Orbital Liquid in Perovskite Transition-Metal Oxides

Sumio Ishihara, Masanori Yamanaka, and Naoto Nagaosa

Department of Applied Physics, University of Tokyo, Bunkyo-ku, Tokyo 113, Japan

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We study the effects of the degeneracy of the $e_g$ orbitals as well as the double exchange interaction with $t_{2g}$ spins in perovskite transition-metal oxides. In addition to the spin field $\vec{S}_i$, the isospin field $\vec{T}_i$ is introduced to describe the orbital degrees of freedom. The isospin is the quantum dynamical variable, and is represented by the boson with a constraint. The dispersion of this boson is flat along $(\pi/a, \pi/a, k_z)$ ($a$: lattice constant) and the other two equivalent directions. This enables the orbital disordered phase down to low temperatures. We interpret some of the anomalous experiments, i.e., optical absorption and d.c. resistivity, in the low temperature ferromagnetic phase of La$_{1-x}$Sr$_x$MnO$_3$ with $x > 0.2$ in terms of this orbital liquid picture.

The colossal negative magneto-resistance observed in transition-metal oxides with perovskite structure, e.g., the double exchange system La$_{1-x}$Sr$_x$MnO$_3$, has revived the interest in these systems [1–4]. The valency of Mn ion is Mn$^{3+}$ for $x = 0$, whose electron configuration is $(t_{2g})^3(e_g)^1$, and all the spins are aligned ferromagnetically due to the strong Hund coupling. Because of the strong on-site repulsion, the double occupancy of $e_g$ orbitals is forbidden, and the system is a Mott insulator. When one La is replaced by Sr, one hole is introduced to Mn and Mn$^{3+}$ turns into Mn$^{4+}$. These doped holes, which contribute to the conduction, can not be described in terms of the one-body theory. For a single band case, which is relevant to high-Tc cuprates, extensive studies have been focused on these doped holes to a Mott insulator. One of the promising approaches is resonating valence bond (RVB) theory [4,5], where the spin and charge are separated. In the orbital-degenerate case, this idea can be generalized also to the orbital degrees of freedom as shown below [6].

Experimentally the orbital ordering has been established in the low hole-concentration region, i.e., $x \sim 0.0$ [10], where the system is insulating with the A-type antiferromagnetic long range ordering (AFLRO) [11]. As $x$ increases the system becomes more and more conductive, and finally shows the metallic conduction below the ferromagnetic transition temperature $T_c$. In this metallic state ($x > 0.2$), there are several anomalous features.

1) The optical conductivity shows a narrow coherent peak up to around 0.02eV followed by a broader “Drude like” band up to around 1eV [12]. The integrated oscillator strength for this two-component Drude absorption changes down to the very low temperature where the ferromagnetic moment already saturates, which suggests that other degrees of freedom still remain active.

2) The photoemission spectra shows only a small discontinuity at the Fermi energy $E_F$ followed by a gap like behavior [13,14]. On the other hand, the specific heat is not enhanced with $\gamma \sim 5mJ/K^2mol$ [13].

3) The anisotropy of the conduction and the spin excitation, which is expected with the orbital ordering, is not observed even at low temperatures [15,16].

4) There is no symptom of the Jahn-Teller (JT) distortion in neutron scattering experiments [17]. The displacements of the oxygen ions are independent of the temperature across the ferromagnetic transition temperature.

It is noted that the on-site repulsive interaction within each orbital plays no role in the ferromagnetic state because of the Pauli’s exclusion principle. Then it is suggested from the above features that the orbital degrees of freedom play some roles in the low temperature phase.

In this paper we study the fluctuation in the orbital degrees of freedom in perovskite transition-metal oxides. These degrees of freedom are represented by the isospin $\vec{T}$, which is the quantum dynamical variable with $T = 1/2$ for the $e_g$ orbitals. We found that its fluctuation has a low dimensional character. Based on this, we propose that the isospin is still disordered, i.e., liquid state, in the ferromagnetic state of La$_{1-x}$Sr$_x$MnO$_3$ with $x > 0.2$. We have done some numerical simulations based on this idea, and their results are at least encouraging.

In order to study fluctuation in the orbital degrees of freedom, we adopt the following Hamiltonian.

$$H = \epsilon_d \sum_{i,\gamma,\sigma} d_{i\gamma\sigma}^\dagger d_{i\gamma\sigma} + \sum_{ij,\gamma,\sigma,\gamma',\sigma'} (t_{ij}^{\gamma\gamma'}^d d_{ij\gamma\sigma}^\dagger d_{j\gamma'\sigma} + h.c.) + H_{e-e} + \frac{1}{2} K \sum_{i,\gamma,\sigma,\sigma'} d_{i\gamma\sigma}^\dagger (\vec{d}_{\sigma\sigma'}^d) d_{i\gamma\sigma'} \cdot \vec{S}_{i}^{2g}.$$  (1)

Here it is assumed that the $2p$ orbitals of oxygen have been integrated over, and only the $d$ orbitals of transition-metal ions are considered. The operator $d_{i\gamma\sigma}^\dagger$ creates an electron with spin $\sigma(=\uparrow, \downarrow)$ in the orbital $\gamma(= a, b)$ at site $i$. The transfer intensity $t_{ij}^{\gamma\gamma'}$ between $\gamma$ orbital in site $i$ and $\gamma'$ orbital in the nearest-neighbor site $j$ is calculated by considering the overlap integral between the $d$ and $p$ orbitals. We choose the up and down isospin state in the orbital space as $a = (3z^2 - r^2)$ and $b = (x^2 - y^2)$ orbitals, respectively. Then $t_{ij}^{\gamma\gamma'}$ is explicitly written by
for $\vec{r}_i^j = \vec{r}_i^j \pm \hat{x}$, $\vec{r}_j^i = \vec{r}_i^j \pm \hat{y}$ and $\vec{r}_j^i = \vec{r}_i^j \pm \hat{z}$, respectively. The constant $t_0$ is positive, and depends on the distance between the $d$ and $p$ orbitals. The electron-electron interaction $H_{e-e}$ is explicitly written by

$$H_{e-e} = U \sum_{i} n_{i\uparrow} n_{i\downarrow} + U' \sum_{i} n_{ia} n_{ib} + I \sum_{i,\sigma,\sigma'} d_{ia \sigma}^d d_{ib \sigma'}^d,$$

where $n_{i\gamma \sigma} = d_{i \gamma \sigma}^\dagger d_{i \gamma \sigma}$ and $n_{i\gamma \sigma} = \sum_{\sigma} n_{i \gamma \sigma}$. The fourth-term in Eq. (3) is the Hund coupling between $e_g$ and $t_{2g}$ spins and $S_{i\gamma \sigma}^{2g}$ is the $t_{2g}$ spin with $S = 3/2$. The electron-electron interaction $H_{e-e}$ in Eq. (3) is rewritten by using the spin operator $\vec{S} = \frac{1}{2} \sum_{a,\sigma} d_{a \sigma}^\dagger (\vec{d}_{a \sigma}) d_{a \sigma}$, and the isospin operator $\vec{T} = \frac{1}{2} \sum_{a,\gamma \sigma} d_{a \gamma \sigma}^\dagger (\vec{d}_{a \gamma \sigma})$ for the orbital degrees of freedom. First notice the identities $\vec{S}^2 = \frac{1}{4} \sum_{a,\gamma \sigma} n_{a \gamma \sigma} + 2 \vec{S}_a \cdot \vec{S}_b$, and $\vec{T}^2 = \frac{1}{4} \sum_{a,\gamma \sigma} n_{a \gamma \sigma} - \frac{1}{2} \vec{S}_a \cdot \vec{S}_b$, where $n = n_a + n_b$. Then $H_{e-e}$ is rewritten as $H_{e-e} = - \sum_{i} \left( \alpha^{(s)} \vec{S}_i \cdot \vec{S}_a + \alpha^{(t)} \vec{T}_i \cdot \vec{T}_a + \beta \vec{S}_a \cdot \vec{S}_b \right)$, where $\alpha^{(s)} = \frac{2}{3} U + \frac{1}{6} U' - \frac{1}{2} I$, $\alpha^{(t)} = U' - \frac{1}{2} I$, and $\beta = -\frac{1}{3} (U - U' - I)$. Because (i) $\beta$ is order of $I$ and is much smaller than $\alpha^{(s)}$ and $\alpha^{(t)}$ and (ii) the large $U'$ forbids the simultaneous occupancy of $a$ and $b$ orbitals, we will neglect the $\vec{S}_a \cdot \vec{S}_b$ term. Since $\alpha^{(s)}$ and $\alpha^{(t)}$ are both positive, the electron-electron interaction tends to induce the spin and isospin moments. By introducing two kinds of Stratonovich-Hubbard auxiality fields, the partition function is given by

$$Z = \int \prod_{\tau} \left[ \prod_{\gamma,\sigma} \left( D \bar{d}_{i \gamma \sigma}(\tau) D d_{i \gamma \sigma}(\tau) \right) \right] \left( D \phi^{(s)}(\tau) D \phi^{(t)}(\tau) \right) e^{-\int d\tau L} ,$$

with

$$L = \sum_{i,\gamma,\sigma} \bar{d}_{i \gamma \sigma} / h_e + \epsilon_d d_{i \gamma \sigma} + \sum_{(ij),\gamma,\sigma,\gamma'} \left( t^{\gamma \gamma'}_{ij} \bar{d}_{i \gamma \sigma} d_{j \gamma' \sigma} + h.c. \right) + K \sum_{i} \vec{S}_i \cdot \vec{S}_i^{2g} + L_{t_{2g}}$$

$$= \sum_{i} \left( \alpha^{(s)} \phi^{(s)}_i \cdot \vec{S}_i + \alpha^{(t)} \phi^{(t)}_i \cdot \vec{T}_i \right)^2 + \sum_{i} \left( \alpha^{(s)} \phi^{(s)}_i \cdot \phi^{(s)}_i + \alpha^{(t)} \phi^{(t)}_i \cdot \phi^{(t)}_i \right)^2 ,$$

where $L_{t_{2g}}$ is the Berry phase term of the $t_{2g}$ spins. Eq. (3) describes the $e_g$ electrons moving in the background of two fluctuating fields $2\alpha^{(s)} \vec{S}^{(s)}$ and $2\alpha^{(t)} \vec{S}^{(t)}$. We introduce at this stage the approximation which is appropriate for the strong correlated case. In this case the magnitude of the local fields $\alpha^{(s)} \vec{S}^{(s)}$ and $\alpha^{(t)} \vec{S}^{(t)}$ are much larger than the transfer intensity $t_0$, and the electron is forced to be aligned in the directions of $\vec{S}^{(s)}$ and $\vec{S}^{(t)}$ at each site. Thus, it is convenient to rotate the spin and isospin axes in each site, in order that its z-axis coincides with $\vec{S}^{(s)}$ and $\vec{S}^{(t)}$. This is accomplished by the unitary matrices $U^{(t)}_i$ and $U^{(s)}_i$ for the spin and orbital spaces, respectively, which transform the fermion operator as $f_{\gamma' \sigma'} = \left( U^{(s)}_i \right)^{\gamma' \gamma}_{\sigma' \sigma} \left( U^{(t)}_i \right)^{\gamma \gamma'}_{\gamma' \gamma} d_{i \gamma \sigma}$ in this rotating frame the fields $\vec{S}^{(s)}$ and $\vec{S}^{(t)}$ are pointing in the direction of $+z$, and accordingly the density of states for f-fermions are divided into four bands separated by the energy gaps. When the concentration of the $e_g$ electrons is one per each transition-metal ion, only the lowest band, which corresponds to $\sigma = \uparrow$ and $\gamma = a$, is occupied and the system becomes a Mott insulator. We keep only this lowest band, because the holes are doped to it and only this is important when the low energy excitations are concerned. We introduce the spinless and orbital-less hole operator $h_i = f^\dagger_{i \sigma \uparrow}$. The virtual transition processes to the higher bands cause the exchange interaction terms $L_J$, i.e., so called $J$ term in the $t$-$J$ type models [15]. Then the effective Lagrangian up to the second-order with respect to the electron transfer is obtained as follows,

$$L = \sum_i \left( h_i (\partial_\tau - \mu_h) h_i + \sum_{(ij)} (1 - \bar{h}_i h_i) \left( (U^{(t)}_i \partial_{\tau} U^{(t)}_i)^{aa} + (U^{(s)}_i \partial_{\tau} U^{(s)}_i)^{at} \right) + \sum_{(ij)} 3 (U^{(s)}_i \partial_{\tau} U^{(s)}_i)^{aa} \right) h_{ij} h_j + L_J ,$$

where the chemical potential $\mu_h$ is determined by the condition $\{ h_i h_i \} = \chi$. The term $3 (U^{(s)}_i \partial_{\tau} U^{(s)}_i)^{aa}$ comes from $L_{t_{2g}}$ in Eq. (3). The Berry phase terms of the original electron $d_{i \gamma \sigma}$ generates those for the rotated fermions $h_i$, spins, and isospins. Here we introduce the spinor boson $z^{(s)}_i = t \left[ z^{(s)}_{i \sigma \uparrow}, z^{(s)}_{i \sigma \downarrow} \right]$ to represent the unitary
matrix $U_i^{(s)} = \left( \begin{array}{cc} z_i^{(s)} & -z_i^{(s)*} \\ z_i^{(s)*} & z_i^{(s)} \end{array} \right)$, where $\phi_i^{(s)} / |\phi_i^{(s)}| = \sum_{\alpha, \beta} z_{i\alpha}^{(s)} (\partial_{\alpha} z_{i\beta}^{(s)})$ and $\sum_{\sigma} |z_i^{(s)}| = 1$. Correspondingly we introduce $z_i^{(t)}$ for $U_i^{(t)}$. Then the Berry phase terms for spins are written as $(U_i^{(s)} \partial U_i^{(s)})_{\uparrow \downarrow} = \sum_{\sigma} z_{i\sigma}^{(s)*} \partial_{\sigma} z_{i\sigma}^{(s)}$, and its coefficient should be regarded as the spin quantum number $2S$. Then in the undoped case $(x = 0)$, the quantum numbers of the spin and isospin are $S = 2$ and $T = 1/2$, respectively. Then it is expected that the quantum fluctuation is stronger for isospin than spin.

Now the original electron operator $d_{\gamma\sigma}$ with the constraint of no double occupancy is expressed as $d_{\gamma\sigma} = h_i z_{i\gamma}^{(t)} z_{i\sigma}^{(s)}$, which is the generalization of the slave-fermion formalism to the orbital degenerate case. Then we call $h_i$, $z_{i\gamma}^{(t)}$, and $z_{i\sigma}^{(s)}$ holon, isospinon, and spinon, respectively. In analogy with the spin-charge separation in high-Tc cuprates [8], one can consider the orbital-charge separation in this formalism, which we discuss below. Then the effective transfer intensity $t_{ij}$ is given by

$$L = \sum_{\vec{k}} x t_0 \left[ \begin{array}{c} z_{\vec{t}}^{(t)}(\vec{k}) \\ z_{\vec{b}}^{(t)}(\vec{k}) \end{array} \right] \left[ \begin{array}{c} \frac{1}{2}(c_x + c_y + 4c_z), \\ \frac{1}{2}(c_x + c_y), \end{array} \right] \left[ \begin{array}{c} \sqrt{2}(-c_x + c_y), \\ -\sqrt{2}(c_x + c_y) \end{array} \right] \left[ \begin{array}{c} z_{\vec{t}}^{(0)}(\vec{k}) \\ z_{\vec{b}}^{(0)}(\vec{k}) \end{array} \right] + \sum_{\gamma, \vec{k}} \lambda |z_{\vec{t}}^{(t)}(\vec{k})|^2. \quad (8)$$

The eigenvalues for each $\vec{k}$ are given by $\epsilon_{\pm}(\vec{k}) = \lambda - x t_0 f_{\pm}(\vec{k})$ where $f_{\pm}(\vec{k}) = -c_x + c_y + c_z \pm \sqrt{c_x^2 + c_y^2 + c_z^2 - c_x c_y - c_y c_z - c_z c_x}/2$, with $c_x = \cos(ak_x)$ etc. The minimum of this energy are given by the flat dispersion along the axis $(\pi/a, \pi/a, k_z)$ and the other two equivalent directions. This situation is quite contrast to the spin case where the dispersion relation is proportional to $\cos(ak_x) + \cos(ak_y) + \cos(ak_z)$. The electron in $x^2-y^2$ orbital can not hop perpendicular to the xy-plane because the overlap with the oxygen p orbital is vanishing due to the symmetry. (Only $(aa)$ component is non-zero in the third matrix in Eq. (2).)

This flat dispersion leads to an important consequence. The chemical potential $\lambda$ is determined by $(\sum_{\gamma} z_{\vec{t}}^{(t)}(\vec{k}) z_{\vec{t}}^{(t)*}(\vec{k})) = 1/N \sum_{\gamma, \vec{k}} n_B(\epsilon_{\gamma}(\vec{k})) = 1$ where $n_B$ is the boson distribution-function. Because of this flat dispersion, the chemical potential $-\lambda$ is always negative at finite temperature although it becomes exponentially small below the effective boson condensation temperature $T^* \sim x t_0$. Then the orbital long range ordering does not occur down to low temperatures.

One may think that the physical quantities behave similarly to the orbital ordered state when the chemical potential is very small and $z^{(t)}$ is almost bond condensed. However this is not the case because there are three-branches of the low lying fluctuations, i.e., along $(\pi/a, \pi/a, k_z)$ and two equivalent directions. In order to show it, we generate the random configuration of $z^{(t)}$ at very low temperature where the chemical potential is already very small. In this case only the static component of $z^{(t)}$ is important, which is obtained by the random numbers generated by the Gaussian function $\exp[-\epsilon_{\gamma}(\vec{k})/T]$. Then $\tilde{t}_{ij}$ is obtained through Eq. (6), and we diagonalize the holon Hamiltonian for that configuration of the transfer. We study the density of states and the optical conductivity $\sigma_h(\omega)$ of the holon system by averaging over 50 random samples for the cubic lattice of $8 \times 8 \times 8$. The results for the optical conductivity is shown in Fig. 1. If one look at $\tilde{t}_{ij}$’s, they fluctuate in sign and magnitude violently, which explains the incoherent nature of $\sigma_h(\omega)$.

To study the nature of the orbital fluctuations in the ferromagnetic state, we derive the effective action for the isospinon by employing the mean-field approximation. We first consider the kinetic energy $\sum_{(ij)} h_i t_{ij} h_j$ assuming that $x t_0 \gg J$ where $J$ is the typical exchange energy and is of the order of $t_0^2/\alpha^{(s)}$ or $t_0^2/\alpha^{(t)}$. Then in the limit of strong correlation, we have the concentration region where $J/t_0 \ll x / 1$, which we are now interested in. The exchange terms $L_j$ will be discussed later. We replace the fermion operators by their average value, i.e., $(\bar{h}_i h_i) = x$, $(\bar{h}_i h_j) = -x$, and quench the magnetic fluctuation by putting $z^{(s)} = 1, 0$. The constraint $\sum_{\gamma}|z^{(t)}_{\gamma\vec{k}}|^2 = 1$ is imposed on average by introducing the chemical potential $-\lambda$. Then the effective Lagrangian of the orbital excitation $z^{(t)}_{\gamma\vec{k}}$ is obtained as

$$\tilde{t}_{ij} = \left( \sum_{\sigma} z_{i\sigma}^{(s)*} z_{j\sigma}^{(s)} \right) \left( \sum_{\gamma, \gamma'} t_{ij}^{(t)} z_{j\gamma'}^{(t)} \right). \quad (7)$$

FIG. 1. The optical conductivity of the holon $\sigma_h(\omega)$ calculated in the $8 \times 8 \times 8$ system. The temperature is chosen to be $T = 0.1 t_0$.

Now we consider the gauge-field fluctuations. There are two kinds of U(1) gauge field corresponding to $z^{(t)}$ and $z^{(s)}$, respectively. The spatial components of which
are given by the phase of the order parameters, i.e.,
\[ \langle z^{(r)}_{a^r \lambda^r} z^{(l)}_{a^l \lambda^l} \rangle = |\langle z^{(r)}_{a^r \lambda^r} z^{(l)}_{a^l \lambda^l} \rangle| \exp(ia^{(r)}_{ij}), \quad (r = s, t, \lambda, \lambda' = \sigma, \gamma). \]
The time components, on the other hand, are the Lagrange multiplier fields which impose the constraint \[ \sum_{\lambda} |\langle z^{(r)}_{a^r \lambda^r} \rangle|^2 = 1. \] In the ferromagnetic state, \( z^{(s)} \) is hole condensed, and \( a^{(s)} \) becomes massive, while \( a^{(t)} \) remains massless in the orbital disordered state. More importantly the Ioffe-Larkin composition rule [19] applies also the orbital-charge separated state, and the orbital conductivity \( \sigma(\omega) \) is given by \( \sigma(\omega) = \sigma_{h}(\omega) + \sigma_{f}(\omega) \). Then the characteristic energy of the orbital fluctuation, which is much smaller than that of holons, can manifest itself in \( \sigma(\omega) \) through \( \sigma_{h}(\omega) \). The photoemission spectrum, on the other hand, is given by the convolution of those for holon and isospinon, because the Green’s function \( G \) in space-time representation is the product \( G(r, \tau) = G_h(r, \tau) G_i(r, \tau) \). According to the flat dispersion of the isospinon, the holon dispersion is averaged over and the Fermi edge will be smeared out as observed experimentally.

Here we discuss several possible effects which break the flat dispersion and/or make the orbitals to be long range ordered. One possibility is so-called \( J \) terms, i.e., \( L_j \) in Eq. (4). It is noted that the transfer matrix \( t_{ij} = (t_{ij}^{(r)}) \) does not commute with any of the Pauli matrices \( \sigma^{\alpha} \). Then there is no continuous rotational symmetry in the isospin space. Neglecting the terms of the order of \( xJ, L_j \) in the ferromagnetic phase has the same form as the first term in Eq. (4) with \( z^{(r)}_{a^r \lambda^r} \) being replaced by \( T_z \) \( (T_x) \) and \( x \) by \( -t^{(r)}_{ij} / (U'-I) \). Note that only \( T_z \) and \( T_x \) appear in \( L_j \). The dispersion has the same form as \( z^{(r)} \)-boson, i.e., \( \epsilon_{f\pm}(\vec{k}) = -t^{(r)}_{ij} / (U'-I) f_{\pm}(\vec{k}) \). Then the minimum of the energy is given by the flat dispersion along the axis \((\pi/a, \pi/a, k_z)\) and the other two equivalent directions. For the lowest dispersion along \((\pi/a, \pi/a, k_z)\), \( T_z = 0 \) and only \( T_x \) is nonzero, which competes with the fact that the kinetic energy prefers nonzero \( T_z \). As before the ordering of the isospin is suppressed because there are three branches of the flat dispersion with the role of \( z^{(r)} \) being replaced by \( T \).

Applying the mean-field approximation to \( L_j \), which gives the two-body interactions between the \( z^{(r)} \)-bosons, \( L_j \) does not generate a dispersion for the flat branch because flatness comes from the fact that the hopping of the \( x^2 - y^2 \) electron along the \( z \)-axis is forbidden. We also note that the orbital angular momentum is quenched in \( \epsilon_{f} \) orbitals, and the spin-orbit interaction is ineffective.

The orbital liquid, on the other hand, should be very sensitive to the anisotropy between \( x \)-, \( y \)-, and \( z \)-axis. In this respect, in the layered materials, e.g., \( L_{a1} \_Sr_{1+2} \_MnO_4 \) and \( L_{a2} \_Sr_{1+2} \_MnO_7 \), the orbital liquid should be absent. Experimentally the incoherent band extending to \( \omega \sim 1 \text{eV} \) seems to be missing in \( \sigma(\omega) \) in these materials [21]. Another test on our scenario is the effects of the uniaxial pressure. We expect \( \sigma(\omega) \) becomes anisotropic and becomes sharp in the more conductive plane.

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