Origin of the Heavy Fermion Behavior in \( \text{Ca}_{2-x}\text{Sr}_x\text{RuO}_4 \): Roles of Coulomb Interaction and the Rotation of \( \text{RuO}_6 \) octahedra

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We study the electronic states for \( \text{Ca}_{2-x}\text{Sr}_x\text{RuO}_4 \) in \( 0.5 \leq x \leq 2 \) within the Gutzwiller approximation (GA) on the basis of the three-orbital Hubbard model for the Ru \( t_{2g} \) orbitals. The main effects of the Ca-substitution are taken into account as the changes of the \( dp \) hybridizations between the Ru \( 4d \) and O \( 2p \) orbitals. Using the numerical minimization of the energy obtained in the GA, we obtain the renormalization factor (RF) of the kinetic energy and total RF, which estimates the inverse of the mass enhancement, for three cases with the effective models of \( x = 2 \) and 0.5 and a special model. We find that the inverse of the total RF becomes the largest for the case of \( x = 0.5 \), and that the van Hove singularity, which is located on (below) the Fermi level for the special model (the effective model of \( x = 0.5 \)), plays a secondary role in enhancing the effective mass. Our calculation suggests that the heavy fermion behavior around \( x = 0.5 \) comes from the cooperative effects between moderately strong Coulomb interaction compared to the total bandwidth and the modification of the electronic structures due to the rotation of \( \text{RuO}_6 \) octahedra (i.e., the variation of the \( dp\pi \) hybridizations and the downward shift for the \( d_{xy} \) orbital). We propose that moderately strong electron correlation and the orbital-dependent modifications of the electronic structures due to the lattice distortions play important roles in the electronic states for \( \text{Ca}_{2-x}\text{Sr}_x\text{RuO}_4 \).

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I. INTRODUCTION

Strongly correlated electron systems with orbital degrees of freedom have attracted much interests due to a diversity of phenomena, e.g., a structure-sensitive superconducting transition temperature\( ^\ast \) a colossal magnetoresistance\, and an orbital ordering and the corresponding collective excitations. Among them, the layered perovskite \( \text{Ca}_{2-x}\text{Sr}_x\text{RuO}_4 \) has rich ground states in which the Ru \( 4d \) orbitals play important roles in determining the electronic states.

In \( \text{Ca}_{2-x}\text{Sr}_x\text{RuO}_4 \), substitution of \( \text{Ca}^{2+} \) for \( \text{Sr}^{2+} \) causes three kinds of lattice distortions, i.e., rotation, tilting, and flattening, which affect the electronic structures. Starting from \( x = 2 \) (i.e., \( \text{Sr}_2\text{RuO}_4 \)), which is a spin-triplet superconductor, the ground state changes from the spin-triplet superconductor to a paramagnetic (PM) metal in the range of \( 0.5 \leq x < 2 \). In particular, in the range of \( 0.5 \leq x < 1.5 \), the Ca substitution induces a rotation of \( \text{RuO}_6 \) octahedra around the \( c \) axis (see Fig. 1), while the crystalline structure remains tetragonal with a unit cell doubled. Except the vicinity of \( x = 2 \), the spin susceptibility behaves like the Curie-Weiss type with a Curie constant corresponding to nearly \( S = 1/2 \), and the Weiss temperature becomes nearly zero at \( x = 0.5 \). In the range of \( 0.2 \leq x < 0.5 \), there occurs a structural transition from tetragonal phase to orthorhombic phase at low temperatures, and the Ca substitution induces the tilting of \( \text{RuO}_6 \) octahedra around a non-symmetric axis in the basal plane. Also, in this range, the spin susceptibility has a peak at some temperature, and the ground state becomes an antiferromagnetically correlated metal. In the range of \( 0 \leq x < 0.2 \), a flattening of \( \text{RuO}_6 \) octahedra along the \( c \) axis is induced and there is a first-order metal-insulator transition: the ground state becomes the antiferromagnetic insulator.\n
Most surprisingly, the coefficient of the electronic specific heat, \( \gamma_e \), at low temperatures becomes large around \( x = 0.5 \). The largest value of \( \gamma_e \) reaches 255 mJ/molK\(^2 \) at \( x = 0.5 \); this value is about 25 times of that obtained in the density-functional calculation for \( \text{Sr}_3\text{RuO}_4 \) within local-density approximation (LDA). A similar mass enhancement has been observed in the optical conductivity measurement by using the extended Drude model. In addition, the spin susceptibility and Hall coefficient measured by applying the magnetic field perpendicular to \( ab \) plane show peak structures at \( T_\ast \sim 10 \text{ K} \) for \( x = 0.3 \) which are similar to those obtained for \( \text{UPt}_3 \). These experimental results indicate a formation of heavy fermions (HFs) around \( x = 0.5 \).

Although there have been extensive theoretical works, the origin of this HF behavior has not been clarified yet. Some studies based on the dynamical mean-field theory (DMFT) have proposed that the HF behavior results from the orbital-selective Mott transition (OSMT) for the \( d_{xz} \) and \( d_{yz} \) orbitals; the OSMT is defined as a partial disappearance of quasiparticles only for some of the conducting bands. However, this contradicts with another DMFT calculation which has used a realistic model of \( \text{Ca}_{2-x}\text{Sr}_x\text{RuO}_4 \) in \( 0.5 \leq x \leq 2 \): the OSMT does not appear.

The OSMT for the \( d_{xz} \) and \( d_{yz} \) orbitals also contradicts with several experiments in \( \text{Ca}_{2-x}\text{Sr}_x\text{RuO}_4 \) around \( x = 0.5 \). The angle-resolved photoemission spectroscopy (ARPES) measurement for \( x = 0.5 \) and 2 has shown that the Ca substitution does not modify the topologies of the Fermi surfaces (FSs) for the \( d_{xz} \) and \( d_{yz} \) orbitals. This result is inconsistent with the proposal of the OSMT.
since the partial Mott gap should drastically affect the topologies of the FSs. In addition, the optical conductivity measurement\[44\] for Ca$_{2-x}$Sr$_x$RuO$_4$ in 0.06 ≤ x ≤ 2 has found that the Drude weights depend weakly on the Ca concentration. This is consistent with the experimentally observed tendency of the HF behavior around consistent with the experimentally observed tendency of the effective mass. These results are consistent with the ARPES measurement since the latter shows a small change of the FS from that for Sr$_2$RuO$_4$. Note that the FS for the $d_{xy}$ orbital changes from an electron pocket for $x = 2$ to a hole pocket for $x = 0.5$.

The aim of this paper is to discuss the qualitative origin of the HF behavior in particular near $x = 0.5$ for Ca$_{2-x}$Sr$_x$RuO$_4$. We study the electronic states for 0.5 ≤ x ≤ 2 within the Gutzwiller approximation (GA) on the basis of the three-orbital Hubbard model for the Ru $t_{2g}$ orbitals (i.e., $d_{xz}$, $d_{yz}$, and $d_{xy}$ orbitals). We assume that the Ca substitution affects the electronic structures mainly by the changes of the $dp$ hybridizations between the Ru $4d$ and O $2p$ orbitals. Actually, the density-functional calculation within the LDA has found that the rotation of RuO$_6$ octahedra affects the electronic structures for Ca$_{2-x}$Sr$_x$RuO$_4$ in 0.5 ≤ x ≤ 2.\[21\] The GA is used to include the effects of electron correlation nonperturbatively, in which the effects lead to the renormalization of the kinetic energy.\[22,23\]

Using the numerical minimization of the energy obtained in the GA, we obtain the renormalization factor (RF) of the kinetic energy for the Ru $t_{2g}$ orbitals and total RF, which estimates the inverse of the mass enhancement, for the effective models of $x = 2$ and 0.5. We find that the difference between the total RFs for the cases of $x = 2$ and 0.5 becomes large as the intraorbital Coulomb interaction is strong; this arises from the criticality approaching the usual Mott transition, where the occupation numbers for the $d_{xz/yz}$ and $d_{xy}$ orbitals are 1 and 2, respectively. In addition, we analyze a special model in which the van Hove singularity (vHs) for the $d_{xy}$ orbital is located on the Fermi level. We find that the total RF is smaller for the effective model of $x = 0.5$ than that for the special model; the vHs plays a secondary role in enhancing the effective mass. These results are consistent with the experimentally observed tendency of the effective mass in 0.5 ≤ x ≤ 2, i.e., monotonic increase of $\gamma_e$ towards $x = 0.5$.\[43\] Our calculation suggests that the HF behavior around $x = 0.5$ comes from the cooperative effects between moderately strong Coulomb interaction compared with the total bandwidth and the significant modification of the electronic structures for the Ru $t_{2g}$ orbitals due to the rotation of RuO$_6$ octahedra; the latter includes both the variation of the $dp\pi$ hybridizations and the downward shift for the $d_{xy}$ orbital.

The paper is organized as follows. Section II is devoted to the explanations of the method to take account of the main effects of the Ca substitution on the electronic structures in 0.5 ≤ x ≤ 2 and the GA for a PM state of the degenerate $d_{xz}$ and $d_{yz}$ orbitals and the $d_{xy}$ orbital. In Sec. III, we show the numerical results of the GA for three cases with the effective models of $x = 2$ and 0.5 and the special model. In Sec. IV, we compare our results with previous theoretical studies and remark on the correspondence of our results with experimental results. The paper concludes with a summary of our results in Sec. V.

II. FORMULATION

In the following, we choose the coordinates, x, y, and z, in the directions of the bonds between Ru and O ions at φ = 0°, where φ is an angle of the rotation of RuO$_6$ octahedra [see Fig. 1(b)]. Namely, the coordinates are fixed in the directions of Sr$_2$RuO$_4$ with φ = 0° even for the cases with finite values of φ. For convenience, the five Ru $4d$ orbitals, $d_{xz}$, $d_{yz}$, $d_{xy}$, $d_{xz/yz}$, and $d_{3z^2−r^2}$, are labeled 1, 2, 3, 4, and 5, respectively.

According to the density-functional calculations\[27,28\] for Sr$_2$RuO$_4$ within the LDA, the antibonding bands of the Ru $t_{2g}$ and O $2p$ orbitals form the conducting bands in the vicinity of the Fermi level, and the density of states (DOS) near the Fermi level is originated mainly from the

![FIG. 1: Schematic pictures of a xy plane of RuO$_6$ octahedra for (a) 1.5 ≤ x ≤ 2 and (b) 0.5 ≤ x < 1.5. Black (white) circles represent Ru (O) ions. φ is the angle of the rotation of RuO$_6$ octahedra. A and B are the indices of two sublattices.](image)

![FIG. 2: (Color online) Band structure of the Ru $t_{2g}$ orbitals for the effective model of x = 2. The dashed black line represents the chemical potential.](image)
Ru $t_{2g}$ orbitals. The partial density of states (pDOS) for the O 2p orbitals is roughly a quarter of those for the Ru $t_{2g}$ orbitals. In addition, the x-ray measurements in Ca$_{2-x}$Sr$_x$RuO$_4$ have shown that the crystalline-electric-field (CEF) energy between the Ru $e_g$ orbitals and Ru $t_{2g}$ orbitals is of the order of 1 eV.\cite{22,29} Thus, the Ru $t_{2g}$ orbitals play main roles in determining the electronic states for Ca$_{2-x}$Sr$_x$RuO$_4$ at low temperatures. In Sec. IV, we remark on the roles of the Ru $e_g$ and O 2p orbitals.

In order to study the electronic states, we use the three-orbital Hubbard model for the Ru $t_{2g}$ orbitals. The unit cell contains one Ru atom for $1.5 \leq x \leq 2$, while it contains two Ru atoms for $0.5 \leq x < 1.5$ due to the rotation of RuO$_6$ octahedra. As shown in Fig. 4(b), the directions of the rotation alternate in the two-dimensional square lattice, leading to a unit cell doubled.

The noninteracting Hamiltonian is

$$
\hat{H}_0 = -\sum_{i,j} \sum_{a,b=1}^3 \sum_\sigma \langle t^{a\sigma}_{ij} (\phi) \hat{c}_{i\sigma a} \hat{c}_{j\sigma b} + \text{H.c.} \rangle - \mu \sum_i \sum_{a=1}^3 \hat{n}_{ia},
$$

(1)

where $\hat{c}_{i\sigma a}^\dagger$ ($\hat{c}_{i\sigma a}$) is the creation (annihilation) operator that creates (annihilates) an electron in $t_{2g}$ orbital $a(=1,2,3)$ with spin $\sigma(=\uparrow, \downarrow)$ at site $i$, $\hat{n}_{ia} = \sum_\sigma \hat{n}_{i\sigma a} = \sum_\sigma \hat{c}_{i\sigma a}^\dagger \hat{c}_{i\sigma a}$, and H.c. means the Hermitian conjugate. Here, $t^{a\sigma}_{ij}(\phi)$ and $\mu$ denote the values of in-plane hopping integrals at an angle $\phi$ and the chemical potential, respectively. $\mu$ is determined so as to satisfy $n_\sigma = 4$ with $n_\sigma$ being the total occupation number for the Ru $t_{2g}$ orbitals. For simplicity, we neglect the effect of the spin-orbit interaction on the electronic structures; the validity is addressed in Sec. IV.

The hopping integrals for Sr$_2$RuO$_4$ with $\phi = 0^\circ$ are determined\cite{22} so as to reproduce the FSs obtained in the de Haas-van Alphen effect.\cite{22} The dispersions are given by

$$
e_{11}(k,0^\circ) = -2t_1 \cos k_x - 2t_2 \cos k_y - \mu,
$$

(2)

$$
e_{22}(k,0^\circ) = -2t_2 \cos k_x - 2t_1 \cos k_y - \mu,
$$

(3)

$$
e_{33}(k,0^\circ) = -2t_3(\cos k_x + \cos k_y) - 4t_4 \cos k_x \cos k_y - \mu,
$$

(4)

$$
e_{ab}(k,0^\circ) = 0 \quad \text{for} \quad a \neq b,
$$

(5)

where $t_1/t_3 = 1.5$, $t_2/t_3 = 0.2$, and $t_4/t_3 = 0.4$. In this tight-binding model, we neglect both the weak hybridization between the $d_{xz}$ and $d_{yz}$ orbitals and the difference of the CEF energy between the $d_{xz}/yz$ and $d_{xy}$ orbitals for simplicity.\cite{23} In this work, we set $t_3 = 0.45$ eV to make $W_{\text{tot}}$ about 4 eV. Figures 2–4 show the band structure of the Ru $t_{2g}$ orbitals, the FSs, and the DOS, respectively.

In the next section, we describe the dependence of the dispersions on $\phi$ for $0.5 \leq x < 1.5$.

The interacting Hamiltonian is

$$
\hat{H}_\text{int} = U \sum_{i\sigma} \hat{n}_{i\sigma a} \hat{n}_{i\sigma b} + U' \sum_{i a>b} \hat{n}_{i\sigma a} \hat{n}_{i\sigma b}
$$

$$
- J_H \sum_{i a>b} (2 \hat{\sigma}_{i\sigma a} \cdot \hat{\sigma}_{i\sigma b} + \frac{1}{2} \hat{n}_{i\sigma a} \hat{n}_{i\sigma b}),
$$

(6)

where $U$, $U'$, and $J_H$ are the intraorbital Coulomb interaction, the interorbital Coulomb interaction, and the Hund's rule coupling; $\hat{\sigma}_{i\sigma a}$ is defined as $\hat{\sigma}_{i\sigma a} = (1/2) \sum_{\sigma',\sigma} \hat{c}_{i\sigma a}^\dagger \sigma \sigma' \hat{c}_{i\sigma a}^\sigma \sigma'$ with $\sigma, \sigma'$ being the Pauli matrices. In the interacting Hamiltonian, we have neglected both the pair hopping $J'$ and the transverse components of $J_H$ for simplicity; the roles of these terms are discussed in Sec. IV. We thus consider the following Hamiltonian in the absence of the rotation of RuO$_6$ octahedra:

$$
\hat{H}_0 + \hat{H}_\text{int}.
$$

(7)

### A. Effects of the Ca substitution on the electronic structures in $0.5 \leq x \leq 2$

As described in Sec. I, the Ca substitution induces the rotation of RuO$_6$ octahedra along the $c$ axis in $0.5 \leq x < 1.5$. In order to take account of effects of the Ca substitution on the electronic structure, we assume that the main effects of the Ca substitution are the changes of the $d_{p}$ hybridizations due to this rotation. As shown in Fig. 4(b), this rotation changes both the Ru-Ru lengths and the overlap integrals between the Ru $4d$...
FIG. 5: (Color online) Schematic picture of the in-plane $dp\pi$ hybridization of the Ru $d_{xz}$ orbital to the O $p_z$ orbital in the presence of the rotation of RuO$_6$ octahedra. $x$ and $y$ ($x'$ and $y'$) are the coordinates in non-rotated (rotated) frame. The difference of a color in the $d_{xz}$ orbital represents that of the sign of the wave function for the $d_{xz}$ orbital.

FIG. 6: FSs for the effective model of $x = 0.5$. The dashed line represents the folded Brillouin zone in the presence of the rotation of RuO$_6$ octahedra.

Fig. 5, we can represent the wave functions for the Ru 4$d$ and O 2$p$ orbitals in the non-rotated frame ($x, y, z$) by those in the rotated frame ($x', y', z'$):

$$
\psi_1(r) = \psi_{d_{xz}}(r) = \psi_{d_{xz}}(r) \cos \phi - \psi_{d_{y'z'}}(r) \sin \phi, \quad (8)
$$

$$
\psi_2(r) = \psi_{d_{xz}}(r) = \psi_{d_{xz}}(r) \sin \phi + \psi_{d_{y'z'}}(r) \cos \phi, \quad (9)
$$

$$
\psi_3(r) = \psi_{d_{y'z'}}(r) = \psi_{d_{y'z'}}(r) \cos 2\phi + \psi_{d_{x'z',y'}}(r) \sin 2\phi, \quad (10)
$$

$$
\psi_4(r) = \psi_{d_{x'z',y'}}(r) = -\psi_{d_{x'z',y'}}(r) \sin 2\phi + \psi_{d_{x'z',y'}}(r) \cos 2\phi, \quad (11)
$$

and $O$ 2$p$ orbitals keeping the Ru-O bond lengths constant. The former leads to negligible effects on the electronic structures since the angle dependence of the Ru-Ru lengths is $\cos \phi$, and the latter results in the change of the $dp$ hybridizations linear in $\phi$.

We first explain the method to construct the tight-binding model by taking into account the effects of the rotation of RuO$_6$ octahedra on the electronic structures. As shown in Fig. 5, the $dp$ hybridizations at $\phi = 0^\circ$ are $V_{1p_x}(0^\circ)$, $V_{3p_y}(0^\circ)$, and $V_{4p_y}(0^\circ)$ along the $x$ direction and $V_{2p_x}(0^\circ)$, $V_{3p_y}(0^\circ)$, and $V_{4p_y}(0^\circ)$ along the $y$ direction, respectively. There-

FIG. 7: (Color online) DOS for the effective model of $x = 0.5$. The dashed black line represents the chemical potential.

FIG. 8: (Color online) DOS for the special model. The dashed black line represents the chemical potential.
hopping integrals among the Ru hybrids, we obtain the following nearest-neighbor order perturbation processes with respect to these $dp_y$ in the $x$ direction, respectively. Using the second-order perturbation processes with respect to these $dp$ hybridizations, we obtain the following nearest-neighbor hopping integrals among the Ru $t_{2g}$ orbitals:

\begin{align}
t_{11}^{AB;x}(\phi) &= t_1 \cos^2 \phi, \\
t_{12}^{AB;x}(\phi) &= -\frac{1}{2} t_1 \sin 2\phi, \\
t_{21}^{AB;x}(\phi) &= -t_{12}^{AB;x}(\phi), \\
t_{22}^{AB;x}(\phi) &= t_2 - t_1 \sin^2 \phi, \\
t_{33}^{AB;x}(\phi) &= t_3 \cos^3 2\phi - t_5 \cos 2\phi \sin^2 2\phi + 2t_6 \cos 2\phi \sin^2 2\phi,
\end{align}

in the $x$ direction, and

\begin{align}
t_{11}^{AB;y}(\phi) &= t_2 - t_1 \sin^2 \phi, \\
t_{12}^{AB;y}(\phi) &= -\frac{1}{2} t_1 \sin 2\phi, \\
t_{21}^{AB;y}(\phi) &= -t_{12}^{AB;y}(\phi), \\
t_{22}^{AB;y}(\phi) &= t_1 \cos^2 \phi, \\
t_{33}^{AB;y}(\phi) &= t_3 \cos^3 2\phi - t_5 \cos 2\phi \sin^2 2\phi + 2t_6 \cos 2\phi \sin^2 2\phi,
\end{align}

in the $y$ direction, respectively. Here, the superscripts $A$ and $B$ denote the sublattices, and $t_1$, $t_2$, $t_3$, and $t_4$ are defined in Eqs. (2)–(4). In deriving Eqs. (23)–(32), we have assumed that the rotation of RuO$_6$ octahedra does not affect $t_2$ in Eqs. (2) and (3), respectively. Using the second-order perturbation process with respect to the $dp$ hybridization of the Ru $d_{xz/yz}$ orbital to the O $2p$ orbital, $t_1$ is given by

\begin{equation}
t_1 = \frac{V_{1p_x}(0^\circ)^2}{E_1(0^\circ) - E_{p_x}(0^\circ)} = \frac{V_{2p_x}(0^\circ)^2}{E_2(0^\circ) - E_{p_x}(0^\circ)}, \tag{33}
\end{equation}

where $E_{a}(\phi)$ and $E_b(\phi)$ are the CEF energies at $\phi$ for the Ru $t_{2g}$ orbital $a$ and the O $2p$ orbital $b$, respectively.
RuO$_6$ octahedra on the next-nearest-neighbor hopping integrals for the Ru 4$d$ orbitals.

The rotation of RuO$_6$ octahedra also induces the hybridization of the $d_{xy}$ orbital to the $d_{yz/zx}$ orbital although it is not included in Eqs. (23)–(32). Since the energy level for the $d_{xy}$ orbital is higher than that for the $d_{yz/zx}$ orbital, this hybridization leads to a downward shift of the $d_{xy}$ orbital. This effect is approximately taken into account as the difference of the CEF energy, $\Delta t_{2g}$, between the $d_{xz/yz}$ and $d_{xy}$ orbitals:

$$\hat{H}_{\text{CEF}} = \frac{\Delta t_{2g}}{3} \sum_i (\hat{n}_i \hat{n}_i + 2\hat{n}_i^2).$$  \hspace{1cm} (47)

In this work, we use $\Delta t_{2g}$ as a parameter. Combining this term and the noninteracting and interacting Hamiltonians, we consider the following Hamiltonian in the presence of the rotation of RuO$_6$ octahedra:

$$\hat{H}_0 + \hat{H}_{\text{int}} + \hat{H}_{\text{CEF}}. \hspace{1cm} (48)$$

In order to discuss the electronic state for $x = 0.5$, we set $\phi = 15^\circ$ and $(t_5, t_6, \Delta p_{2g}) = (0, 0, 0.42)$ (eV) so as to reproduce the FSs obtained in the ARPES measurements.\cite{Figures 8 and 7} The absence of the FS around $k = (\pi, 0)$ corresponds to the change of the FS for the $d_{xy}$ orbital from an electron pocket to a hole pocket. There are three main changes of the electronic structures due to the rotation of RuO$_6$ octahedra: the reduction of the bandwidth for the $d_{xy}$ orbital, the increase of the pDOS for the $d_{xy}$ orbital near the Fermi level, and the change of the FS for the $d_{xy}$ orbital from an electron pocket to a hole pocket. The bandwidth and pDOS for the $d_{xz/yz}$ orbital are little affected. These results are qualitatively consistent with those obtained in the density-functional calculation within the LDA\cite{Figures 8} or local-spin-density approximation.\cite{Figures 8}

We thus think that the present model is reasonable for the study of the electronic states in Ca$_{2-x}$Sr$_x$RuO$_4$ although the experimental value of $\phi$ is about 12.8$^\circ$ at $x = 0.5$.\cite{Figures 8}

In addition, we study a special model in which the vhs for the $d_{xy}$ orbital is located on the Fermi level in order to clarify the role of the vhs in enhancing the effective mass. We use the dispersions in Eqs. (38)–(46) setting $\phi = 15^\circ$ and $(t_5, t_6, \Delta t_{2g}) = (0, 0, 0.3)$ (eV); the difference between this case and the case of $x = 0.5$ is that in the values of $\Delta t_{2g}$. Figure 8 shows the DOS in this case.

**B. Gutzwiller approximation**

In this section, we explain the GA for a PM state consisting of the degenerate $d_{xz}$ and $d_{yz}$ orbitals and the $d_{xy}$ orbital. Let us define the Gutzwiller-type variational wave function as

$$|\Psi_G\rangle = \prod_{j=0}^{63} \prod_{l=0}^{63} (1 - (1 - g_l)\hat{P}_{j,l}) |\Psi_0\rangle. \hspace{1cm} (49)$$

where $|\Psi_0\rangle$ is the ground state for $\hat{H}_0$, $\hat{P}_{j,l}$ are the projection operators, and $g_l$ are the corresponding variational parameters for the $l$th configuration. There are $4^3 = 64$ configurations for each site $j$ since we have three orbitals and two kinds of spin degrees of freedom. The variational energy is given by

$$E_{\text{gs}} = \min_{\{g_l\}} \langle \Psi_G | \hat{H} | \Psi_G \rangle, \hspace{1cm} (50)$$

where $\min_{\{g_l\}}$ denotes the optimization with respect to $\{g_l\}$, and $\hat{H}$ is the total Hamiltonian given by Eq. (38). To calculate the expectation values, we use the GA\cite{Figures 8} in which the dependence of the Slater determinants on the configurations is neglected. For example, the square of the Slater determinant, $|\det U_{\uparrow\uparrow}(|\{r_{1\uparrow}^{N_\uparrow}\}|)^2$, for the electrons in $a = 1$ with $\sigma = \uparrow$ can be approximated as

$$|\det U_{\uparrow\uparrow}(|\{r_{1\uparrow}^{N_\uparrow}\}|)^2 \xrightarrow{\text{GA}} \prod_{a=1}^{N_\uparrow} (1 - n_{1\uparrow}^a)^{L - N_{\uparrow}}, \hspace{1cm} (51)$$

where $\{r_{1\uparrow}^{N_\uparrow}\}$ is a set of sites occupied by these electrons, $L$ is the number of sites, $N_{\uparrow}$ is the number of these electrons, and $n_{1\uparrow}^a$ is defined as an expectation value without the projection operators:

$$n_{1\uparrow}^a = \frac{1}{L} \sum_{j=0}^{L} \langle \hat{n}_{j\uparrow}^a | \Psi_G \rangle = \frac{1}{L} \sum_{j=0}^{L} \langle \hat{n}_{j\uparrow}^a | \Psi_G \rangle. \hspace{1cm} (52)$$

Using the GA, we can rewrite the denominator in Eq. (50) as

$$\langle \Psi_G | \Psi_G \rangle = \sum_{\{N_{\sigma}\}} \sum_{\{r_{a\sigma}^{N_{\sigma}}\}} \prod_{l=1}^{3} g_l^{2\Gamma_l(|\{r_{a\sigma}^{N_{\sigma}}\}|)} \prod_{a=1}^{N_\sigma} (1 - n_{a\sigma}^0)^{L - N_{a\sigma}} \prod_{l=1}^{L} P(L; \{N_{\sigma}\}). \hspace{1cm} (53)$$

with

$$P(L; \{N_{\sigma}\}) = \prod_{a=1}^{N_\sigma} (1 - n_{a\sigma}^0)^{L - N_{a\sigma}}. \hspace{1cm} (54)$$

Here, $\sum_{\{N_{a\sigma}\}}$ denotes the summation with respect to all the possible values $N_{a\sigma}$ ($a = 1, 2, 3, \sigma = \uparrow, \downarrow$), $\Gamma_l$ is the number of sites with the $l$th configuration, and the summation $\sum_{\{r_{l\uparrow}^{N_\uparrow}\}}$ is taken over all the possible values $\Gamma_l$ ($l = 0 - 63$) under the constraints

$$\sum_{l=0}^{63} \Gamma_l = L, \hspace{1cm} (55)$$

$$\sum_{l=0}^{63} \sum_{a=1,2} \Gamma_l n_{a\sigma} = \sum_{a=1,2} N_{a\sigma}, \hspace{1cm} (56)$$

$$\sum_{l=0}^{63} \Gamma_l n_{3\uparrow} = N_{3\uparrow}, \hspace{1cm} (57)$$

respectively.
where \( n_{l\alpha\sigma} \) is the number of electrons in orbital \( a \) with spin \( \sigma \) for the \( l \)th configuration; as we shall show, \( n_{l\alpha\sigma} \) plays important roles in calculating the expectation values within the GA.

Since the occupation number for each orbital is same in \( A \) and \( B \) sublattices, we do not need to take care of the sublattices in the GA. In other words, the formulation for a PM state consisting of the \( t_{2g} \) orbitals without the sublattice indices is sufficient to calculate the expectation values for a PM state consisting of the \( t_{2g} \) orbitals with the sublattice indices.

\((N_{1\sigma} + N_{2\sigma})\) and \(N_{3\sigma}\) are conserved quantum numbers although \( N_{1\sigma} \) and \( N_{2\sigma} \) are not conserved quantum numbers due to the finite hopping integral between the \( d_{xz} \) and \( d_{yz} \) orbitals. In general, the values of \((N_{1\sigma} + N_{2\sigma})\) and \(N_{3\sigma}\) may change in the presence of interactions for a system with orbital degrees of freedom. In the following, however, we assume that these values are equal to those in the absence of the interactions; e.g., for the effective model of \( x = 2 \), \((N_{1\sigma} + N_{2\sigma})/L = (n_1 + n_2) = 2.66\), \(N_{3\sigma}/L = n_3^0 = 1.33\). In Sec. IV, we address the effect of the variation of the occupation numbers due to electron correlation.

In the thermodynamic limit, we can approximate the summation with respect to \( \Gamma_l \) in Eqs. (53) to their largest terms:

\[
\langle \Psi_G | \Psi_G \rangle \overset{\text{GA}}{\to} \left( \prod_l g_l^2 \right) \frac{L!}{(\prod_l \Gamma_l)} P(L; \{ N_{l\alpha\sigma} \}),
\]

(58)

where \( \{ \Gamma_l \} \) is the set of \( \{ \Gamma_l \} \) that gives the largest term, \( \Gamma_l \) is given by

\[
\Gamma_l = L g_l^2 \exp \left( 1 + \lambda_0 + \sum_{\sigma} \lambda_{\sigma} n_{l\alpha\sigma} \right),
\]

(59)

where \((\lambda_0, \{ \lambda_{\sigma} \})\) are the Lagrange multipliers determined so as to satisfy the constraints Eqs. (63)-(67) for \( \{ \Gamma_l \} \). For simplicity, we assume that the following relations hold in the thermodynamic limit:

\[
\frac{N_{l\alpha\uparrow}}{L} = N_{l\alpha\downarrow},
\]

(60)

\[
\frac{N_{1\sigma}}{L} = \frac{N_{2\sigma}}{L}.
\]

(61)

Correspondingly, the Lagrange multipliers satisfy

\[
\lambda_{\alpha\uparrow} = \lambda_{\alpha\downarrow},
\]

(62)

\[
\lambda_{2\sigma} = \lambda_{1\sigma}.
\]

(63)

Similarly, the expectation values of \( \hat{n}_{i\alpha\sigma} \hat{n}_{j\beta\sigma'} \) and \( \hat{c}_{i\alpha\sigma}^\dagger \hat{c}_{j\beta\sigma'} \) can be rewritten within the GA as

\[
\langle \Psi_G | \hat{n}_{i\alpha\sigma} \hat{n}_{j\beta\sigma'} | \Psi_G \rangle \overset{\text{GA}}{\to} \sum_{l \Gamma_l} \left( \prod_l g_l^2 \right) \left( \prod_l \Gamma_l \right) P(L - 1; \{ N_{l\alpha\sigma} \}),
\]

\[
\times \frac{(L - 1)!}{(\prod_l \Gamma_l)} P(L - 1; \{ N_{l\alpha\sigma} \}),
\]

(64)

and

\[
\langle \Psi_G | \hat{c}_{i\alpha\sigma}^\dagger \hat{c}_{j\beta\sigma'} | \Psi_G \rangle \overset{\text{GA}}{\to} \sum_{l \Gamma_l} \left( \prod_l g_l^2 \right) \left( \prod_l \Gamma_l \right) P(L - 2; \{ N_{l\alpha\sigma} \}),
\]

(65)

with the constraints

\[
\sum_{l=0}^{63} \Gamma_l = L - 1,
\]

(66)

\[
\sum_{l=0}^{63} \sum_{a=1,2} \Gamma_l n_{l\alpha\sigma} = \sum_{a=1,2} N'_{l\alpha\sigma},
\]

(67)

\[
\sum_{l=0}^{63} \sum_{a=1,2} \Gamma_l n_{l\beta\sigma} = N'_{l\beta\sigma},
\]

(68)

\[
\sum_{l=0}^{63} \sum_{a=1,2} \Gamma_l n_{l\alpha\sigma} n_{l\beta\sigma'} = \sum_{a=1,2} N''_{l\alpha\sigma},
\]

(69)

\[
\sum_{l=0}^{63} \sum_{a=1,2} \Gamma_l n_{l\beta\sigma} n_{l\beta\sigma'} = \sum_{a=1,2} N''_{l\beta\sigma},
\]

(70)

\[
\sum_{l=0}^{63} \sum_{a=1,2} \Gamma_l n_{l\alpha\sigma} n_{l\beta\sigma} = \sum_{a=1,2} N''_{l\alpha\sigma}.
\]

(71)

Here, the summation with respect to \( l_i \) in Eq. (64) is taken for the configurations of site \( i \) in which there are at least an electron in orbital \( a \) with spin \( \sigma \) and an electron in orbital \( \beta \) with spin \( \sigma' \). In Eq. (65), \( l_i \) and \( l_j \) are the configurations of sites \( i \) and \( j \) after the hopping process \( \hat{c}_{i\alpha\sigma}^\dagger \hat{c}_{j\beta\sigma'} \) in which there are no electrons in orbital \( \beta \) with spin \( \sigma' \) at site \( j \) and there is at least an electron in orbital \( a \) with spin \( \sigma \) at site \( i \); \( l'_i \) and \( l'_j \) are similar configurations of sites \( i \) and \( j \) before the hopping process. The prime and double prime in the summations of Eqs. (64) and (65) represent these restrictions.

In the thermodynamic limit, we approximate the summation with respect to \( \Gamma_l \) in Eq. (64) to their largest terms for each configuration of \( l_i \) and the summation with respect to \( \Gamma''_l \) in Eq. (65) to their largest terms for the configurations of \( l_i, l'_j, l'_i, \) and \( l'_j \). Thus, these
expectation values become

\[
\langle \Psi_G| \hat{n}_{i\alpha\sigma} \hat{n}_{i\bar{\alpha}\sigma'}| \Psi_G \rangle \xrightarrow{\text{GA}} \sum_{i, l_i} g^{2}_{l_i} \langle \hat{P}_{i,l_i} \hat{n}_{i\alpha\sigma} \hat{n}_{i\bar{\alpha}\sigma'} \hat{P}_{i,l_i} \rangle_0 \left( \prod_{l} g^{2\Gamma_l} \right) \\
\times \left( \frac{(L-1)!}{\prod_{l} \Gamma_l} \right) P(L-1; \{N'_{\alpha\sigma}\}), \tag{72}
\]

and

\[
\langle \Psi_G| \hat{c}_{i\alpha\sigma}^\dagger \hat{c}_{j\bar{\alpha}\sigma'}| \Psi_G \rangle \xrightarrow{\text{GA}} \sum_{i, l_i, j, l'_j} g_{l_i} g_{l'_j} \langle \hat{P}_{i,l_i} \hat{P}_{j,l'_j} \hat{c}_{i\alpha\sigma}^\dagger \hat{c}_{j\bar{\alpha}\sigma'} \hat{P}_{i,l_i} \hat{P}_{j,l'_j} \rangle_0 \\
\times \left( \prod_{l} g^{2\Gamma_l} \right) \left( \frac{(L-2)!}{\prod_{l} \Gamma_l} \right) P(L-2; \{N'_{\alpha\sigma}\}), \tag{73}
\]

where \(\tilde{\Gamma}'_l\) and \(\tilde{\Gamma}''_l\) are given by

\[
\tilde{\Gamma}'_l = L g^2_l \exp\left( 1 + \lambda'_0 + \sum_{a=1}^{3} \lambda'_{\alpha a} n_{l\alpha a} \right), \tag{74}
\]

\[
\tilde{\Gamma}''_l = L g^2_l \exp\left( 1 + \lambda''_0 + \sum_{a=1}^{3} \lambda''_{\alpha a} n_{l\alpha a} \right), \tag{75}
\]

respectively. The Lagrange multipliers, \((\lambda'_0, \{\lambda'_{\alpha a}\})\) and \((\lambda''_0, \{\lambda''_{\alpha a}\})\), are determined so as to satisfy the constraints Eqs. (65)–(68) for \(\{\Gamma'_l\}\) and Eqs. (69)–(72) for \(\{\Gamma''_l\}\), respectively. For simplicity, we also assume that the following relations hold in the thermodynamic limit:

\[
\frac{N'_{\alpha a}}{L} = \frac{N'_{\bar{\alpha} \bar{a}}}{L}, \tag{76}
\]

\[
\frac{N'_{1\alpha}}{L} = \frac{N'_{2\bar{\alpha}}}{L}, \tag{77}
\]

and

\[
\frac{N''_{\alpha a}}{L} = \frac{N''_{\bar{\alpha} \bar{a}}}{L}, \tag{78}
\]

\[
\frac{N''_{1\alpha}}{L} = \frac{N''_{2\bar{\alpha}}}{L}. \tag{79}
\]

Correspondingly, the Lagrange multipliers satisfy

\[
\lambda'_{a \bar{a}} = \lambda'_{\bar{a} a}, \tag{80}
\]

\[
\lambda'_{2\alpha} = \lambda'_{1\bar{\alpha}}, \tag{81}
\]

and

\[
\lambda''_{a \bar{a}} = \lambda''_{\bar{a} a}, \tag{82}
\]

\[
\lambda''_{2\alpha} = \lambda''_{1\bar{\alpha}}. \tag{83}
\]

Using Eqs. (68), (72), and (73), we obtain the normalized expectation values of \(\hat{n}_{i\alpha\sigma} \hat{n}_{i\bar{\alpha}\sigma'}\) and \(\hat{c}_{i\alpha\sigma}^\dagger \hat{c}_{j\bar{\alpha}\sigma'}\) within the GA in the thermodynamic limit:

\[
\frac{\langle \Psi_G| \hat{n}_{i\alpha\sigma} \hat{n}_{i\bar{\alpha}\sigma'}| \Psi_G \rangle}{\langle \Psi_G| \Psi_G \rangle} \xrightarrow{\text{GA}} \frac{1}{L} \sum_{i, l_i} g^{2}_{l_i} \langle \hat{P}_{i,l_i} \hat{n}_{i\alpha\sigma} \hat{n}_{i\bar{\alpha}\sigma'} \hat{P}_{i,l_i} \rangle_0 \\
\times \left( \frac{\prod_{l} 2\Delta\Gamma'_l}{\prod_{l} \Gamma'_l} \right) \left( \frac{\prod_{l} \Gamma''_l}{\prod_{l} \Gamma''_l} \right) P(L-1; \{N'_{\alpha\sigma}\}), \tag{84}
\]

and

\[
\frac{\langle \Psi_G| \hat{c}_{i\alpha\sigma}^\dagger \hat{c}_{j\bar{\alpha}\sigma'}| \Psi_G \rangle}{\langle \Psi_G| \Psi_G \rangle} \xrightarrow{\text{GA}} \frac{1}{L} \sum_{i, l_i, j, l'_j} g_{l_i} g_{l'_j} \langle \hat{P}_{i,l_i} \hat{P}_{j,l'_j} \hat{c}_{i\alpha\sigma}^\dagger \hat{c}_{j\bar{\alpha}\sigma'} \hat{P}_{i,l_i} \hat{P}_{j,l'_j} \rangle_0 \\
\times \left( \frac{\prod_{l} 2\Delta\Gamma''_l}{\prod_{l} \Gamma''_l} \right) \left( \frac{\prod_{l} \Gamma''_l}{\prod_{l} \Gamma''_l} \right) P(L-2; \{N'_{\alpha\sigma}\}). \tag{85}
\]

where \(\Delta\Gamma'_l\) and \(\Delta\Gamma''_l\) are defined as

\[
\Delta\Gamma'_l = \Gamma'_l - \tilde{\Gamma}'_l, \quad \text{and} \quad \Delta\Gamma''_l = \Gamma''_l - \tilde{\Gamma}''_l, \tag{86}
\]

respectively. From Eqs. (85)–(88) for \(\{\Gamma'_l\}\) and Eqs. (89)–(91) for \(\{\Gamma''_l\}\), we have the following constraints for \(\Delta\Gamma'_l\) and \(\Delta\Gamma''_l\):

\[
\sum_{l=0}^{63} \Delta\Gamma'_l = -1, \tag{87}
\]

\[
\sum_{l=0}^{63} \Delta\Gamma''_l = -2, \tag{88}
\]

Calculating \(\langle \hat{P}_{i;l_i} \hat{n}_{i\alpha\sigma} \hat{n}_{i\bar{\alpha}\sigma'} | \Psi_G \rangle\) and \(\langle \hat{P}_{i;l_i} \hat{c}_{i\alpha\sigma}^\dagger \hat{c}_{j\bar{\alpha}\sigma'} | \Psi_G \rangle\) in Eq. (83) and \(\langle \hat{P}_{i;l_i} \hat{P}_{j;l'_j} \hat{c}_{i\alpha\sigma}^\dagger \hat{c}_{j\bar{\alpha}\sigma'} | \Psi_G \rangle\) and \(\langle \hat{P}_{i;l_i} \hat{P}_{j;l'_j} | \Psi_G \rangle\) in Eq. (85) explicitly for each possible configuration, we find

\[
\frac{\langle \Psi_G| \hat{n}_{i\alpha\sigma} \hat{n}_{i\bar{\alpha}\sigma'}| \Psi_G \rangle}{\langle \Psi_G| \Psi_G \rangle} \xrightarrow{\text{GA}} \frac{1}{L} \sum_{l} g_{l_i} \left( \prod_{l} 2\Delta\Gamma'_l \right) \left( \prod_{l} \Gamma'_l \right) \left( \prod_{l} \Gamma''_l \right) P(L-1; \{N'_{\alpha\sigma}\}); \tag{89}
\]

and

\[
\frac{\langle \Psi_G| \hat{c}_{i\alpha\sigma}^\dagger \hat{c}_{j\bar{\alpha}\sigma'}| \Psi_G \rangle}{\langle \Psi_G| \Psi_G \rangle} \xrightarrow{\text{GA}} \frac{1}{L} \sum_{l} g_{l_i} g_{l'_j} \left( \prod_{l} 2\Delta\Gamma''_l \right) \left( \prod_{l} \Gamma''_l \right) P(L-2; \{N'_{\alpha\sigma}\}); \tag{90}
\]
\[
\frac{\langle \Psi_G | ^{\dagger}c_{i\sigma} \hat{c}_{j\sigma} | \Psi_G \rangle}{\langle \Psi_G | \Psi_G \rangle} \xrightarrow{\text{GA}} \frac{1}{L^2} \sum_{l_i,j,l_i',l_j}'' g_{t_i} g_{t_j} g_{t_{i'}} g_{t_{j'}} \langle \hat{c}_{i\sigma} \hat{c}_{j\sigma} \rangle_0 \left( \prod_l g_l^{2\Delta\Gamma'_l} \right) \left( \prod_i \Gamma'_i \right) \frac{1}{(1 - n_{a_b}^0) n_b^0}. \tag{93}
\]

In addition, we have the following relation in the thermodynamic limit:

\[
\frac{\langle \hat{\Gamma}_i \rangle}{(\hat{\Gamma}_i + \Delta \Gamma_i)!} \sim (\hat{\Gamma}_i)^{-\Delta \Gamma_i}. \tag{94}
\]

Using this relation, we can rewrite Eqs. (92) and (93) as

\[
\frac{\langle \Psi_G | \hat{v}_{i\sigma} \hat{v}_{j\sigma} | \Psi_G \rangle}{\langle \Psi_G | \Psi_G \rangle} \xrightarrow{\text{GA}} \frac{1}{L^2} \sum_{l_i,j} g_{t_i} \prod_l \left( \frac{\Gamma'_i}{g_l} \right)^{-\Delta \Gamma'_i}, \tag{95}
\]

\[
\frac{\langle \Psi_G | ^{\dagger}c_{i\sigma} \hat{c}_{j\sigma} | \Psi_G \rangle}{\langle \Psi_G | \Psi_G \rangle} \xrightarrow{\text{GA}} \frac{1}{L^2} \sum_{l_i,j}'' g_{t_i} g_{t_j} g_{t_{i'}} g_{t_{j'}} \langle \hat{c}_{i\sigma} \hat{c}_{j\sigma} \rangle_0 \frac{1}{(1 - n_{a_b}^0) n_b^0} \prod_l \left( \frac{\Gamma'_i}{g_l} \right)^{-\Delta \Gamma''_i}, \tag{96}
\]

respectively. Substituting Eq. (93) into these equations and using relations \( L^2 \sum_i \Delta \Gamma'_i = L \) and \( L^2 \sum_i \Delta \Gamma''_i = L^2 \) from Eqs. (80) and (81), we find

\[
\frac{\langle \Psi_G | \hat{v}_{i\sigma} \hat{v}_{j\sigma} | \Psi_G \rangle}{\langle \Psi_G | \Psi_G \rangle} \xrightarrow{\text{GA}} \sum_{l_i,j} g_{t_i} \exp \left[ - \sum_l (1 + \lambda_0) \Delta \Gamma'_i - \sum_{l_i,a',a''} \lambda_{a'a''} n_{l_i a'a''} \Delta \Gamma'_i \right]
\]

\[
= \sum_{l_i} g_{t_i} \exp \left[ (1 + \lambda_0) + \sum_{a',a''} \lambda_{a'a''} n_{l_i a'a''} \right]
\]

\[
= \sum_{l_i} \tilde{\Gamma}_i L, \tag{97}
\]

\[
\frac{\langle \Psi_G | ^{\dagger}c_{i\sigma} \hat{c}_{j\sigma} | \Psi_G \rangle}{\langle \Psi_G | \Psi_G \rangle} \xrightarrow{\text{GA}} \sum_{l_i,j}'' g_{t_i} g_{t_j} g_{t_{i'}} g_{t_{j'}} \langle \hat{c}_{i\sigma} \hat{c}_{j\sigma} \rangle_0 \frac{1}{(1 - n_{a_b}^0) n_b^0} \exp \left[ - \sum_l (1 + \lambda_0) \Delta \Gamma''_i \right] \exp \left[ - \sum_{l_i,a',a''} \lambda_{a'a''} n_{l_i a'a''} \Delta \Gamma''_i \right]
\]

\[
= \sum_{l_i,j}'' g_{t_i} g_{t_j} g_{t_{i'}} g_{t_{j'}} \langle \hat{c}_{i\sigma} \hat{c}_{j\sigma} \rangle_0 \frac{1}{(1 - n_{a_b}^0) n_b^0} \exp \left[ 2(1 + \lambda_0) \right]
\]

\[
\times \exp \left[ \frac{1}{2} \sum_{a',a''} \lambda_{a'a''} \left( n_{l_i a'a'} + n_{j a'a'} + n_{l_i a'a''} + n_{j a'a''} \right) \right]
\]

\[
= \frac{1}{(1 - n_{a_b}^0) n_b^0} \langle \hat{c}_{i\sigma} \hat{c}_{j\sigma} \rangle_0 \sum_{l_i,j}'' \sqrt{\tilde{\Gamma}_i \tilde{\Gamma}_j \tilde{\Gamma}_i' \tilde{\Gamma}_j'} \frac{1}{L^2}. \tag{98}
\]

In deriving Eq. (98), we have also used the following relation due to Eq. (63):

\[
\sum_{a=1,2} \lambda_{a\sigma} (n_{l_i a\sigma} + n_{l_j a\sigma}) = \sum_{a=1,2} \lambda_{a\sigma} (n_{l i a\sigma} + n_{l j a\sigma}). \tag{99}
\]

Finally, the variational energy becomes

\[
E_{\text{var}} \xrightarrow{\text{GA}} \min_{\{g_l\}} \left[ - \sum_{l_i,j} \sum_{a,b=1}^2 \sum_{\sigma=\uparrow,\downarrow} t_{a,b}^{i,j}(\phi) \frac{1}{(1 - n_{l_i}^0) n_{l_j}^0} \langle \hat{c}_{i\sigma} \hat{c}_{j\sigma} \rangle_0 \sum_{l_i,j}'' \sqrt{\tilde{\Gamma}_i \tilde{\Gamma}_j \tilde{\Gamma}_i' \tilde{\Gamma}_j'} \frac{1}{L^2}
\]

\[
- \sum_{l_i,j} \sum_{a,b=3}^2 \sum_{\sigma=\uparrow,\downarrow} t_{a,b}^{i,j}(\phi) \frac{1}{(1 - n_{l_i}^0) n_{l_j}^0} \langle \hat{c}_{i\sigma} \hat{c}_{j\sigma} \rangle_0 \sum_{l_i,j}'' \sqrt{\tilde{\Gamma}_i \tilde{\Gamma}_j \tilde{\Gamma}_i' \tilde{\Gamma}_j'} \frac{1}{L^2}
\]

\[+ U \sum_k \sum_{a=b}^2 \sum_{\sigma=\uparrow,\downarrow} \sum_{\sigma'=\uparrow,\downarrow} \sum_{l_i}'' \tilde{\Gamma}_i \frac{1}{L} + U' \sum_k \sum_{a=b}^2 \sum_{\sigma=\uparrow,\downarrow} \sum_{l_i}'' \tilde{\Gamma}_i \frac{1}{L} - J_H \sum_k \sum_{a=b}^2 \sum_{\sigma=\uparrow,\downarrow} \sum_{l_i}'' \tilde{\Gamma}_i \frac{1}{L} \right]. \tag{100}
\]
Here, the restrictions about the summations with respect to $l_i$, $l_j$, $l_i'$, and $l_j'$ in the first and second terms are those for the hopping process $\hat{c}_{i\sigma} \hat{c}_{j\sigma}^\dagger$ $(a, b = 1, 2)$ and hopping process $\hat{c}_{i\sigma} \hat{c}_{j\sigma}$, and the restrictions about the summations with respect to $l_i$ in the third, fourth, and final terms are those for the interaction terms $U$, $U'$, and $J_H$. In deriving Eq. (100), we have neglected the term of $\hat{H}_{CEF}$ in the variational energy since this term only gives a constant energy shift which is independent on the strength of the onsite interactions within the present treatment. Note that $E_{gs}$ can be written as the products of the component for orbital $a$ with spin $\sigma$ since we have neglected both $J'$ and the transverse components of $J_H$ in the interacting Hamiltonian as denoted in Sec. II.

For simplicity of the numerical calculation, we classify the possible 64 configurations into 23 groups in which the energies are same. These are shown in Table I where $X_k$ denotes the optimized number of sites with the configuration in the $k$ group; e.g., $X_1 = \Gamma_l$ for $l = 1 - 4$, and so on. Denoting $x_k = X_k/L$, we obtain

$$E_{gs} \overset{GA}{\underset{x_{3, x_{4}, \ldots, x_{22}}}{\min}} \left[ - \sum_{i,j,a,b=1}^3 \sum_{\sigma} q_{ab}(x_3, x_4, \cdots, x_{22}) \delta_{a,b} \langle \phi \rangle \langle \hat{c}_{i\sigma}^\dagger \hat{c}_{j\sigma} \rangle 0 
+ U(2x_3 + x_4 + 4x_9 + 4x_{10} + 4x_{11} + 4x_{14} + 4x_{15} + 4x_{16} + 2x_{17} + 2x_{18} + 4x_{19} + 8x_{20} + 4x_{21} + 3x_{22}) 
+ U'(2x_5 + 4x_6 + 4x_9 + 4x_{10} + 4x_{11} + 12x_{12} + 12x_{14} + 6x_{15} + 8x_{16} + 4x_{17} + 2x_{18} + 4x_{19} + 16x_{20} + 8x_{21} + 6x_{22}) 
+ (U' - J_H)(2x_7 + 4x_8 + 4x_9 + 4x_{10} + 4x_{11} + 6x_{12} + 6x_{13} + 8x_{14} + 4x_{15} + 12x_{16} + 6x_{17} + 2x_{18} + 4x_{19} + 16x_{20} + 8x_{21} + 6x_{22}) \right].$$

(101)
Here, $q_{ab}(x_3, x_4, \ldots, x_{22})$ is the RF of the kinetic energy for the Ru $t_{2g}$ orbital, which satisfies

$$q_{11}(x_3, x_4, \ldots, x_{22}) = q_{12}(x_3, x_4, \ldots, x_{22}) = q_{21}(x_3, x_4, \ldots, x_{22}) = q_{22}(x_3, x_4, \ldots, x_{22}).$$  

The RFs for the $d_{xz/y^2}$ and $d_{xy}$ orbitals are given by

$$q_{11}(x_3, x_4, \ldots, x_{22}) = \frac{1}{n_1^0(1 - n_1^0)} \left[ \sqrt{x_1}(\sqrt{x_0} + \sqrt{x_3} + \sqrt{x_5} + \sqrt{x_7}) + \sqrt{x_6}(\sqrt{x_2} + \sqrt{x_4} + 2\sqrt{x_9} \right]$$

$$+ \sqrt{x_8}(\sqrt{x_2 + \sqrt{x_10} + \sqrt{x_{12}} + \sqrt{x_{13}}) + \sqrt{x_9}(\sqrt{x_3 + \sqrt{x_14} + \sqrt{x_18} + \sqrt{x_19})$$

$$+ \sqrt{x_{11}}(\sqrt{x_4 + \sqrt{x_{15}} + \sqrt{x_{17}} + \sqrt{x_{19}}) + \sqrt{x_{14}}(\sqrt{x_{10} + \sqrt{x_{12}} + \sqrt{x_{21}})$$

$$+ \sqrt{x_{16}}(\sqrt{x_{10} + \sqrt{x_{12}} + \sqrt{x_{13}} + \sqrt{x_{21}}) + \sqrt{x_{20}}(\sqrt{x_{15} + \sqrt{x_{17}} + \sqrt{x_{19}} + \sqrt{x_{22}}) \right]^2,$$

and

$$q_{13}(x_3, x_4, \ldots, x_{22}) = \frac{1}{n_3^0(1 - n_3^0)} \left[ \sqrt{x_2}(\sqrt{x_0} + \sqrt{x_3} + \sqrt{x_5} + \sqrt{x_7}) + 2\sqrt{x_1}(\sqrt{x_6} + \sqrt{x_8}) + 2\sqrt{x_{10}}(\sqrt{x_3 + \sqrt{x_{19}}})$$

$$+ 2\sqrt{x_{11}}(\sqrt{x_6 + \sqrt{x_8}) + 2\sqrt{x_{12}}(\sqrt{x_{15} + \sqrt{x_{19}}) + \sqrt{x_{14}}(\sqrt{x_{12} + \sqrt{x_{17}} + \sqrt{x_{19}})$$

$$+ \sqrt{x_{20}}(\sqrt{x_{15} + \sqrt{x_{17} + \sqrt{x_{19}} + \sqrt{x_{22}})})^2,$$

respectively. Note that the optimization with respect to $\{g_{X_k}\}$ is equivalent that with respect to $\{x_k\}$ due to the relation $x_k = g_{X_k}^n \exp(1 + \lambda_0 + \sum_{a \sigma} \lambda_{a \sigma} n_{a \sigma})$. In the numerical calculations, we use the following constraints instead of determining the Lagrange multipliers $\lambda_0$ and $\lambda_{a \sigma}$:

$$1 = x_0 + 4x_1 + 2x_2 + 2x_3 + x_4 + 2x_5 + 4x_6 + 2x_7 + 4x_8 + 4x_9 + x_{10} + 4x_{11} + 6x_{12} + 2x_{13} + 4x_{14} + 2x_{15} + 4x_{16} + 2x_{17} + x_{18} + 2x_{19} + 4x_{20} + 2x_{21} + x_{22},$$

$$n_1^0 = x_1 + x_3 + x_5 + x_6 + x_7 + x_8 + 3x_9 + 2x_{10} + 2x_{11} + 3x_{12} + 3x_{13} + 3x_{14} + 3x_{15} + 3x_{16} + x_{17} + x_{18} + x_{19} + 3x_{20} + 2x_{21} + x_{22},$$

$$n_3^0 = x_2 + x_4 + 2x_6 + 2x_8 + 2x_{10} + 4x_{11} + 3x_{12} + 3x_{13} + 2x_{14} + 2x_{15} + 2x_{16} + 2x_{17} + 2x_{19} + 4x_{20} + 2x_{21} + x_{22}. \quad (107)$$

### III. RESULTS

In this section, we show the numerical results of the GA for three cases with the effective models of $x = 2$ and 0.5 and the special model. The variational energy Eq. (101) is numerically minimized with respect to $\{x_k\}$ under the constraints (105) – (107) by Powell's method \[^{27}\] which is one of the numerical methods to minimize a function with more than one variable. In this work, we use the value of $U$ as the parameter, and set $U' = U - 2J_{1\text{H}}, J_{3\text{H}} = U/4$, and $W_{\text{tot}} = 4.1$ eV, which is obtained in the effective model of $x = 2$.

#### A. Mass enhancement for the effective models of $x = 2$ and 0.5

We first show the results for the effective models of $x = 2$ and 0.5. Figures \[5\] and \[6\] represent the RFs of the kinetic energy for the Ru $t_{2g}$ orbitals as a function of $U/W_{\text{tot}}$ for these models. We see from Fig. \[5\] that the RFs for the $d_{xz/y^2}$ and $d_{xy}$ orbitals are nearly the same for the case of $x = 2$. This is probably originated from the fact that these orbitals have nearly the same occupation numbers (i.e., $n_1^0 = n_2^0 = n_3^0 = 4/3$) in the absence of the interactions. On the other hands, for the case of $x = 0.5$, we find from Fig. \[6\] that the RFs for the $d_{xz/y^2}$ and $d_{xy}$ orbitals are different, and that the increase of $U/W_{\text{tot}}$ leads to the large difference between these RFs. The occupation number for each Ru $t_{2g}$ orbital becomes $(n_1^0, n_2^0, n_3^0) = (1.17, 1.17, 1.66)$ for the case of $x = 0.5$. This change of the occupation numbers results mainly from the downward shift of the $d_{xy}$ orbital since we have $(n_1^0, n_2^0, n_3^0) = (1.32, 1.32, 1.35)$, which are little different from those for the case of $x = 2$, for the model setting $\phi = 15^\circ$ and $\Delta_{t_{2g}} = 0$ eV in Eq. (108). By using the analogy with the result for the single-orbital Hubbard model, the difference of the RFs between the cases of $x = 2$ and $x = 0.5$ will be due to this change of the occupation numbers approaching the integer values towards $x = 0.5$, which is expected in the usual Mott transition; in the present case, the occupation numbers expected in the Mott insulator are 1 for the $d_{xz/y^2}$ orbital and 2 for the $d_{xy}$ orbital, respectively.

In order to compare our results with the experimen-
tally observed mass enhancement, we define a total RF,

$$q_{\text{tot}} = \sqrt{\frac{1}{3} \sum_{a=1}^{3} q_{aa}^2},$$  \hfill (108)

which estimates the inverse of the mass enhancement. Figure 11 shows the total RFs as a function of $U/W_{\text{tot}}$ for the effective models of $x = 2$ and 0.5. We see that $q_{\text{tot}}$ for the case of $x = 0.5$ becomes much smaller than that for the case of $x = 2$ as $U/W_{\text{tot}}$ increases. Therefore, our results suggest that moderately strong Coulomb interaction and the modifications of the electronic structures for the Ru $t_{2g}$ orbitals due to the rotation of RuO$_6$ octahedra lead to mass enhancement for $x = 0.5$ than that for $x = 2$.

B. Primary effect of the Ca substitution

In order to clarify the role of the Ca substitution in forming the HF, we calculate the RF for the special model. Figure 12 shows the RFs for each Ru $t_{2g}$ orbital. We see that the RF for the $d_{xz/yz}$ orbital is slightly larger than that for the case of $x = 0.5$, while the RF for the $d_{xy}$ orbital is slightly smaller. The former results mainly from the decrease of the occupation number for the $d_{xz/yz}$ orbital from 1.21 to 1.17, and the latter results mainly from the increase of the occupation number for the $d_{xy}$ orbital from 1.57 to 1.66; both changes of the occupation numbers arise from the downward shift for the $d_{xy}$ orbital, which is induced by the rotation of RuO$_6$ octahedra.

Figure 13 shows the total RFs for both the effective model of $x = 0.5$ and the special model. We find that the inverse of $q_{\text{tot}}$ for the effective model of $x = 0.5$ is larger than that for the special model, and that Coulomb
interaction enhances this difference of the inverse of $q_{\text{tot}}$. Therefore, our result indicates that the vHs for the $d_{xy}$ orbital plays a secondary role in enhancing the effective mass around $x = 0.5$; the primary one arises from the change of the occupation numbers approaching the integer values. Note that these occupation numbers are different from those expected in the usual Mott transition, where the occupation numbers for the $d_{xz/yz}$ and $d_{xy}$ orbitals are 1 and 2, respectively.

IV. DISCUSSION

A. Comparison with previous theoretical studies

We first remark on the physical meaning of the enhancement of the effective mass obtained in the GA. For simplicity, we consider a PM state consisting of a single orbital. The following argument is based on the discussion in Ref. 33. One of the origins of the HF behavior is the criticality approaching the Mott transition. Namely, the formation of the HF results from separation of energy scale between spin and charge degrees of freedom due to electron correlation; on-site charge fluctuation suppresses at the higher scale corresponding to $U$, and the lower one, $T_F$, associates with the local spin fluctuation. Below $T_F$, a Fermi-liquid description applies; the mass enhancement is inversely proportional to a ratio of $T_F$ to the noninteracting Fermi temperature. Although the analysis using the GA restricts to the discussion about the properties for the ground states and can not address the possibility of the above separation of energy scale, the GA can analyze the effective mass for systems with a different parameter. A similar argument can apply to a system with orbital degrees of freedom. Therefore, we think that the analysis using the GA can capture the tendency of mass enhancement in $\text{Ca}_{2-x}\text{Sr}_x\text{RuO}_4$ for $0.5 \leq x \leq 2$.

In the present calculation, we have not discussed Mott transition. From a theoretical point of view, the previous DMFT calculation based on the models for $\text{Ca}_{2-x}\text{Sr}_x\text{RuO}_4$ in $0.5 \leq x \leq 2$ has shown that the critical value of $U$ for the Mott transition, $U_c$, at $x = 0.5$ is larger than 6 eV (i.e., $U/W_{\text{tot}} > 1.4$) at $T = 0.02$ eV. In principle, the Gutzwiller-type variational wave function gives the Mott transition as a function of $U$, when charge fluctuations, which play an important role in the vicinity of the Mott transition, are included. However, the present study using the GA is inappropriate to address the possibility of the Mott transition. Thus, we have shown the results only for the case with $U/W_{\text{tot}} \leq 1.4$ where the system will remain metallic.

The present formalism of the GA neglects the variation of the occupation number for each orbital due to electron correlation for simplicity. The previous DMFT calculation based on the models for $\text{Ca}_{2-x}\text{Sr}_x\text{RuO}_4$ with $0.5 \leq x \leq 2$ has observed a drastic variation of the occupation numbers ($\sim 20 - 30\%$) for values of $U$ near $U_c$, while the variation is about 10\% (a few \%) for $U \sim 0.8U_c$ ($U \sim 0.7U_c$). This indicates that the variation of the occupation numbers due to electron correlation is important near the Mott transition. In this paper, we have discussed the HF behavior only in the regions where the effects of the variation of the occupation numbers is small.

Although it will be necessary to include the variation of the occupation number for each orbital for the quantitative argument, we think from the following arguments that the obtained tendency of the mass enhancement in $0.5 \leq x \leq 2$ does not change qualitatively even if the variation of the occupation number for each orbital is included. According to the DMFT study for the three-orbital Hubbard model, $U_c$ decreases when the occupation number for each orbital in the absence of interactions approaches to an integer value. Simultaneously, the occupation number for each orbital changes as a function of $U/W_{\text{tot}}$. Since the decrease of $U_c$ leads to the increase of the effective mass at a fixed value of $U/W_{\text{tot}}$ and $J_H/U$, the mass enhancement will be largest at $x = 0.5$ where the occupation numbers in the absence of interactions are nearest to integer values in $0.5 \leq x \leq 2$. Therefore, our results about the mass enhancement in $0.5 \leq x \leq 2$ will not change qualitatively even if the variation of the occupation number for each orbital is included.

DMFT studies proposed that the Hund’s rule coupling plays an important role in stabilizing a metallic state with large effective mass. For example, a DMFT study for the degenerate three-orbital Hubbard model showed that the increase of $J_H/U$ leads to a decrease of $U_c$ at 1/3-filling and an increase of $U_c$ at 5/6-filling. (Note that there are three electrons per a site at 1/3-filling and there is one electron per a site at 5/6-filling.) From this result, they claimed that the increase of $J_H/U$ extends a region for the metallic state with large effective mass at the filling away from 1/3-filling; this metallic state is called Hund’s metal. However, in $\text{Ca}_{2-x}\text{Sr}_x\text{RuO}_4$, the
total filling number does not change in $0.5 \leq x \leq 2$ (i.e., $\frac{4}{5}$ filling) and the value of $J_H/U$ does not change either. The main changes due to the Ca substitution are both the bandwidth for each Ru $t_{2g}$ orbital and the occupation number for each Ru $t_{2g}$ orbital. Therefore, the effect of the Hund’s rule coupling is not important for the difference between $x = 0.5$ and 2. Instead, the criticality approaching the Mott transition plays a more important role in enhancing the effective mass in $\text{Ca}_{2-x}\text{Sr}_x\text{RuO}_4$ towards $x = 0.5$.

We now address the effect of the neglected terms in the interacting Hamiltonian (i.e., $J'$ and the transverse components of $J_H$) on the electronic states. According to the previous study\cite{1} of the PM state for the two-orbital Hubbard model in the GA, these terms slightly stabilize a PM metal against a nonmagnetic insulator. This result suggests that the effect of these neglected terms little affects the properties for the PM state studied in the present study within the GA. On the other hand, the transverse components of $J_H$ will strongly affect the stability of the magnetically ordered states. Therefore, these neglected terms will not change the obtained tendency of the mass enhancement in PM states.

According to the density-functional calculation for $\text{Ca}_{2-x}\text{Sr}_x\text{RuO}_4$ in $0.5 \leq x \leq 2$ within the LDA\cite{2}, the total bandwidth for the Ru $t_{2g}$ orbitals becomes smaller for $x = 0.5$ than that for $x = 2$. Although this reduction is partially included in our calculation through the $\phi$ dependence of the dispersions, it seems that these are other effects which reduce the total band width. Thus, if this effect is fully included, the difference between the values of $q_{\text{tot}}^{-1}$ for $x = 2$ and 0.5 will become larger than for the present calculation.

In our analysis, we have assumed that the roles of the O 2$p$ orbitals are only to change the $dp$ hybridizations. However, the previous theoretical work\cite{2} based on the $dp$ model for $\text{Sr}_2\text{RuO}_4$ has proposed that Coulomb interaction for the O 2$p$ orbitals plays an important role in stabilizing spin-triplet superconductivity. We expect that the Coulomb interaction for the O 2$p$ orbitals leads to a larger mass enhancement than the present calculation. The more detailed theoretical study about the role of the O 2$p$ orbitals is deserved.

There is a theoretical proposal that the vHs for the $d_{xy}$ orbital plays a primary role in forming HF states around $x = 0.5$ on the basis of the density-functional calculation within the LDA\cite{3}. This work has proposed that the rotation-induced hybridization of the $d_{xy}$ orbital to the $d_{x^2-y^2}$ orbital causes the magnetic instability due to the nesting of the FS for the $d_{xy}$ orbital, and that the instability will lead to the mass enhancement around $x = 0.5$. In contrast, our results suggest that the primary role arises from the criticality approaching the usual Mott transition resulting from the change of the occupation numbers for the Ru $t_{2g}$ orbitals due to the downward shift of the $d_{xy}$ orbital, and not from the vHs. It will be necessary to study the effect of the vHs on the formation of HF states around $x = 0.5$ more systematically.

B. Correspondence with experimental results

We first discuss the roles of the Ru $e_g$ and O 2$p$ orbitals in determining the electronic states for $\text{Ca}_{2-x}\text{Sr}_x\text{RuO}_4$ in $0.5 \leq x \leq 2$. In this study, we have taken account of the effects of these orbitals as the changes of the $dp$ hybridization and the CEF energy for the Ru $t_{2g}$ orbitals; the latter is the downward shift of the $d_{xy}$ orbital due to the hybridization with the $d_{x^2-y^2}$ orbital. There is no experimental evidence that the Ru $e_g$ orbitals play an important role in determining the electronic states except the possible change of the CEF energy through the hybridization of the Ru $t_{2g}$ orbitals; thus, our treatment about the Ru $e_g$ orbitals will be valid. In contrast, a polarized neutron diffraction measurement for $\text{Ca}_{1.5}\text{Sr}_{0.5}\text{RuO}_4$ has observed a field-induced magnetic moment on the in-plane O ions, which is about 20% of that for Ru ions\cite{4}. This result indicates that not only the $dp$ hybridizations, but also the Coulomb interaction for the O 2$p$ orbitals will play non-negligible roles in determining the electronic states. It is thus necessary to study the role of the O 2$p$ orbitals systematically.

Let us remark on the role of the spin-orbit interaction, which has been neglected in this work. The experimentally observed FSs\cite{5,6} for $x = 2$ and 0.5 are reproducible by the density-functional calculations without the spin-orbit interaction\cite{7,8,9}. Therefore, the spin-orbit interaction will be negligible in determining the electronic states.

We have also neglected the effect of the disorder induced by the Ca substitution in this work. A measurement with a SQUID magnetometer for $\text{Ca}_{1.5}\text{Sr}_{0.5}\text{RuO}_4$ has observed glassy behavior (i.e., the time-dependent magnetization)\cite{10} which is similar to the behavior observed in $\text{Ca}_{0.95}\text{Sr}_{0.05}\text{RuO}_4$. This behavior is related to the disorder by the Ca substitution. It is thus necessary to include the effect of the disorder on the electronic state in order to discuss the electronic states for $\text{Ca}_{2-x}\text{Sr}_x\text{RuO}_4$. This remains as a future problem.

Let us discuss the role of the vHs for the $d_{xy}$ orbital. Experimentally, substitution of La$^{3+}$ for Sr$^{2+}$ in $\text{Sr}_2\text{RuO}_4$ leads to the downward shift of the vHs towards the Fermi level without any structural distortions\cite{11}. In this case, the coefficient of the electronic specific heat for $\text{Sr}_1\text{La}_{0.2}\text{RuO}_4$ reaches 1.3 times of that in $\text{Sr}_2\text{RuO}_4$. This mass enhancement is mainly due to the increase of the DOS by the vHs for the $d_{xy}$ orbital; the density-functional calculation within the LDA and the ARPES measurement support this mechanism\cite{12,13}. However, in the case of $\text{Ca}_{2-x}\text{Sr}_x\text{RuO}_4$ with $x = 0.5$, the ARPES measurement\cite{14} has shown that the vHs is located below the Fermi level. Therefore, there must be other factors other than the vHs in enhancing the effective mass in $\text{Ca}_{2-x}\text{Sr}_x\text{RuO}_4$; our results indicate that one of the factors is the criticality approaching the usual Mott transition.

We next remark on the roles of the spin fluctuations. Around $x = 0.5$, the resistivity behaves metallic (i.e.,
$d\rho/dT > 0$, and the spin susceptibility shows Curie-Weiss behavior, as described in Sec. I. These experimental facts indicate that the mode-mode coupling for the spin fluctuations plays an important role in the electronic states around $x = 0.5$ since the enhancement of the mode-mode coupling generally leads to the Curie-Weiss behavior. The study taking account of the mode-mode coupling is a remaining future problem.

There are several experimental results which indicate that ferromagnetic spin fluctuation also plays an important role in the electronic states around $x = 0.5$. One of the examples is the enhancement of the Wilson ratio towards $x = 0.5$. This result indicates that the system is a nearly ferromagnetic metal near $x = 0.5$. In addition, the inelastic neutron scattering measurement has claimed that the value of $\gamma_e$ for $x = 0.62$ is reproducible by a phenomenological theory including the over-damped magnetic excitations for the ferromagnetic fluctuation. However, the additional Ca substitution does not lead to ferromagnetism but evolves to a simple nearly ferromagnetic metal near $x = 0.5$. We propose that moderately strong electron correlation and the orbital-dependent modifications of the electronic structures due to the lattice distortions play important roles in the electronic states for $\text{Ca}_{2-x}\text{Sr}_x\text{RuO}_4$.

### V. SUMMARY

In order to clarify the origin of the HF behavior around $x = 0.5$, we have studied the electronic states for $\text{Ca}_{2-x}\text{Sr}_x\text{RuO}_4$ in $0.5 \leq x \leq 2$ within the GA on the basis of the three-orbital Hubbard model for the Ru $t_{2g}$ orbitals. We have assumed that the Ca substitution affects the electronic structures mainly by the changes of the $dp$ hybridizations between the Ru $4d$ and O $2p$ orbitals, and have estimated the mass enhancement on the basis of the models taking account of these effects on the electronic structures. In particular, we have numerically calculated the RF within the GA for three cases with the effective models of $x = 2$ and $0.5$ and the special model. We have found that the inverse of the total RF becomes the largest for the case of $x = 0.5$, and that the vHs for the $d_{xy}$ orbital plays a secondary role in enhancing the effective mass. Our results can reproduce the experimentally observed tendency of the effective mass $\gamma_e$. It is thus needed to study the role of the ferromagnetic spin fluctuation.

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