) electrons in a non-degenerate $e_g$ conduction band ferromagnetically coupled with $t_{2g}$ localized spins of $S=3/2$, there remain open problems which cannot be understood within the framework of this model. One of them is that La$_{1-x}$Sr$_x$MnO$_3$ in the ferromagnetic and metallic phase near the insulator ($x$=0.175) shows a large and broad structure of incoherence in the optical response together with a relatively small Drude weight at low temperatures, although the spin degrees of freedom cannot contribute to the incoherence under the perfect polarization of spins. Some other degrees of freedom not contained in the DE model must be involved. Possible origins of the incoherence are the dynamical Jahn-Teller (JT) distortion, orbital degeneracy and electronic correlations. In ref. 3 employing the dynamical mean-field approximation, the electronic correlations are not taken into account although they are not negligible and play an essential role as shown later. In this work, we focus on the latter two and make it clear how large incoherence is induced in a minimal model of these two origins.

On this subject, related studies have already been done under some approximations. Shiba, Shinya and Taka-hashii claimed that the large incoherence in the optical absorption originates in the degeneracy of the $e_g$ orbitals, although the Mott insulator in the undoped system is not reproduced because the strong correlation effect is not seriously considered. Ishihara, Yamanaka and Nagaosa derived an effective $t$-$J$ type Hamiltonian considering the degeneracy of the $e_g$ orbitals and the strong interaction. They obtained incoherent part of the optical conductivity in a mean-field treatment. In such a mean-field treatment, unfortunately, the Drude weight is absent with a diverging specific heat coefficient $\gamma$ in contrast to the experimental results. Horsch et al. applied a finite-temperature Lanczos method to the ‘orbital’ $t$-$J$ model. In their method, however, the accessible temperature range is much higher than the experimental conditions. Consequently their Drude weight is largely suppressed simply by thermal fluctuations, which makes hard to compare with the experimental results. In order to discuss this metal-insulator transition, fluctuation effects are important; a reliable way to calculate beyond biased approximations is required.

In this work, we examine the Hamiltonian given by

$$\mathcal{H} = \sum_{ij} \sum_{\nu \nu'} t_{ij}^\nu \epsilon_{ij}^\nu \epsilon_{ij}^{\nu'} + U \sum_{\nu} (n_{1\nu} - \frac{1}{2})(n_{2\nu} - \frac{1}{2}), \quad (1)$$

as a minimal model mentioned above. This model is derived from the generalized DE model with $e_g$-orbital degeneracy under the assumptions of strong Hund’s rule coupling and perfect spin polarization. Here $t_{ij}^{\nu \nu'}$ denotes the hopping integral and $U$ is the effective interorbital Coulomb interaction obtained after subtracting the Hund’s rule coupling energy between $e_g$ electrons. The orbitals $d_{x^2-y^2}$ and $d_{3z^2-r^2}$ correspond to $\nu = 1$ and $\nu = 2$, respectively. Note that this model is essentially different from the usual Hubbard model. Actually, the difference appears even in the NI case as shown later. We consider here only the nearest-neighbor hopping given by $t_{ij}^1 = -3/4 t_0$, $t_{ij}^2 = -1/4 t_0$, $t_{ij}^2 = -1/2 t_0$, and $t_{ij}^2 = t_{ij}^1 = -\gamma_0$ along the $\langle x,y \rangle$-direction in two dimensions. Here, we investigate the two-dimensional (2D) model given by eq. (1) based on the following reasons. One is that the three-dimensional (3D) system of $R_{1-x}A_x$MnO$_3$ keeps a perfectly spin-polarized plane not only in the ferromagnetic doped phase but also in the $A$-type antiferromagnetic insulating phase at $x$=0 so that the spin polarization is retained in a 2D plane over all regions of interest. The...
We first show our results of the doping dependence of the total weights, the effective carrier densities and the Drude weights in Fig. 1. Even in the NI case, as was reported in the 3D model in ref. [1], the present model (1) in 2D exhibits a different doping dependence between the Drude weight and the total weight due to the hopping between the $d_{x^2-y^2}$ and $d_{z^2-r^2}$ bands. (See the gray curves in Fig. 1.) However, the Drude weight remains finite even at half filling, which indicates that the system is metallic in this NI case. When $U/t_0 = 16$, on the other hand, the Drude weight at half filling has a very small value $\sim 0.0005$ in the case of $\sqrt{10} \times \sqrt{10}$-site system. This small value indicates that the system is Mott insulating and that even a cluster of $\sqrt{10} \times \sqrt{10}$ sites can reproduce well the bulk quantities. In the dilute-electron-density region ($\delta \sim 1$), the total weights, the effective carrier density and the Drude weights for $U/t_0 = 16$ behave close to the corresponding quantities for the NI case, which indicates that effects of Coulomb interaction are small in this region. At $\delta = 0.5$, the Drude weight shows a significant dip, which reminds us of a charge ordering with a CE-type magnetic structure observed in such materials as Nd$_{0.5}$Sr$_{0.5}$MnO$_3$[2,23] and Pr$_{0.5}$Ca$_{0.5}$MnO$_3$[2,24]. Although the value of the Drude weight is still finite, this dip is neither seen in the NI case of the present model nor in the usual Hubbard model with finite $U$. We will discuss this issue later. With decreasing $\delta$ further, the Drude weight and the effective carrier density vanish for $U/t_0 = 16$ while the two quantities increase for $U = 0$. It should be emphasized here that the overall behaviors of the Drude weight and the effective carrier density except for the dip at $\delta = 0.5$ in the Drude weight are qualitatively similar to the ones of the usual Hubbard model in 2D. We, however, also note that the critical region of suppressed Drude weight near $\delta = 0$ seems to be narrower than that in the 2D Hubbard model due to the imbalanced populations of electrons in $d_{x^2-y^2}$ and $d_{z^2-r^2}$.

In Fig. 2, we present results for the incoherent part of $\sigma(\omega)$. One can see in Fig. 2 (a) that, at half filling, a large gap exists and that only the weight transfer across the gap to the UH band appears. As shown in Figs. 2 (b) and (c), the more holes from half filling are doped, the more weights are transferred from the region above the gap to the region within the lower-Hubbard (LH) band. Especially, note that weights for $U/t_0 = 16$ spread in a wider region than those in the NI case shown in the inset of Fig. 2 (b). The QMC study shows a critical enhancement of the orbital correlation length induced by $U$ which would cause the incoherence of the charge dynamics.

The orbital correlation in the present calculation is in agreement with that in the QMC. The present calculations indeed show a close relation between the orbital fluctuation and the mid-gap incoherence. The qualitative feature of the incoherent charge response experimentally observed in $\sigma(\omega)$ is reproduced in the present calculation, which supports the importance of combined effects from orbital degeneracy and strong correlations. On a quantitative level, however, $D/K \sim 0.51$ at $\delta \sim 0.125$ in the present result is still larger than the experimental indications, $\sim 0.2$.

To understand the dip at $\delta = 0.5$ in Fig. 1, let us dis-
cuss the orbital and charge structures in the ground state at $\delta = 0.5$. The basic point is that an orbital-polarized state with a spatially anisotropic overlap seems to enhance the charge ordering as we see below. To gain the kinetic energy in such a state at finite $U$ and $\delta = 0.5$, an occupied site favors a vacant site as the nearest neighbors. In the model (i), the orbital polarization (OP) defined by \( \langle n_{i,x} - n_{i,y} \rangle / \langle n_{i,x} + n_{i,y} \rangle \) grows because \( d_{x^2-y^2} \) orbital has larger hopping matrix than \( d_{3z^2-r^2} \) orbital. The strong interaction also enhances the polarization. Actually the OP is \( \sim 0.756 \) at $U/t_0 = 10$ in the 4×4-site system. Note here that, on the other hand, the usual Hubbard model does not show such a spin polarization in the ground state at $\delta = 0.5$. When one uses $|\theta| = \cos \theta |d_{x^2-y^2}| + \sin \theta |d_{3z^2-r^2}|$ as a notation for a single-site state, the above polarization leads to $|\theta|/\pi \simeq 0.114$, where each occupied orbital is strongly anisotropic and has a large overlap only in the $x$- or $y$-direction. We have next calculated the charge density correlation defined as $\Delta(k) = N_{\sigma}^{-1} \sum_{i,j} \langle n_{i \sigma} - n_{j \sigma} \rangle \exp[k \cdot (\mathbf{x}_i - \mathbf{x}_j)]$ in the 4×4 sites, where $n_i \equiv n_{i \uparrow} + n_{i \downarrow}$. The results at $\delta = 0.5$ show a peak at $k = (\pi, \pi)$ which makes staggered charge correlation (CC). The doping dependence of the above CC at $(\pi, \pi)$ is shown in Fig. 3. An anomalous peak appears at $\delta = 0.5$ only for the model (i) while the usual Hubbard model exhibits a monotonic $\delta$ dependence. A similar behavior at $\delta = 0.5$ of the CC and the charge dynamics was reported in ref. [25] where a spinless and orbitless system with the usual Hubbard-type hoppings and the nearest-neighbor interaction $V$ was studied. Although the size treated here is too small to judge whether the present system is metallic or insulating, an anomalous behavior of $\Delta(\pi, \pi)$ at $\delta = 0.5$ occurs even in the present case without $V$. The enhanced CC at $\delta = 0.5$ which makes the suppressed coherence in the charge dynamics can be induced only by the anisotropic hopping and the on-site interaction while the static charge order will be more stabilized with the help of the intersite Coulomb repulsion $V$. The JT distortion, studied theoretically by means of LDA+$U$[26] and Hartree-Fock[27] methods, will also enhance the above tendency of the CC and the incoherence of the charge dynamics. Although three dimensionality would reduce the OP, which influences the stability of this staggered CC, our results in 2D system are important because the charge-ordering phenomena essentially appear with strong 2D anisotropy in experiments[28,29,30,31]. To obtain information of orbital patterns at $\delta = 0.5$, in addition, we calculate orbital correlations defined by $C \equiv \sum_{i'j'} \langle W_{i'}W_{j'} \rangle$, where $W_i$ denotes a pseudo-spin operator of $3x^2 - r^2$ or $3y^2 - r^2$ $(W_i \equiv -\frac{1}{2} T_{i}^{x} + (-\frac{3}{2} T_{i}^{x} + T_{i}^{z})$ for $3x^2 - r^2$ and $T_{i}^{\mu} = \frac{1}{2} \sum_{\nu\nu'} \delta_{\nu\nu'} c_{i\nu} c_{i\nu'}$ with the Pauli matrix $\delta_{\nu\nu'}$). Prime at the sum means that $i$ and $j$ run over one sublattice. The possible patterns on the lattice are illustrated in Fig. 3. The results reveal that $C$ for (a) is the largest. The pattern (a) agrees with the experimental indication. Thus, the basic orbital structure in charge-ordering phenomena is determined irrespective of magnetic structure due to difference of energy scales. This situation is captured well within the model (i) in which the spin degrees of freedom are frozen out.

Finally, it is worth mentioning effects of the three dimensionality neglected above. In 2D, there happens the imbalance of populations in $d_{z^2-r^2}$ and $d_{3z^2-r^2}$ as described above. In 3D case, a hopping along $z$-axis would reduce the imbalance. We note that, in the NI case, such a reduction of OP in 3D from that in 2D decreases the coherence as inferred from the comparison between 3D case in ref. [16] and 2D one in Fig. 1. This is simply because the charge incoherence can not be induced if the orbital is completely polarized. The orbital depolarization may also be simulated by introducing a chemical potential difference between the two orbitals to compensate the existing OP. We have performed calculations for the $\sqrt{10} \times \sqrt{10}$-site 2D Hamiltonian with such a chemical potential difference. The results show that the Drude weight becomes more suppressed. For example, if the chemical potential difference is tuned to keep the vanishing OP, $\frac{D}{\rho_{D}} \sim 0.45$ at $\delta = 0.2$ as compared to $\frac{D}{\rho_{D}} \sim 0.67$ in the case of Fig. 1. The broad shape of incoherence within the LH band near the Mott transition is found to be qualitatively unchanged after the chemical potential is introduced. These suggest the possibility that the depolarization due to the three dimensionality would also make the charge transport more incoherent.

In summary, we have investigated the optical conductivity $\sigma(\omega)$ of the double-exchange model with both the $c_{g}$-orbital degeneracy and the Coulomb interaction. Assuming the spin polarization and the strong Hund’s-rule coupling in the 2D system, we have examined the effects of the orbital degeneracy and the on-site interaction. We have obtained in $\sigma(\omega)$ a suppressed Drude weight and a mid-gap incoherence with a broad structure in the metallic state near the Mott transition. The results reproduce to a considerable extent the incoherent charge dynamics observed experimentally in Mn oxides. On a quantitative level, however, the calculated Drude weight does not appear to be sufficiently small[32]. Effects of fluctuations of JT distortion would be an additional source of the incoherence, which is an interesting subject of further studies for more quantitative comparison. We have also found an anomalous feature in charge transport and the charge correlation at quarter filling, which reproduces basic structure of the orbital and charge ordering observed in experiments.

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[1] A. P. Ramirez: J. Phys. Condens. Matter 9 (1997) 8171 and references therein.
Fig. 1. Doping dependences of (a) the total weight $K$, (b) the effective carrier density $N_{\text{eff}}$ and the Drude weight $D$ at $U/t_0=16$. For comparison, gray lines show results in the non-interacting case, where the total weight, the effective carrier density and the Drude weight in the thermodynamic limit $N_s \to \infty$ are shown by the dotted line in (a), dotted one in (b) and solid one in (b), respectively.

Fig. 2. Incoherent part of the optical conductivity at $U/t_0=16$ for (a) the half-filled case in the 10-site system under the anti-periodic BC, (b) 2 holes in the 4$\times$4 sites under the mixed BC, (c) 4 holes in the 4$\times$4 sites under the anti-periodic BC. Inset in (b) shows the non-interacting case at the same filling and the same BC. Delta functions are broadened with width of 0.05$t_0$. We choose the BC to realize the lowest-energy ground state.

Fig. 3. Doping dependences of the charge correlation. An anomaly at $\delta=0.5$ for the model (c) is obtained while only the monotonic behavior is seen in the usual Hubbard model. Insets (a), (b) and (c) display possible staggered patterns of orbitals at $\delta=0.5$ in 4$\times$4 cluster. Simple circles and anisotropic symbols denote Mn$^{4+}$ and Mn$^{3+}$ with $3x^2-r^2/3y^2-r^2$, respectively.
Free $N_s = \infty$

(a) $K_c$

(b) $D_c$ and $N_{\epsilon_{\text{eff}}}$

U/t_0 = 16
