Microscopic Study of Electronic and Magnetic Properties for Ir Oxide

Tomonori Shirakawa*, Hiroshi Watanabe, and Seiji Yunoki

Computational Condensed Matter Physics Laboratory, RIKEN ASI, Wako, Saitama 351-0198, Japan, CREST, Japan Science and Technology Agency (JST), Kawaguchi, Saitama 332-0012, Japan, and Computational Materials Science Research Team, RIKEN AICS, Kobe, Hyogo 650-0047, Japan

The exact diagonalization and the variational cluster approximation (VCA) are used to study the nature of a novel Mott insulator induced by a strong spin-orbit coupling for a two-dimensional three-band Hubbard model consisting of the $t_{2g}$ manifold of 5d orbitals. To characterize the ground state, we introduce a local Kramer's doublet which can represent a state with effective angular momentum $J_{\text{eff}} = \frac{|S - \mathbf{L}|}{2}$ as well as spin $S = \frac{1}{2}$. Our systematic study of the pseudo-spin structure factor defined by the Kramer's doublet shows that the $J_{\text{eff}} = \frac{1}{2}$ Mott insulator is smoothly connected to the $S = \frac{1}{2}$ Mott insulator. Using the Kramer's doublet as a variational state for the VCA, we examine the one-particle excitations for the Mott insulating phase. These results are compared with recent experiments on Sr$_2$IrO$_4$.

KEYWORDS: 5d electrons, spin-orbit coupling, Mott insulator, three-band Hubbard model, variational cluster approximation

1. Introduction

5d transition metal oxides have attracted much attention because of their unique properties caused by a strong spin-orbit coupling (SOC) $\lambda$ for 5d transition elements. One of such materials is Sr$_2$IrO$_4$ in a layered perovskite structure of K$_2$NiF$_4$ type.$^{1,2}$ While Sr$_2$IrO$_4$ was first synthesized more than fifty years ago,$^1$ it is only in 90’s that its electronic properties has been studied systematically as an analogous system to high-T$_c$ cuprate superconductors. An inelastic neutron scattering experiment has found that the ground state of Sr$_2$IrO$_4$ is antiferromagnetically ordered with weak ferromagnetic moment, similar to that for the parent compounds of cuprates.$^2$ The early studies then concluded that the ground state of Sr$_2$IrO$_4$ was a spin $S = 1/2$ Mott insulator with unpaired electrons occupying a half-filled $d_{xy}$ band, which is split off upward compared to $d_{yz}$ and $d_{zx}$ orbitals due to the crystalline electrostatic field with elongation of the Ir-O bond along $z$ direction.$^{3}$ However, very recently, x-ray scattering experiments have revealed that the ground state is instead close to a $J_{\text{eff}} = 1/2$ Mott insulator.$^4$ Here, $J_{\text{eff}} = |S - \mathbf{L}|$ is an effective total angular momentum defined in the $t_{2g}$ manifold with the orbital angular momentum $\mathbf{L}$. Note also that the $J_{\text{eff}} = 1/2$ state corresponds to the ground state in the atomic limit with large $\lambda$.

Motivated by these experiments, we shall study theoretically the electronic and magnetic properties of Sr$_2$IrO$_4$ using a three-band Hubbard model with the SOC.$^5$ First, we introduce a local Kramer’s doublet which can represent a $S = 1/2$ state as well as a $J_{\text{eff}} = 1/2$ state.$^6$ Employing the exact diagonalization method, we show that the local Kramer’s doublet can describe smoothly both the $S = 1/2$ and $J_{\text{eff}} = 1/2$ Mott insulators with varying $\lambda$. This strongly indicates that there exists no apparent symmetry change between these two extreme states. We then employ the variational cluster approximation$^7$ (VCA) method based on the self-energy functional theory$^8$ (SFT) to examine the one-particle excitations in the Mott insulating phase. We find that, for a realistic set of model parameters for Sr$_2$IrO$_4$, most of the unoccupied state, i.e., the upper Hubbard band, can be well describe by the $J_{\text{eff}} = 1/2$ state. This result is in good qualitative agreement with the recent experimental observation.$^4$ We also discuss the effects of SOC and local Coulomb interactions on the one-particle excitations.

The paper is organized as follows. After describing the three-band Hubbard model in Sec. 2, the local Kramer’s doublet is introduced in Sec. 3 and compared with the numerically exact ground state of the model. Using VCA based on SFT, the one-particle excitations are studied in Sec. 4. The paper is concluded in Sec. 5.

2. Model

Since the crystalline electrostatic field is much larger than the SOC and the local Coulomb interactions,$^10$ the local electronic configuration of Ir$^{4+}$ ion in Sr$_2$IrO$_4$ is the low-spin state of ($t_{2g}$)$^5$. Therefore, we consider the following effective three-band Hubbard model, consisting of three $d$ orbitals ($d_{xy}$, $d_{yz}$, and $d_{zx}$), on the square lattice

$\begin{align*}
H &= H_{\text{kin}} + H_{\text{so}} + H_{\text{int}} \\
H_{\text{kin}} &= \sum_{k\alpha\sigma} \epsilon_k c_{k\alpha\sigma}^\dagger c_{k\alpha\sigma} \\
H_{\text{so}} &= \lambda \sum_{r} \mathbf{L}_r \cdot \mathbf{s}_r \\
H_{\text{int}} &= U \sum_{r\alpha} n_{r\alpha\uparrow} n_{r\alpha\downarrow} + \frac{U'}{2} \sum_{r\alpha} \sum_{\alpha'\beta} n_{r\alpha\alpha'} n_{r\beta\beta'} \\
&+ \frac{1}{2} (U' - J) \sum_{r\sigma} \sum_{\alpha'\beta} n_{r\alpha\sigma} n_{r\beta\sigma}
\end{align*}$

$^*$E-mail: t-shirakawa@riken.jp
Here, $c_{\rho \sigma}$ ($c_{\rho \sigma}^\dagger$) is the annihilation (creation) operator of an electron with spin $\sigma$ ($\sigma = \uparrow, \downarrow$) and orbital $\alpha$ ($\alpha = xy, yz, zy, and zx$) at site $r$. $c_{\rho \alpha \sigma}$ is the Fourier transform of $c_{\rho \sigma}$, $c_k$ is the dispersion of orbital $\alpha$

\[ c_k^{xy} = -2t_1 \cos k_x \cos k_y - t_2 \cos k_x \cos k_y - 2t_3 \cos k_x \cos k_y + \Delta, \]

\[ c_k^{yz} = -2t_4 \cos k_y - 2t_5 \cos k_z, \]

\[ c_k^{zx} = -2t_4 \cos k_x - 2t_5 \cos k_y, \]

where $t_1$, $t_2$, and $t_3$ correspond to the hopping integrals for $d_{xy}$ orbitals located at the nearest, next nearest, and third nearest neighbor sites, respectively, $t_4$ and $t_5$ are the next nearest hopping integrals for $d_{yz}$ ($d_{zx}$) orbital in $y$ ($x$) and $x$ ($y$) directions, respectively. $\Delta$ is an energy level difference between $d_{xy}$ orbital and the other orbitals ($d_{yz}$ and $d_{zx}$), which is naturally expected due to the large crystalline electrostatic field inducing tetragonal splitting. $H_{so}$ is the SOC term represented in the following matrix form

\[ 2\ell_r \cdot s_r = \sum \left( \begin{array}{ccc} c_{rxy\sigma} & c_{ryz\sigma} \r c_{rxz\sigma} \end{array} \right) \times \left( \begin{array}{ccc} 0 & -s & i \r -s & 0 & is \r i & is & 0 \end{array} \right) \left( \begin{array}{c} c_{rxy\sigma} \r c_{ryz\sigma} \r c_{rxz\sigma} \end{array} \right), \]

where $s = +1$ ($-1$) for $\sigma = \uparrow$ ($\downarrow$), and $\bar{\sigma}$ indicates the opposite spin of $\sigma$. Finally, we introduce, for the local Coulomb interactions, the intra-orbital ($U$) and the inter-orbital ($U'$) Coulomb interactions, the Hund’s coupling $J$, and the pair-hopping $J'$, with $U = U' + 2J$ and $J = J'$.

As shown in Table I, we use two sets of parameters indicated by ”Simplified model” and ”Sr$_2$IrO$_4$”. The parameter set ”Sr$_2$IrO$_4$” is a realistic set of parameters determined by fitting the band dispersion obtained from the first principles calculations based on density functional theory.  

### 3. Exact diagonalization study

First, we have obtained the phase diagram for the simplified model with $U/t_1 = 8$ and $J/U = 0.15$ using exact diagonalization technique for a 4-site cluster.

Let us briefly summarize the phase diagram of $\Delta$ vs. $\lambda$. In region (I) $\Delta/t_1 \lesssim -0.3$ and $\lambda/t_1 \lesssim 0.15$, $d_{yz}$ and $d_{zx}$ orbitals are magnetically active, whereas most of $d_{xy}$ orbital is fully occupied. The degeneracy of $d_{xy}$ and $d_{zx}$ orbital leads to a ferromagnetic state with antiferro orbital ordering, which is expected by the second-order perturbation theory from the strong coupling limit in the presence of Hund’s coupling. In region (II) $-0.3 \lesssim \Delta/t_1 \lesssim 0.4$ and $\lambda/t_1 \lesssim 0.2$, the hole density is $n_{xy} \sim n_{yz} + n_{xz} = 1/2 : 1/2$ for $\lambda = 0$, and stripe-like spin correlations, characterized by $q = (\pi, 0)$ and $(0, \pi)$, become dominant. Finally, in region (III) $\Delta/t_1 \sim 1$ or $\lambda/t_1 \gtrsim 0.2$, an antiferromagnetic insulating phase appears, including both $S = 1/2$ and $J_{eff} = 1/2$ Mott insulators in the limit of $\lambda = 0$ and $\infty$, respectively.

Let us now discuss closely the ground state properties in region (III). We first introduce the following local Kramer’s doublet

\[ a_{\rho \bar{\sigma}} = s \cos \theta c_{rxy\sigma} + \frac{\sin \theta}{\sqrt{2}} (c_{ryz\sigma} + i s c_{rxz\sigma}), \]

which includes the two limiting states, namely, $S = 1/2$ ($d_{xy}$) for $\theta = 0$ and $J_{eff} = 1/2$ for $\theta = \text{arctan} \sqrt{2}/3 \sim 54.74^\circ$. In the atomic limit, the eigenstate of the highest level of $H_{so}$ in the presence of $\Delta$ is generally expressed by this state. Here, we shall optimize $\theta$ by minimizing the hole density $n_{\rho \bar{\sigma}} = \langle \psi_0 | a_{\rho \bar{\sigma}} c_{r\rho\sigma}^\dagger | \psi_0 \rangle$. This quantity should be $n_{\rho \bar{\sigma}} = 0.5$ if $c_{r\rho\sigma}^\dagger$ is a well-defined particle. The numerically obtained optimized $\theta$ is summarized in Fig. 1 (d) for the simplified model, where we can see that the optimized $\theta$ varies smoothly with $\lambda$. The deviation of $n_{\rho \bar{\sigma}}$ from 0.5 is found less than 1.2% for a range of $\lambda$ studied, indicating that the ground state is well described by the Kramer’s doublet.

Next, let us study the magnetic properties in region (III) of the phase diagram. For this purpose, we first

| Parameters | Simplified model | Sr$_2$IrO$_4$ |
|------------|-----------------|--------------|
| $t_1$      | 0.36 eV         | 0.36 eV      |
| $t_2$      | 0.00 eV         | 0.18 eV      |
| $t_3$      | 0.00 eV         | 0.09 eV      |
| $t_4$      | 0.36 eV         | 0.37 eV      |
| $t_5$      | 0.00 eV         | 0.06 eV      |
| $\Delta$   | 0.36 eV         | -0.36 eV     |
| $\lambda$  | —               | 0.37 eV      |

**Table 1.** Two sets of parameters used.
define the structure factor for a local angular momentum operator $O_r^\mu$

$$C_\mu(q) = \frac{1}{N} \sum_{r,r'} e^{iq \cdot (r-r')} \langle \psi_0 | O_r^\mu \cdot O^\mu_{r'} | \psi_0 \rangle,$$

where $N$ is the number of lattice sites, and $|\psi_0\rangle$ indicates the ground state. The spin structure factor $C_S(q)$ is then obtained simply by setting

$$O_r^z = S_r = \frac{1}{2} \sum_{\alpha \sigma \sigma'} c^\dagger_{r \alpha \sigma} \sigma \sigma' c_{r \alpha \sigma'},$$

where $\sigma$ is the vector representation of Pauli matrices. The structure factor for the effective total angular momentum $C_{J_{eff}}(q)$ is defined by introducing the following local angular momentum operator

$$O_r^{J_{eff}} = S_r - \sum_{\alpha \sigma \sigma'} c^\dagger_{r \alpha \sigma} L_{\alpha \sigma} c_{r \alpha \sigma'},$$

where $L$ is the orbital angular momentum operator. Note that as long as the local bases are confined within $t_{2g}$ manifold, the matrix elements among $t_{2g}$ states are equivalent to those among $p$ states apart from minus sign.\(^{13}\) Finally, we define the structure factor for the Kramer’s doublet $C_{KD}(q)$ by introducing the following pseudo-spin $1/2$ operator

$$O_r^{KD} = \frac{1}{2} \sum_{\sigma \sigma'} a^\dagger_{r \theta \sigma} \sigma \sigma' a_{r \theta \sigma'},$$

where $a^\dagger_{r \theta \sigma}$ is given in Eq. (9).

The numerical results for these structure factors are shown in Fig. 1. For $\lambda = 1$, the ground state is the $S = 1/2$ Mott insulator, where the hole density of $d_{xy}$ orbital is exactly 1 whereby the model is equivalent to the single-band Hubbard model. With increasing $\lambda$, we can see in Fig. 1 (a)–(c) that the values of $C_{J_{eff}}(q)$ approach to those of $C_S(q)$ for $\lambda = 1$. This indicates that the ground state in the limit of large $\lambda$ is represented simply by an antiferromagnetic ordering of $J_{eff} = 1/2$ angular momentum. Finally, we also find in Fig. 1 (a)–(c) almost no $\lambda$ dependence on $C_{KD}(q)$, which strongly suggests that the ground state for different values of $\lambda$ can be well described by a state with alternative alignment of the Kramer’s doublet pseudo-spin. Therefore, we conclude that the $S = 1/2$ and $J_{eff} = 1/2$ Mott insulators, the two extreme states for $\lambda = 0$ and $\infty$, are smoothly connected with no apparent symmetry change.

4. Variational Cluster Approximation Study

We now adopt the VCA method\(^7\) based on the SFT\(^8\) to study the low-energy one-particle excitations. This method takes into account precisely the effects of short-range static and dynamical correlations, and thus it is superior to a simple mean field approximation. The SFT introduces a reference Hamiltonian $H'$ with the same two-body interactions as $H$ but with a different one-body part $t'$, and $H'$ may be solved numerically exactly on a finite cluster. An approximate grand potential for $H$ is given in a functional form by $\Omega(t') = \Omega' - \text{Tr} \ln(-\tilde{G}_0^{-1} + \tilde{\Sigma}(t')) + \text{Tr} \ln(-\tilde{G}^{-1}(t'))$, where $\Omega'$, $\tilde{\Sigma}(t')$, and $\tilde{G}(t')$ are the ground potential, self-energy, and Green’s function of the reference system $H'$, respectively. $\tilde{G}_0$ is the non-interacting Green’s function of $H$. The variational condition $\partial \Omega(t')/\partial t' = 0$ determines an appropriate reference system $H'$ which describes the original system $H$ approximately.

To study the symmetry-broken long-range-ordered states in the VCA, we introduce suitably chosen fictitious Weiss fields in a set of variational parameters $t'$. In this study, we introduce the Weiss field acting on the Kramer’s doublet

$$H_{AF} = h_{AF} \sum_{r \theta \sigma} c_{r \theta \sigma'}^\dagger c_{r \theta \sigma'},$$

with $Q = (\pi, \pi)$. Note that we only consider the Weiss field corresponding to the in-plane antiferromagnetic ordering since the energy for the states with the out-of-plane antiferromagnetic ordering is always higher than that for the in-plane one, as reported previously.\(^5\)

Fig. 2 shows $\Omega(h_{AF}, \theta) - \Omega(0, \theta)$ per site for different values of $\theta$ and with $U = 1.44$ eV, $J/U = 0.15$, and the realistic set of parameters for Sr$_2$IrO$_4$ listed in Table I. The fact that this quantity has a minimum at a finite value of $h_{AF}$ indicates that the ground state is antiferromagnetically ordered. Carrying out careful calculations, we also find that the optimal value of $\theta$ is $\theta \approx 25^\circ$ for this set of model parameters.

Let us now study the one-particle excitations using the Green’s function optimized above. The results for the momentum resolved one-particle excitation spectra and the density of states are shown in Fig. 3. Here, to understand the effects of $\lambda$ as well as $U$, we choose three different sets of parameters with (a) and (d): $\lambda = U = J = 0$, (b) and (e): $\lambda = 0.37$ eV and $U = J = 0$, and (c) and (f): $\lambda = 0.37$ eV, $U = 1.44$ eV, and $J/U = 0.15$.

As clearly seen in Fig. 3 (a), when the SOC and the local Coulomb interactions are absent, the bands consist of two one-dimension-like narrower bands (ranging from $-1$ eV to 0 eV), which are originated from $d_{xz}$ and $d_{yz}$ orbitals, and the remaining band with broader band width extending from $-3.2$ eV to $0.5$ eV, which has a characteristic of $d_{xy}$. As shown in Fig. 3 (d), the projected density of states onto $J_{eff} = 1/2$ extends to the
whole energy band, indicating that $J_{\text{eff}} = 1/2$ is not a good quantity to describe the one-particle excitations. When the SOC is turned on in Fig. 3 (b) and (e), the three different bands are observed, i.e., the highest one located from $-1.1$ to $0.6$ eV in energy, the intermediate one ranging from $-1.4$ to $0.2$ eV, and the lowest one extending from $-3.2$ to $-0.2$ eV. For this case, we can observe that while the partial density of states projected onto $J_{\text{eff}} = 1/2$ is still extended to the whole energy region, most of the unoccupied states (from $\sim 0.2$ to $\sim 0.6$ eV) have a characteristic of $J_{\text{eff}} = 1/2$. Finally, when we include the Coulomb interactions in Fig. 3 (c) and (f), we can clearly see that the “upper Hubbard band”, which is located above the Fermi level, is well separated from the valence band. We can also see in Fig. 3 (f) that almost all the unoccupied states is of $J_{\text{eff}} = 1/2$ characteristic, which provides a numerical evidence that the ground state is well characterized by the $J_{\text{eff}} = 1/2$ Mott insulator. This finding is in good qualitative agreement with the recent experiments on Sr$_2$IrO$_4$.\(^4\)

5. Conclusions

We have employed the exact diagonalization method to study the ground state phase diagram for the three-band Hubbard model with the SOC. We have found that in the Mott insulating phase the ground state can be well described by the Kramer’s doublet. This suggests that no apparent symmetry change exists between the two extreme states, i.e., the $S = 1/2$ Mott insulator and the $J_{\text{eff}} = 1/2$ Mott insulator, which appear for $\lambda = 0$ and $\infty$, respectively. We have also studied the one-particle excitations using the VCA, and found that both $\lambda$ and $U$ are essential to realize the $J_{\text{eff}} = 1/2$ Mott insulator, where the unoccupied states are mostly of $J_{\text{eff}} = 1/2$ characteristic.

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