Construction of microscopic model for $f$-electron systems on the basis of $j$-$j$ coupling scheme

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We construct a microscopic model for $f$-electron systems, composed of $f$-electron hopping, Coulomb interaction, and crystalline electric field (CEF) terms. In order to clarify the meaning of one $f$-electron state, here the $j$-$j$ coupling scheme is considered, since the spin-orbit interaction is generally large in $f$-electron systems. Thus, the $f$-electron state at each site is labelled by $\mu$, namely, the $z$-component of total angular momentum $j$. By paying due attention to $f$-orbital symmetry, the hopping amplitudes between $f$-electron states are expressed using Slater’s integrals. The Coulomb interaction terms among the $\mu$-states are written by Slater-Condon or Racah parameters. Finally, the CEF terms are obtained from the table of Hutchings. The constructed Hamiltonian is regarded as an orbital degenerate Hubbard model, since it includes two pseudo-spin and three pseudo-orbital degrees of freedom. For practical purposes, it is further simplified into a couple of two-orbital models by discarding one of the three orbitals. One of those simplified models is here analyzed using the exact diagonalization method to clarify ground-state properties by evaluating several kinds of correlation functions. Especially, the superconducting pair correlation function in orbital degenerate systems is carefully calculated based on the concept of off-diagonal long-range order. We attempt to discuss a possible relation of the present results with experimental observations for recently discovered heavy fermion superconductors CeMIn$_5$ ($M=$Ir, Co, and Rh), and a comprehensive scenario to understand superconducting and antiferromagnetic tendencies in the so-called “115” materials such as CeMIn$_5$, UMGa$_5$, and PuCoGa$_5$ from the microscopic viewpoint.

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I. INTRODUCTION

Since the pioneering discovery of superconductivity in CeCu$_2$Si$_2$, elucidation of the mechanism of unconventional superconductivity in heavy fermion compounds has been one of the central issues both in the experimental and theoretical research fields of condensed matter physics. In particular, further discoveries of superconductivity in uranium compounds such as UBe$_{13}$, URu$_2$Si$_2$, UPt$_3$, UPd$_2$Al$_3$, and UNi$_2$Al$_2$ have triggered a rapid increase of vigorous investigations on exotic properties of superconductivity in $f$-electron materials.

Recently there has occurred a second rush of new discoveries of superconductivity in $f$-electron compounds. One such is the coexistence of superconductivity and ferromagnetism in UGe$_2$ and URhGe. After this discovery, much attention has been attracted to the mechanism of unconventional triplet superconductivity in $f$-electron systems, since it is naively believed that triplet pairing can coexist in the ferromagnetic phase. A second example is the family of Ce-based heavy fermion superconductors CeMIn$_5$ ($M=$Ir, Rh, and Co). Surprisingly, CeCoIn$_5$ exhibits a superconducting transition temperature $T_c=2.3K$, which is the highest among those yet observed for heavy fermion materials at ambient pressure. On the other hand, CeIrIn$_5$ shows $T_c=0.4K$, which is much less than that of CeCoIn$_5$. Note that CeRhIn$_5$ is an antiferromagnet with a Neél temperature $T_N=3.8K$ at ambient pressure, while under high-pressure it becomes superconducting at $T_c=2.1K$. It is interesting that the ground state properties of these compounds are easily changed by transition metal ions. Third is the superconductivity of the filled skutterudite compound PrOs$_4$Sb$_{12}$ with $T_c=1.85K$ and a mass enhancement factor as large as fifty. Again, a relatively high $T_c$ is surprising, while an interesting point is that the ground state is suggested to belong to $\Gamma_3$, leading to a potential role played by quadrupole fluctuations in the mechanism of superconductivity. Another amazing result is the discovery of superconductivity in PuCoGa$_5$ with $T_c=18.5K$. Although it is difficult to synthesize this compound and to measure various physical quantities, owing to the inclusion of plutonium, this is truly high $T_c$ and its mechanism is rather mysterious.

Among several remarkable features both of new and old $f$-electron superconductors, one interesting and important point is the common observation of anisotropic Cooper-pairing, experimentally suggested by the power-law behavior of physical quantities in the low-temperature region. As is well known, the value of the power sensitively depends on the node structure of the gap function on the Fermi surface. Thus, by analysing carefully the temperature dependence of physical quantities in experiments, it is possible to deduce the symmetry of the Cooper pairs under the group-theoretical restrictions. As a result of this phenomenological analysis, it has been clarified that the superconducting gap in $f$-electron materials has nodes on the Fermi surface, indicating that non-$s$-wave Cooper pairing occurs in heavy fermion superconductors.

The appearance of non-$s$-wave pairing itself is easily
understood as an effect of strong short-range correlation, if we recall the fact that the Cooper pair is composed of a pair of f electrons with heavy effective mass. Since superconductivity in heavy fermion materials is a second-order transition phenomenon, the Ginzburg-Landau theory is still applicable to f-electron superconductors if we take account the symmetry of the Cooper pairs as well as the crystal structure with the help of group-theoretical arguments. Such efforts have been quite useful to promote the understanding of the nature of unconventional superconductivity without considering the mechanism of the Cooper-pair formation.

As for the microscopic aspects of the mechanism of unconventional superconductivity, it has at least been confirmed that the strong short-range Coulomb interaction plays a crucial role. For instance, it brings about antiferromagnetic spin fluctuations which induce singlet d-wave superconductivity consistent with the node structure suggested by some experiments. It is true that in some f-electron materials, anisotropic singlet pairing is stabilized, but in UPt$_3$, it has been experimentally confirmed that triplet pairing occurs. Quite recently, also in UNi$_2$Al$_3$, a possibility of triplet pairing has been discussed. Unfortunately, the triplet pair formation as well as the coexistence of superconductivity and ferromagnetism cannot be simply explained as the effect of antiferromagnetic spin fluctuations.

One may naively consider that instead, we can include the effect of ferromagnetic spin fluctuations, which was proposed for the origin of superfluidity in helium 3. However, we then immediately face another problem, i.e., how to obtain such fluctuations from the strong short-range Coulomb interaction. It may be possible to derive this based on a realistic electronic band structure, but we do not find that paramagnons are always dominant in the spin fluctuation spectrum when we survey the magnetic properties of those materials. In fact, in ruthenate Sr$_2$RuO$_4$ which is experimentally confirmed to be a triplet superconductor, instead we find that the incommensurate antiferromagnetic spin fluctuation is enhanced, as observed in neutron scattering experiments. Namely, in contrast to our naive expectation, paramagnons do not seem to play a central role in the occurrence of triplet superconductivity in the solid state. Thus, it is still a puzzling and challenging problem to clarify what is the key issue which determines the symmetry of Cooper pairs, singlet or triplet, in f-electron superconductors.

In order to understand this point, it is necessary to perform a microscopic analysis based on a model Hamiltonian appropriate for f-electron systems, but unfortunately, we find such a model to be lacking. It may be possible to consider this problem based on the single-band Hubbard model, which is believed to describe well the properties of strongly correlated electron systems. In fact, several basic features of high $T_c$ cuprates have been understood based on the Hubbard model by analyzing it using various kinds of analytical and numerical techniques. However, this model is too simplified to include differences among materials characterized by orbital degrees of freedom, although recently, the active role of orbitals has been widely recognized in several materials as a means for understanding novel magnetism and unconventional superconductivity. For instance, in manganites, $e_g$ orbitals play a primary role for electronic properties since orbital ordering has been successfully observed in manganites by means of the resonant X-ray scattering measurement. In order to investigate systems with active orbital degrees of freedom, it is necessary to analyze the multi-orbital Hubbard model. Such an extension of the model does not bring essential difficulty, at least in d-electron materials. For instance, in 4d electron systems such as ruthenate Sr$_2$RuO$_4$ introduced above, it has been found that a three $t_{2g}$-orbital tight-binding model can well reproduce the experimental results, as can band-structure calculations.

However, if we try to construct such a model also for f-electron materials, we immediately find a serious problem. Since the spin-orbit interaction is fairly strong in f-electron systems, the meaning of a single f-electron state is unclear. Even if this point is overcome, we find another difficulty in the evaluation of hopping amplitudes as well as Coulomb interactions based on a good representation for one f-electron state. In addition, we need to include correctly the important effects of crystalline electric fields (CEF), which are very often essential for some f-electron systems.

In this paper, we attempt to go beyond all those problems through use of the j-j coupling scheme, in order to construct an appropriate microscopic Hamiltonian for f-electron compounds, including the hopping amplitudes, Coulomb interactions, and CEF terms. The Hamiltonian obtained is a multi-orbital Hubbard-like model. After construction of the model, we exhibit a couple of practical models, simplified by discarding one orbital degree of freedom. Then, as an typical example, one simplified model is analyzed by using exact diagonalization techniques to evaluate several kinds of correlation functions. Especially, the superconducting pair correlation function is carefully analyzed based on the concept of off-diagonal long-range order. Finally, we will discuss the relation between the present theoretical results and some properties of CeMn$_5$. We also try to give a possible explanation for superconducting and antiferromagnetic tendencies in “115” materials including CeMn$_5$, UMGa$_5$, and PuCoGa$_5$, based on our microscopic picture.

The organization of this paper is as follows. In Sec. 2, the construction of the microscopic model Hamiltonian based on the j-j coupling scheme is discussed in detail. The Coulomb interaction terms, CEF terms, and the hopping amplitudes are evaluated by paying due attention to f-orbital symmetry. Two types of simplified models are also introduced. In Sec. 3, one of the simplified models will be analyzed by showing the results of spin, charge, orbital, and pair correlation functions. A prescription to measure the pair correlation will be also
discussed. Finally in Sec. 4, the paper is summarized and properties of 115-materials such as CeMn$_5$, UMGa$_5$, and PuCoGa$_5$ are discussed. Throughout the paper, we use units such that $\hbar=k_B=1$.

II. MODEL CONSTRUCTION

In this section we construct a microscopic model Hamiltonian for $f$-electron systems in order to discuss unconventional superconductivity and novel magnetism from the microscopic viewpoint. For this purpose, the model must include correctly the itinerant nature of $f$ electrons as well as strong electron correlation and the effect of CEF. Namely, the Hamiltonian $H$ should be composed of three parts as

$$H = H_{\text{kin}} + H_{\text{int}} + H_{\text{CEF}},$$  \hspace{1cm} (1)

where $H_{\text{kin}}$, $H_{\text{int}}$, and $H_{\text{CEF}}$ are $f$-electron hopping, Coulomb interactions among $f$ electrons, and the CEF term, respectively.

In order to express the Hamiltonian in the form of Eq. (1), it is requested that the one $f$-electron state should be well-defined by using a label $\mu$. The physical meaning of $\mu$ will be discussed later in detail, but here it is convenient to define a second quantized operator to express the state $|\mu\rangle_i$ as

$$|\mu\rangle_i = a_{i\mu}^\dagger |0\rangle,$$  \hspace{1cm} (2)

where $|0\rangle$ denotes the vacuum and $a_{i\mu}^\dagger$ is the creation operator for $f$ electrons at site $i$. By using the second-quantized operator $a_{i\mu}^\dagger$ defined above, the kinetic term can be written as

$$H_{\text{kin}} = \sum_{i,a,\mu,\nu} t_{\mu\nu} a_{i\mu}^\dagger a_{i+a\nu},$$  \hspace{1cm} (3)

where $t_{\mu\nu}$ is the overlap integral between the $\mu$- and $\nu$-states connected by the vector $a$. The Coulomb interaction term is given in the form of

$$H_{\text{int}} = \frac{1}{2} \sum_{i,\mu,\nu,\mu',\nu'} I(\mu,\nu;\mu',\nu') a_{i\mu}^\dagger a_{i\nu}^\dagger a_{i\nu'} a_{i\mu'},$$  \hspace{1cm} (4)

where $I$ is the matrix element for Coulomb interactions. Finally, the CEF term is expressed by

$$H_{\text{CEF}} = \sum_{i,\mu,\nu} B_{\mu\nu} a_{i\mu}^\dagger a_{i\nu},$$  \hspace{1cm} (5)

where $B_{\mu\nu}$ indicates the potential energy for $f$ electrons which expresses the effect of the CEF.

Now our tasks in this section are as follows: (i) Specification of the meaning of $\mu$ for one $f$-electron state. (ii) Evaluation of the hopping amplitude, Coulomb matrix elements, and CEF coefficients. (iii) Simplification of the model for practical purposes. In the following subsections, all of these points will be clarified in this order.

A. $j$-$j$ coupling scheme

First let us discuss the meaning of $\mu$ in the Hamiltonian Eq. (1). To make it clear, it is instructive to start the discussion with the single ion problem using two typical approaches, the $LS$ coupling and $j$-$j$ coupling schemes. In general, we consider the $f^n$ configuration, where $n$ is the number of $f$ electrons included on a localized ion. In the $LS$ coupling scheme, first the spin $S$ and angular momentum $L$ are formed by following Hund’s rules as $S=\sum_{i=1}^{n} \lambda_i$ and $L=\sum_{i=1}^{n} \ell_i$, where $\lambda_i$ and $\ell_i$ are spin and angular momentum for $i$-th $f$-electron. Note here that the Hund’s rules are based on the Pauli principle and Coulomb interactions among $f$ electrons. After forming $S$ and $L$, we include the effect of spin-orbit interaction $AL\cdot S$, where $\lambda$ is the spin-orbit coupling. Note that $\lambda$ is $>0$ for $n<7$, while $\lambda$ is $<0$ for $n>7$. Note also that a good quantum number to label such a state is the total angular momentum $J$, given by $J=L+S$. Following from simple algebra, the ground-state level is characterized by $J=|L-S|$ for $n<7$, while $J=L+S$ for $n>7$.

As is easily understood from the above discussion, the $LS$ coupling scheme is valid under the assumption that the Hund’s rule coupling is much larger than the spin-orbit interaction, since $S$ and $L$ are formed by the Hund’s rule coupling prior to the inclusion of spin-orbit interaction. It is considered that this assumption is valid for insulating compounds with localized $f$ electrons. However, when the spin-orbit interaction is not small compared with the Hund’s rule coupling, especially in actinide ions, the above assumption is not always satisfied. In addition, if the $f$ electrons become itinerant owing to hybridization with the conduction electrons, the effect of Coulomb interactions would thereby be effectively reduced. In rough estimation, the effective size of the Coulomb interaction may be as large as the bandwidth of $f$ electrons, leading to a violation of the assumption required for the $LS$ coupling scheme.

For $f$-electron systems in which the spin-orbit interaction becomes larger than the effective Coulomb interactions, it is useful to consider the problem in the $j$-$j$ coupling scheme. Here we emphasize that the $j$-$j$ coupling scheme is also quite convenient for including many-body effects using the standard quantum-field theoretical techniques, since individual $f$-electron states can be clearly defined, as explained below. First, we include the spin-orbit coupling so as to define the state labelled by the total angular momentum $J_i$ for the $i$-th electron, given by $J_i=\lambda_i+\ell_i$. For $f$-orbitals with $\ell=3$, we immediately obtain an octet with $J=7/2(=3+1/2)$ and a sextet with $J=5/2(=3-1/2)$, which are well separated by the spin-orbit interaction. Note here that the level for the octet is higher than that of the sextet. Then, we take into account the effect of Coulomb interactions to accommodate $n$ electrons among the sextet and/or octet, leading to the ground-state level in the $j$-$j$ coupling scheme.

Here, the meaning of $\mu$ in our Hamiltonian becomes clear. In the case of $n<7$, $\mu$ should be the label to specify
the state in the $j=5/2$ sextet, namely, the $z$-component of the total angular momentum $j=5/2$ and takes the values of $\mu=-5/2$, $-3/2$, $\cdots$, $5/2$. Note here that for $3<n<7$, $j=7/2$ octet is not occupied, since we presume that the effect of spin-orbit interaction is larger than that of the Hund’s rule coupling in the $j-j$ coupling scheme. On the other hand, for the case of $n\geq7$, $\mu$ should be considered to specify the state in the $j=7/2$ octet, since $j=5/2$ sextet is fully occupied. Note again that spin-orbit interaction is larger than that of the Hund’s rule coupling. In this paper, we concentrate only on the case of $n<7$, especially the situation with $n=1$ and 2, corresponding to $\text{Ce}^{3+}$ and $\text{U}^{4+}$ ions. Thus, in the following, $\mu$ indicates the $z$-component of the total angular momentum which specifies the state in the $j=5/2$ sextet.

B. Coulomb interaction term

Now let us consider the ground-state multiplet appearing in the $j-j$ coupling scheme. For this purpose, first it is necessary to define the Coulomb interaction $I$ in $H_{\text{int}}$, which is the sum of two contributions, written as

$$I(\mu, \nu; \nu', \mu') = K_{\mu\nu, \mu'\nu'} - K_{\mu', \mu\nu'},$$

(6)

where the former indicates the Coulomb term, while the latter denotes the exchange one. It should be noted that $I$ vanishes unless $\mu+\nu=\mu'+\nu'$ due to the conservation of $z$-component of total angular momentum. The matrix element $K_{\mu_1\mu_2; \mu_3\mu_4}$ is explicitly given by

$$K_{\mu_1\mu_2; \mu_3\mu_4} = \sum_{\sigma\sigma'} C_{\mu_1\sigma} C_{\mu_2\sigma'} C_{\mu_3\sigma'} C_{\mu_4\sigma} \times \langle \mu_1 - \sigma, \mu_2 - \sigma' | \mu_3 - \sigma, \mu_4 - \sigma \rangle,$$

(7)

where $C_{\mu\sigma}$ is the Clebsch-Gordan coefficient, given as

$$C_{\mu\sigma} = -\sigma \sqrt{\frac{7/2 - \mu\sigma}{7}}.$$

(8)

with $\sigma=+1$ (-1) for up (down) real spin. The Coulomb matrix element among $\ell$-orbitals is given by

$$\langle m_1, m_2 | m_3, m_4 \rangle = \int dr_1 dr_2 \varphi_{m_1}(r_1) \varphi_{m_2}(r_2) g_{12} \varphi_{m_3}(r_2) \varphi_{m_4}(r_1),$$

(9)

where $g_{12}=e^2/|r_1 - r_2|$ and $\varphi_m(r)$ is the wavefunction for the $m$ state in $\ell=3$ orbitals, expressed by the product of the radial function and spherical harmonic $Y_{\ell m}$. The matrix element $\langle m_1, m_2 | m_3, m_4 \rangle$ can be written in the form of

$$\langle m_1, m_2 | m_3, m_4 \rangle = \sum_{k=0}^{6} F^{k} c_{k}(m_1, m_4) c_{k}(m_2, m_3),$$

(10)

where the sum on $k$ includes only even values ($k=0, 2, 4$, and 6), $F^{k}$ is the Slater-Condon parameter including the complex integral of the radial function, and $c_{k}$ is the Gaunt coefficient which is tabulated in the standard textbooks of quantum mechanics (see, for instance, Ref. 30).

When two electrons are accommodated in the $j=5/2$ sextet, the allowed values for total angular momentum $J$ are 0, 2, and 4 due to the Pauli principle. Thus, the Coulomb interaction term should be written in a $15 \times 15$ matrix form. Note that “15” is the sum of the basis numbers for singlet ($J=0$), quintet ($J=2$), and nonet ($J=4$). As is easily understood, this $15 \times 15$ matrix can be decomposed into a block-diagonalized form labelled by $J_z$, including one $3 \times 3$ matrix for $J_z=0$, four $2 \times 2$ matrices for $J_z=\pm2$ and $\pm1$, and four $1 \times 1$ for $J_z=\pm1$ and $\pm1$. We skip the details of tedious calculations for the matrix elements and here only summarize the results in the following by using the Racah parameters $E_k$ ($k=0,1,2,3$) which are related to the Slater-Condon parameters $F^k$ as

$$E_0 = F^0 - \frac{80}{1225} F^2 - \frac{12}{441} F^4,$$

$$E_1 = \frac{120}{1225} F^2 + \frac{18}{441} F^4,$$

(11)

$$E_2 = \frac{12}{1225} F^2 - \frac{1}{441} F^4.$$

For $J_z=4$ and 3, we obtain

$$I(5/2, 3/2; 3/2, 5/2) = E_0 - 5E_2,$$

(12)

and

$$I(5/2, 1/2; 1/2, 5/2) = E_0 - 5E_2,$$

(13)

respectively. For $J_z=2$ and 1, we obtain

$$I(3/2, 1/2; 1/2, 3/2) = E_0 + 4E_2,$$

$$I(5/2, -1/2; -1/2, 5/2) = E_0,$$

(14)

$$I(3/2, 1/2; -1/2, 5/2) = -3\sqrt{5}E_2,$$

and

$$I(3/2, -1/2; -1/2, 3/2) = E_0 - E_2,$$

$$I(5/2, -3/2; -3/2, 5/2) = E_0 + 5E_2,$$

(15)

$$I(3/2, -1/2; -3/2, 5/2) = -2\sqrt{10}E_2,$$

Finally, for $J_z=0$, we obtain

$$I(1/2, -1/2; -1/2, 1/2) = E_0 + 2E_2 + E_1,$$

$$I(3/2, -3/2; -3/2, 3/2) = E_0 - 3E_2 + E_1,$$

(16)

$$I(5/2, -5/2; -5/2, 5/2) = E_0 + 5E_2 + E_1,$$

$$I(1/2, -1/2; -3/2, 3/2) = -E_1 - 3E_2,$$

$$I(1/2, -1/2; -5/2, 5/2) = E_1 - 5E_2,$$

$$I(3/2, -3/2; -5/2, 5/2) = -E_1.$$

Note here the following relations:

$$I(\mu, \nu; \nu', \mu') = I(\mu', \nu'; \nu, \mu),$$

(17)

and

$$I(\mu, \nu; \nu', \mu') = I(-\nu, -\mu; -\mu', -\nu').$$

(18)
By using these two relations and Eqs. (12, 13, 14), we can obtain all the Coulomb matrix elements. 

As a typical example, let us consider the \( J^2 \) configuration. In the \( j-j \) coupling schemes, two electrons are accommodated in the \( J=5/2 \) sextet. When we diagonalize the \( 15 \times 15 \) matrix for the Coulomb interaction terms, we can easily obtain the eigen energies as \( E_{0} - 5E_{2} \) for the \( J=4 \) nonet, \( E_{o} + 9E_{1} \) for the \( J=2 \) quintet, and \( E_{o} + 3E_{1} \) for the \( J=0 \) singlet. Since the Racah parameters are all positive, the ground state is specified by \( J=4 \) in the \( j-j \) coupling scheme. In the \( LS \) coupling scheme, on the other hand, we obtain the ground-state level as \( ^3H_4 \) with \( S=1 \) and \( L=5 \) from the Hund's rules. On further inclusion of the spin-orbit interaction, the ground state becomes characterized by \( J=4 \), expressed as \( ^3H_4 \) in the traditional notation. Note that we are now considering a two-electron problem. Thus, if we correctly include the effects of Coulomb interactions, it is concluded that the same quantum number as that in the \( LS \) coupling scheme is obtained in the \( j-j \) coupling scheme for the ground-state multiplet.

In order to understand the physical meaning of Racah parameters, let us consider a simplified Coulomb interaction term. In the above discussion, the expressions using Racah parameters are not convenient since they depend on the orbitals in a very complicated manner, although they keep the correct symmetry required by group theory. To clarify their meanings, it may be useful to restart the discussion from the following interaction form among \( \ell = 3 \) orbitals:

\[
\begin{align*}
H_{\text{int}} &= U \sum_{i,m} \rho_{im\uparrow} \rho_{i\downarrow} + U'/2 \sum_{i,\sigma',m \neq m'} \rho_{im\sigma} \rho_{im'\sigma'} \\
&\quad + J/2 \sum_{i,\sigma',m \neq m'} f_{im\sigma}^\dagger f_{im'\sigma'}^\dagger f_{im'\sigma'} f_{im\sigma},
\end{align*}
\tag{19}
\]

where \( f_{im\sigma} \) is the annihilation operator for an \( f \) electron with spin \( \sigma \) in the \( m \) state of angular momentum \( \ell \) at site \( i \) and \( \rho_{im\sigma} = f_{im\sigma}^\dagger \rho_{im\sigma} \). In this equation, we include only three interactions: intra-orbital Coulomb interaction \( U \), inter-orbital Coulomb interaction \( U' \), and the exchange interaction \( J \). Note that the relation \( U = U' + J \) holds among Coulomb interactions to ensure rotational invariance in the orbital space.

By using Clebsch-Gordan coefficients, \( f_{im\sigma} \) with real-spin \( \sigma \) can be related to \( a_{im} \) as

\[
f_{im\sigma} = -\sigma \sqrt{\frac{3 - \sigma m}{2}} a_{im+\sigma/2}.
\tag{20}
\]

Note here that we consider only the \( j = 5/2 \) sextet. The Coulomb interaction term for \( j=5/2 \) is given by

\[
H_{\text{int}} = U_{\text{eff}} \sum_{i,j} n_{ij} n_{i'j'} - J_{H} J_{H}^2 + (35 J_{H}/4) N_{I},
\tag{21}
\]

where \( n_{ij} = a_{ij}^\dagger a_{ij} \), \( N_{I} = \sum_{\mu} n_{i\mu} \), \( U_{\text{eff}} = U' - J/2 \), \( J_{H} = J/49 \), and \( J_{H} \) is the operator for total angular momentum with \( J=5/2 \). Explicitly, \( J_{H}^2 \) is written as

\[
J_{H}^2 = \sum_{\mu,\mu'} \left[ \phi_{\mu}^+ \phi_{\mu'}^+ n_{\mu\mu'} + (\phi_{\mu}^+ \phi_{\mu'}^- n_{\mu\mu'} + 1 a_{\mu\mu'}^\dagger a_{\mu'\mu}^\dagger \right] \phi_{\mu'} \phi_{\mu} a_{\mu\mu'} a_{\mu'\mu'}^\dagger / 2],
\tag{22}
\]

with \( \phi_{\mu}^\dagger = \sqrt{(j+1) - \mu(\mu + 1)} = \sqrt{35/4 - \mu(\mu + 1)} \).

For two electrons in the \( j=5/2 \) sextet, based upon the simplified Coulomb interaction term, we can easily obtain the energy levels as \( U_{\text{eff}} - 5J_{H}/2 \) for the \( J=4 \) nonet, \( U_{\text{eff}} + 23J_{H}/2 \) for the \( J=2 \) quintet, and \( U_{\text{eff}} + 35J_{H}/2 \) for the \( J=0 \) singlet. When we compare these energy levels with the results obtained using Racah parameters, we understand the correspondence such as \( E_{0} \sim U_{\text{eff}} \) and \( E_{2} \sim J_{H} \). Namely, \( E_{0} \) is the effective inter-orbital Coulomb interaction, while \( E_{2} \) denotes the Hund’s rule coupling. Note that \( E_{1} \) does not appear, since it is not included in the pair-hopping interaction which is not included here.

Finally, we note the smallness of \( J_{H} \), given as \( J_{H} = J/49 \). The origin of the large reduction factor \( 1/49 \) is, in one word, due to the neglect of \( j=7/2 \) octet. In the Coulomb interaction term Eq. (19), the Hund’s rule term is simply written as \( -J S^2 \). Note the relation \( S=(g_{J} - 1)J \) with \( g_{J} \) the Landé’s \( g \)-factor. For \( j = 5/2 \), we easily obtain \( g_{J} = 6/7 \), indicating \( S = -(1/7)J \). Thus, the original Hund’s rule term is simply rewritten as \( -(J/49)J^2 \).

C. CEF term

As is well known, the ground-state multiplet is further split due to the effect of the CEF. In this paper we take into account the effect of the CEF by simply accommodating several electrons in the one-electron potential. Namely, \( B_{\mu \mu'} \) in Eq. (3) is expressed by the CEF parameters for \( j=5/2 \). Since the CEF term depends on the crystal structure, it is convenient to write down the CEF formula for \( j=5/2 \) in the typical lattice structure, expressed as

\[
H_{\text{CEF}}^{\text{cub}} = B_{2}^{2}(\hat{O}_{2}^{0} + 5\hat{O}_{4}^{0}),
\tag{23}
\]

for a cubic lattice,

\[
H_{\text{CEF}}^{\text{tet}} = B_{2}^{2}\hat{O}_{2}^{0} + B_{4}^{2}\hat{O}_{4}^{0} + B_{4}^{2}\hat{O}_{4}^{0},
\tag{24}
\]

for a tetragonal lattice, and

\[
H_{\text{CEF}}^{\text{hex}} = B_{2}^{2}\hat{O}_{2}^{0} + B_{4}^{2}\hat{O}_{4}^{0}.
\tag{25}
\]

for a hexagonal lattice. In each equation above, \( \hat{O}_{m}^{n} \) is the Stevens equivalent operator composed of \( J_{z} \), \( J_{z}^{2} \), and \( J_{+} \). The matrix formulae have been tabulated in a paper by Hutchings. The coefficients \( B_{n}^{m} \) are conventionally called the CEF parameters, which are, in actuality, determined by the fitting of experimental results for physical quantities such as magnetic susceptibility.
Note here that the above formulæ have been obtained from the case of \( J = 5/2 \). In general, the CEF term is expressed in matrix form, depending on the value of \( J \); for \( J \) larger than 5/2, higher terms in \( B_n^m \) should occur. However, as already mentioned above, since in this paper the effect of the CEF is considered as a one-electron potential based on the \( j \)-\( j \) coupling scheme, it is enough to use the CEF term for \( J = 5/2 \).

In order to check the validity of our viewpoint regarding the CEF term, let us see, for instance, the case of cubic structure, in which we can easily obtain

\[
\begin{align*}
B_{\pm5/2,\pm5/2} & = 60B_4^0, \\
B_{\pm3/2,\pm3/2} & = -180B_4^0, \\
B_{\pm1/2,\pm1/2} & = 120B_4^0, \\
B_{\pm5/2,\pm5/2} & = B_{\pm3/2,\pm5/2} = 60\sqrt{3}B_4^0, \\
\end{align*}
\]

and zero for other \( \mu \) and \( \nu \). In the following we consider the cases of both \( f^1 \) and \( f^2 \) configurations.

When one electron exists in \( f \)-orbitals, i.e., in the case of the Ce\(^{3+} \) ion, the ground state is easily obtained by the diagonalization of Eq. (26). Then we immediately obtain two eigen energies, \( E(\Gamma_7) = -240B_4^0 \) for the \( \Gamma_7 \) doublet and \( E(\Gamma_8) = 120B_4^0 \) for the \( \Gamma_8 \) quartet. Thus, the ground state is changed due to the sign of \( B_4^0 \), as shown in Eq. (26). Qualitatively, the ground state is deduced from the positions of ligand anions and the shape of wavefunctions. As in the case of the Ce monopnictide, when anions are located along the direction of \([1,0,0]\) from the Ce\(^{3+} \) ion, the \( \Gamma_8 \) level is energetically penalized, since the corresponding wavefunctions are expanding along the axis directions. On the other hand, as in the case of Ce hexaborides with anions located along the \([1,1,1]\) directions from the Ce\(^{3+} \) ions, the \( \Gamma_7 \) levels are higher due to the shape of \( \Gamma_8 \) wavefunction.

In order to consider the \( f^2 \) configurations such as \( Pr^{4+} \) and \( U^{4+} \) ions based on the \( j \)-\( j \) coupling scheme, we put two electrons in the potential for the \( J = 5/2 \) CEF term. Here some readers may have a naive question regarding its validity. To clarify this point, we analyze the CEF level schemes for the \( f^2 \) configuration by diagonalizing \( H_{\text{int}} + H_{\text{CEF}} \). In Fig. 1(b), we show the eigen energies as a function of \( B_4^0 \) for a set of typical values of Racah parameters, \( E_0 = 5, E_1 = 2, \) and \( E_2 = 0.5 \). For \( B_4^0 < 0 \), the ground state is the \( \Gamma_5 \) triplet, while the \( \Gamma_1 \) singlet appears for \( B_4^0 > 0 \). At \( B_4^0 = 0 \), the ground-state is the \( J = 4 \) nonet. Here it should be noted that the ground-state wavefunction consists of a mixture of the \( J = 4, J = 2, \) and \( J = 0 \) states. Note also that \( J_z \), not \( J \), is a good quantum number to label the state, since the rotational invariance in \( J \) space is broken by the effect of the CEF for \( J = 5/2 \). However, we confirm that the contribution of the \( J = 4 \) component is the largest in the ground state wave function.

In the \( LS \) coupling scheme, on the other hand, we need to consider a \( 9 \times 9 \) matrix form for the \( J = 4 \) nonet. The CEF term for \( J = 4 \) under cubic symmetry is given by \( H_{\text{CEF}} = B_3^0 (O_4^0 + 5O_4^0) + B_0^0 (O_4^0 - 21O_8^0) \). Note that for the case of \( J = 4 \), there appears a higher order term including \( B_4^0 \). Referring to the paper by Hutchings, we obtain the CEF coefficients as

\[
\begin{align*}
B_{\pm2,\pm2} & = -660(B_4^0 - 42B_6^0), \\
B_{\pm2,\mp2} & = 180(5B_4^0 + 294B_6^0), \\
\end{align*}
\]

for the \( J = \pm 2 \) sector,

\[
\begin{align*}
B_{\pm3,\pm3} & = -1260(B_4^0 + 17B_6^0), \\
B_{\pm1,\mp1} & = 180(3B_4^0 + 7B_6^0), \\
B_{\pm3,\mp1} & = 180(3B_4^0 + 7B_6^0), \\
\end{align*}
\]

for the \( J = \pm 3 \) and \( \mp 1 \) sectors, and

\[
\begin{align*}
B_{\pm4,\pm4} & = 840(B_4^0 + 6B_6^0), \\
B_{0,0} & = 360(3B_4^0 - 7B_6^0), \\
B_{\pm4,0} & = 60\sqrt{70}(B_4^0 - 126B_6^0), \\
\end{align*}
\]

for the \( J = \pm 4 \) and 0 sectors. Note that we obtain three \( 2 \times 2 \) and one \( 3 \times 3 \) matrices. After diagonalization, we obtain four eigen energies as

\[
\begin{align*}
E(\Gamma_1) & = 1680(B_4^0 - 60B_6^0), \\
E(\Gamma_3) & = 240(B_4^0 + 336B_6^0), \\
E(\Gamma_4) & = 840(B_4^0 + 6B_6^0), \\
E(\Gamma_5) & = -120(13B_4^0 + 210B_6^0), \\
\end{align*}
\]

As shown in Fig. 1(c), for \( B_4^0 > 0 \), the ground state is a \( \Gamma_5 \) triplet for \( B_6^0 > 0 \), while it is a \( \Gamma_1 \) singlet for \( B_6^0 < 0 \). On the other hand, for \( B_4^0 < 0 \), the ground state is also a \( \Gamma_5 \) triplet for \( B_6^0 > 0 \) and a \( \Gamma_1 \) singlet for \( B_6^0 < 0 \), respectively, except for the region around \( B_4^0 \sim 0 \), in which the case the \( \Gamma_3 \) becomes the ground state, as shown in Fig. 1(d).

When we compare the \( LS \) coupling results with those for the \( j \)-\( j \) coupling, the following two points are noted:
(i) Although we commonly observe conversion of the ground state between a Γ₅ triplet and a Γ₁ singlet, the correspondence with the sign of B₀₂ is reversed between the LS and the j-j coupling schemes. (ii) The Γ₃ doublet does not appear as the ground state in the j-j coupling scheme. The point (i) may not be serious, since it is just a problem of parametrization. However, point (ii) looks strange at first glance. In order to clarify this point, it is useful to change the basis in the j-j coupling. As shown in Fig. 1(a), in the one f-electron case, for B₀₂>0 (<0), the Γ₇ doublet is the ground state (excited state), while the Γ₆ quartet is the excited state (ground state). If we introduce pseudo-spin to distinguish the Kramers doublet, Γ₇ indicates a single orbital, while Γ₆ denotes doubly degenerate orbitals. When we put two electrons into the situation shown in Fig. 1(a), owing to the Hund’s rule coupling we obtain three cases: (i) Two electrons occupy Γ₇ for B₀₂>0. (ii) They occupy Γ₆ for B₀₂<0. (iii) One occupies Γ₇ and the other does Γ₆ around B₀₂≈0.

After algebraic calculations, we confirm that (i) and (ii) correspond to a Γ₁ singlet and a Γ₅ triplet, respectively, in agreement with the above result. However, in contrast to the naive expectation, (iii) results in a Γ₄ triplet due to the Hund’s rule coupling. Note that this Γ₄ triplet does not become the unique ground state, as shown in Fig. 1(b), except at B₀₂=0. In this case, the Γ₃ doublet appears only as an excited state, since this Γ₃ doublet is found to be composed of two singlet states, each of which includes a pair of electrons, one in Γ₇ and the other in Γ₆. As is easily understood, a local singlet state in multi-orbital systems is energetically penalized due to the Hund’s rule coupling, and thus, the Γ₃ doublet is always the excited state, higher than the Γ₄ triplet.

As long as we consider the j-j coupling scheme for the j=5/2 sextet, the Γ₃ doublet never appears as the ground state, which is attributed to ignoring the j=7/2 octet. However, it is not allowed to include the effect of this octet in the present j-j coupling scheme, since it just contradicts the original assumption. Namely, if the Hund’s rule coupling is strong enough so that j=7/2 cannot be neglected, we must not consider the j-j coupling schemes, but take the LS coupling scheme from the outset. Here we have an interesting conclusion: In the j-j coupling scheme, Γ₃ never becomes the ground state. Only in the LS coupling scheme with B₀₂<0 and B₁₂≈0, the ground state becomes Γ₃. Except for the disappearance of the Γ₃ doublet, it is concluded that the CEF terms can be treated within the j-j coupling schemes.

D. Hopping term

Now we consider the hopping motion of f electrons based on the j-j coupling scheme. As discussed in the previous subsections, the one f-electron state is labelled by μ. Within the second-order perturbation, the hopping amplitude t⁺µν includes two contributions, as shown in Fig. 2: (a) The direct hopping of f electrons between the µ-state at i site and the ν-state at i+a site and (b) the hopping via ligand anions located along the a-direction from the f-ion site. In order to evaluate both contributions, basically we employ Slater’s two-center integral method as has been done in d-electron systems. However, as emphasized in the previous subsections, it is necessary to pay due attention to the fact that spin and orbital are mixed. Thus, in this case, it is not allowed to simply use the Slater-Koster table.

To avoid any confusion, it is convenient to step back to f-electron operators in the ℓ=3 multiplet, defined as f₃µσ. Using Clebsch-Gordan coefficients, f₃µσ with real-spin σ is related to aₘ as

$$aₘ = \sum_σ C_{⟨σ,\ell⟩} f₃,µ−σ/2,σ.$$

Note again here that σ is defined to be +1 (−1) for up (down) spin.

First, let us consider the direct hopping of f electrons along the a-direction, as shown in Fig. 2(a). Since the real spin should be conserved in the hopping process, t⁺µν is given as

$$t⁺µν = \sum_σ C_{σ,ℓ} C_{ν,σ} T₃,µ−σ/2,σ,$$

where T₃,µ−σ/2,σ is the hopping amplitude of electrons between (ℓ,m)- and (ℓ′,m′)-states along the a-direction.

Now the problem is reduced to the evaluation of T₃,µ−σ/2,σ. Although we can simply consult the paper of Slater and Koster, a convenient formula has been obtained by Sharma for the overlap integral between two orbitals, (ℓ,m) and (ℓ′,m′) connected by unit vector a. It is expressed as

$$T₃,µ−σ/2,σ = (ℓℓ′σ) \sqrt{\frac{4π}{2ℓ+1}} \sqrt{\frac{4π}{2ℓ′+1}} Yₗₗ^*(θ,φ) Yₗₗ′(θ,φ),$$

where (ℓℓ′σ) denotes Slater’s two-center integral through the σ bond, for instance, it is (fσf) for ℓ=ℓ′=3 and (fpσ)
for $\ell=3$ and $\ell’=1$. $Y_{\ell m}$ is the spherical harmonic function with $m=-\ell, \ldots, \ell$. $\theta$ and $\varphi$ are polar and azimuth angles, respectively, to specify the vector $\mathbf{a}$ as

$$
\mathbf{a} = (\sin \theta \cos \varphi, \sin \theta \sin \varphi, \cos \theta).
$$

Let us consider the direct hopping between $f$ orbitals in nearest neighbor sites by putting $\ell=\ell’=3$. After some calculations, we obtain the hopping amplitudes as follows. For diagonal elements, we obtain

$$
\begin{align*}
t_{a}^{\pm 5/2, \pm 5/2} &= 5t_0 \sin^4 \theta, \\
t_{a}^{\pm 3/2, \pm 3/2} &= t_0 \sin^2 \theta (1 + 15 \cos^2 \theta), \\
t_{a}^{\pm 1/2, \pm 1/2} &= 2t_0 (1 - 2 \cos^2 \theta + 5 \cos^4 \theta),
\end{align*}
$$

where the energy unit $t_0$ is given by

$$
t_0 = \frac{3}{50} (f f \sigma),
$$

where $(f f \sigma)$ is the Slater-Koster two-center integral between adjacent $f$ orbitals. Note that $t_{\mu,-\mu} = 0$. For off-diagonal elements, we obtain

$$
\begin{align*}
t_{a}^{\pm 5/2, \pm 1/2} &= -t_0 \sqrt{10} e^{\mp 2i\varphi} \sin^2 \theta (1 - 3 \cos^2 \theta), \\
t_{a}^{\pm 3/2, \pm 3/2} &= t_0 \sqrt{5} e^{\pm 4i\varphi} \sin^4 \theta, \\
t_{a}^{\pm 1/2, \pm 3/2} &= -t_0 \sqrt{2} e^{\mp 2i\varphi} \sin^2 \theta (1 + 5 \cos^2 \theta),
\end{align*}
$$

and

$$
\begin{align*}
t_{a}^{5/2,-1/2} &= -t_{a}^{1/2,-5/2} = t_0 \sqrt{10} e^{-3i\varphi} \sin^2 \theta \sin 2 \theta, \\
t_{a}^{5/2,3/2} &= -t_{a}^{3/2,-5/2} = -2t_0 \sqrt{5} e^{-i\varphi} \sin^2 \theta \sin 2 \theta, \\
t_{a}^{1/2,3/2} &= -t_{a}^{3/2,-1/2} = t_0 \sqrt{2} e^{i\varphi} \sin 2 \theta (1 - 5 \cos^2 \theta).
\end{align*}
$$

Note that $t_{\mu \nu}^{a} = t_{\mu \nu}^{a*}$.

Next we consider the hopping of $f$ electrons $t_{\mu \nu}^{a}$ through ligand anions, as shown in Fig. 2(b). Assume that $\ell$-orbitals are situated along the $\mathbf{a}$-direction and $f$-electrons hop to the neighboring $f$-site through these $\ell$-orbitals. Again we note that the real spin is conserved in the hopping process. In second-order perturbation, we can easily obtain

$$
t_{\mu \nu}^{a} = \sum_{\mu, \sigma} C_{\mu \sigma} C_{\nu \sigma} T_{a, \mu - \sigma; 2/\ell, \ell} T_{a, \mu; 3/\ell, \ell} / \varepsilon_{\ell} - \varepsilon_{\ell},
$$

where $\varepsilon_{\ell}$ and $\varepsilon_{\ell}$ are the energy levels for $\ell$- and $f$-orbitals and $m$ runs between $-\ell$ and $\ell$. Due to the orthogonality of spherical harmonics, it is easily reduced to

$$
t_{\mu \nu}^{a} = (f f \sigma)^2 t_{\mu \nu}^{a} / \varepsilon_{\ell} - \varepsilon_{\ell} (f f \sigma).
$$

It is stressed that the $\mathbf{a}$-dependence of $t_{\mu \nu}^{a}$ is the same as that of $t_{\mu \nu}^{a}$, although the energy unit is changed from $(f f \sigma)^2/\varepsilon_{\ell} - \varepsilon_{\ell})$. Note that in general, the sign is also changed.

### E. Simplified models

In previous subsections, we have completed the construction of a model Hamiltonian which is expected to be a basic model to investigate the microscopic properties of $f$-electron systems. However, it includes six states per site, i.e., three Kramers doublets. For practical purposes, it is more convenient to simplify the model further by discarding one of the three Kramers doublets. Although the hopping amplitudes are obtained in a general form applicable to any type of crystal structure, it is necessary to set the crystal structure for the purpose of actual calculations.

#### 1. $\Gamma_8$ model

First let us consider a simple cubic lattice composed of ions with $f$ electrons. Under the cubic CEF, as discussed above, for $B_4^0 < 0$ the $\Gamma_8$ quartet becomes the ground state, while the $\Gamma_7$ doublet is the excited state. This situation is considered to be realized when ligand anions are situated in the face-centered or body-centered position, due to a naive discussion of the point-charge picture. Note that the effect of ligand anions is included only through the CEF term, and we do not consider its effect on $f$-electron hopping. Then, it is possible to consider a model consisting of $\Gamma_8$, neglecting $\Gamma_7$ under the condition of $B_4^0 < 0$.

To consider the model including $\Gamma_8$ levels, it is useful to define new operators with “orbital” degrees of freedom to distinguish two Kramers doublets included in $\Gamma_8$ as

$$
\begin{align*}
c_{10}^{\uparrow} &= \sqrt{5/6} a_{4-5/2} + \sqrt{1/6} a_{43/2}, \\
c_{10}^{\downarrow} &= \sqrt{5/6} a_{45/2} + \sqrt{1/6} a_{4-3/2},
\end{align*}
$$

for $\alpha$ orbital electrons and

$$
\begin{align*}
c_{1\beta}^{\uparrow} &= a_{14-1/2}, \\
c_{1\beta}^{\downarrow} &= a_{141/2},
\end{align*}
$$

for $\beta$ orbital electrons, respectively. Note that the $\Gamma_7$ state is given as a $\gamma$ orbital as

$$
\begin{align*}
c_{1\gamma}^{\uparrow} &= \sqrt{1/6} a_{4-5/2} - \sqrt{5/6} a_{43/2}, \\
c_{1\gamma}^{\downarrow} &= \sqrt{5/6} a_{415/2} - \sqrt{1/6} a_{4-3/2}.
\end{align*}
$$

For the standard time reversal operator $K=-i\sigma_y K$, where $K$ denotes an operator to take the complex conjugate, we can easily show the relation

$$
Kc_{\ell \sigma} = \sigma_{\ell \sigma} c_{\ell \sigma}.
$$

Note that this has the same definition for real spin.

For hopping in the $xy$ plane and along the $z$-axis, we simply set $(\theta, \varphi)$ to be $(\pi/2, 0)$, $(\pi/2, \pi/2)$, and $(0, 0)$ for $\mathbf{a}=x=[1,0,0]$, $y=[0,1,0]$, and $z=[0,0,1]$, respectively. Then, by using the general results in the previous subsection, we easily obtain $t_{\mu \nu}^{a}$ between neighboring $f$ orbitals.
in the $xy$ plane and along the $z$ axis. Further we transform the basis by the above definitions for operators with orbital degrees of freedom. The results are given as:

\[
t^x_{\tau\tau'} = t \begin{pmatrix}
1 & -1/\sqrt{3} & 0 \\
-1/\sqrt{3} & 1/3 & 0 \\
0 & 0 & 0
\end{pmatrix},
\]

(45)

for the $x$ direction,

\[
t^y_{\tau\tau'} = t \begin{pmatrix}
1 & 1/\sqrt{3} & 0 \\
1/\sqrt{3} & 1/3 & 0 \\
0 & 0 & 0
\end{pmatrix},
\]

(46)

for the $y$ direction, and

\[
t^z_{\tau\tau'} = t \begin{pmatrix}
0 & 0 & 0 \\
0 & 4/3 & 0 \\
0 & 0 & 0
\end{pmatrix},
\]

(47)

for the $z$ direction. Note that $t=6t_0=(9/28)(ff\sigma)$. Here we note two points: (i) Hopping amplitudes among $\Gamma_8$ orbitals are just the same as those for the $v_\epsilon$ orbitals of $3d$ electrons. This is quite natural if we recall the fact that $\Gamma_8$ is isomorphic to $\Gamma_3 \times \Gamma_6$, where $\Gamma_3$ indicates $E$ representation for the orbital part and $\Gamma_6$ denotes the spin part. (ii) The $\Gamma_7$ orbital is localized, since the corresponding wavefunction has nodes along the axis direction. Since $\Gamma_7$ is the excited state for $D_{3h}^0<0$ and it is also localized, electrons do not occupy the $\Gamma_7$ orbital.

After lengthy and tedious calculations to transform the basis of the Coulomb interaction terms, the Hamiltonian for $\Gamma_8$ is given by

\[
H_8 = \sum_{i,a,\sigma,\tau,\tau'} t^a_{\tau\tau'} c^\dagger_{i\tau\sigma} f_{i+a\tau'\sigma} - \varepsilon \sum_i (\rho_{i\alpha} - \rho_{i\beta})/2
+ U \sum_{i,\tau} \rho_{i\uparrow}\rho_{i\downarrow} + U' \sum_i \rho_{i\alpha}\rho_{i\beta}
+ J/2 \sum_{i,\sigma,\sigma',\tau\neq\tau'} c^\dagger_{i\tau\sigma} c_{i\tau\sigma'} c^\dagger_{i\tau'\sigma'} c_{i\tau'\sigma'}
+ J' \sum_{i,\tau\neq\tau'} c^\dagger_{i\tau\sigma} c^\dagger_{i\tau'\sigma'} c_{i\tau'\sigma'} c_{i\tau\sigma'},
\]

(48)

where $\rho_{i\tau\sigma} = c^\dagger_{i\tau\sigma} c_{i\tau\sigma}$ and $\rho_{i\tau} = \sum_{\sigma} \rho_{i\tau\sigma}$. Note that in the second term, the level splitting $\varepsilon$ is simply included to include partially the effect of a tetragonal CEF. In the Coulomb interaction terms, $U$, $U'$, $J$, and $J'$ denote intra-orbital, inter-orbital, exchange, and pair-hopping interactions, respectively, expressed by the Racah parameters $E_k$ as

\[
U = E_0 + E_1 + 2E_2,
U' = E_0 + (2/3)E_2,
J = 5E_2,
J' = E_1 - (11/3)E_2.
\]

(49)

Note that the relation $U=U'+J+J'$ holds, ensuring rotational invariance in pseudo-orbital space for the interaction part.

We believe that this $\Gamma_8$ Hamiltonian provides a simple, but non-trivial model to consider superconductivity and magnetism in $f$-electron systems. Note again that it is essentially the same as the model for $v_\epsilon$ electron systems such as manganites, although the coupling with Jahn-Teller distortion is not included in the present model. Due to the complex interplay and competition among charge, spin, and orbital degrees of freedom, a rich phase diagram has been obtained for manganites. Thus, it is definitely expected that a similar richness will also be unveiled for $f$-electron systems based on the $\Gamma_8$ model Hamiltonian.

2. $\Gamma_7$ model

The $\Gamma_8$ Hamiltonian $H_8$ is believed to be a non-trivial model for $f$-electron systems, since we can immediately grasp some essential aspects of $f$-electron materials viewed as charge-spin-orbital complex systems. In fact, based on $H_8$, we can have insight into the effect on superconductivity of cooperation and competition among spin and orbital fluctuations in the new family of heavy fermion materials CeMIn$_5$ ($M=$Ir, Co, and Rh), with the HoCoGa$_5$-type tetragonal structure.

Among CeMIn$_5$ materials, the de Haas-van Alphen (dHvA) effect has been successfully observed in CeIrIn$_5$ and CeCoIn$_5$ both of which have huge electronic specific heat coefficients of several hundreds of mJ/K$^2$·mol. The angular dependence of major experimental dHvA frequency branches is well explained by a quasi two-dimensional Fermi surface. This is a clear advantage when we construct a model Hamiltonian, since it is enough to consider the two-dimensional case.

In order to analyze further the electronic properties from a quantitative viewpoint, it is desirable to include more precisely the effect of the actual crystal structure. For instance, in the previous subsection, we have introduced the level splitting $\varepsilon$ between $\Gamma_8$ levels in a simple way, in order to take into account partially the effect of a tetragonal CEF. However, in an actual tetragonal situation, there occur three Kramers doublets, two $\Gamma_7$ and one $\Gamma_6$. Thus, in this subsection, we attempt to incorporate the effect of a tetragonal CEF more faithfully into the model.

First let us consider the tetragonal CEF term. After the diagonalization, we obtain three Kramers doublets, two $\Gamma_7$ and one $\Gamma_6$, expressed as

\[
|\Gamma^{(1)}_7\rangle = (pa^\dagger_{i\pm 5/2} + qa^\dagger_{i\pm 3/2})|0\rangle,
|\Gamma^{(2)}_7\rangle = (-qa^\dagger_{i\pm 5/2} + pa^\dagger_{i\pm 3/2})|0\rangle,
|\Gamma_6\rangle = a^\dagger_{i\pm 1/2}|0\rangle.
\]

(50)

The coefficients $p$ and $q$ are determined by the CEF parameters as

\[
p = \sqrt{(1+\alpha)/2}, \quad q = \theta \sqrt{(1-\alpha)/2},
\]

(51)
where $\theta = B_4^1/B_4^5$ and

$$\alpha = 12(B_2^0 + 20B_4^0)/\varepsilon_7,$$  \hspace{1cm} (52)

with

$$\varepsilon_7 = 12\sqrt{(B_2^0 + 20B_4^0)^2 + 20(B_4^1)^2}. \hspace{1cm} (53)$$

The corresponding eigen energies are given by

$$E(\Gamma^{(1)}) = 4(B_2^0 - 15B_4^0) + \varepsilon_7/2,$$

$$E(\Gamma^{(2)}) = 4(B_2^0 - 15B_4^0) - \varepsilon_7/2,$$

$$E(\Gamma_6) = -8(B_2^0 - 15B_4^0), \hspace{1cm} (54)$$

respectively.

If the $\Gamma_6$ level is higher than the other two $\Gamma_7$ levels, it is possible to obtain another simplified model for the $\Gamma_7$ levels. In fact, in some experimental papers on CeMIn$_5$, we have found that the position of the $\Gamma_6$ level is the highest among the three Kramers doublets. Thus, a simplified and realistic model for CeMIn$_5$ can be constructed by including only two $\Gamma_7$ levels.

In this crystal structure, the Ce ions form a two-dimensional tetragonal lattice, while the In ions are located in the face-centered positions of this Ce-ion network, as shown in Fig. 3. We include the nearest-neighbor hopping between Ce 4$f$ orbitals as well as next-nearest neighbor hopping via In 5$p$ orbitals. Due to the symmetry, the latter process contributes only along the diagonal direction, while hopping via $p$-orbitals along the bond direction vanishes.

Based on the two-dimensional lattice, we have further constructed a Hamiltonian called the "f-p model" by keeping the $f-p$ hybridization explicitly. In order to compare the tight-binding dispersion directly with the results of a relativistic band-structure calculation, it is important to keep the hybridization term. However, here we consider an $f$-electron model wherein we include the effects of $f-p$ hybridization in the next-nearest neighbor hopping of $f$ electrons. We believe it will be adequate for the treatment of superconductivity and magnetism if we further add the Coulomb interaction terms to the model.

Since two $\Gamma_7$'s are given by the linear combinations of $\mu = \pm 3/2$ and $\pm 5/2$, we obtain the $\Gamma_7$ model just by discarding the $\mu = \pm 1/2$ states. It is convenient to define additional new operators as

$$c_{1\uparrow} = a_{5/2}, \quad c_{1\downarrow} = a_{-5/2},$$

$$c_{2\uparrow} = a_{-3/2}, \quad c_{2\downarrow} = a_{3/2}. \hspace{1cm} (55)$$

Again, we can easily show the relation $Kc_{i\sigma\tau} = \sigma c_{i\tau - \sigma}$.

For the nearest neighbor hopping, we obtain

$$t_{\tau\tau'} = (t/6) \left( \frac{5}{\sqrt{5}} - 1 \right). \hspace{1cm} (56)$$

Note that $t$ has the same definition as for the $\Gamma_8$ model. On the other hand, for the next-nearest neighbor hopping via the $p$ orbitals, we obtain

$$t'_{\tau\tau'} = (t'/6) \left( \frac{5}{\sqrt{5}} - 1 \right), \hspace{1cm} (57)$$

for both $[1,1,0]$ and $[1,-1,0]$ directions. The next-nearest neighbor hopping amplitude is given by

$$t' = \frac{9}{28}(f_p\sigma)^2 \frac{28}{\varepsilon_1 - \varepsilon_p}, \hspace{1cm} (58)$$

where $(f_p\sigma)$ is the Slater-Koster two-center integral for $f$ and $p$ orbitals. Note that in general $t' < 0$.

The $\Gamma_7$ model is then written as

$$H_7 = \sum_{i,\sigma}^{} t_{\tau\tau'} c^\dagger_{i\sigma\tau} c_{i+\alpha\tau' \sigma} + \sum_{i,\alpha,\sigma,\tau,\tau'}^{} t_{\tau\tau'} c^\dagger_{i\sigma\tau} c_{i+\alpha\tau' \sigma} + \frac{\varepsilon_7}{2} \sum_{i,\sigma,\tau,\tau'}^{} (\alpha \tau_z + \theta \sqrt{1 - \alpha^2 \tau_x}) c^\dagger_{i\sigma\tau} c_{i\tau' \sigma}$$

$$+ \sum_{i,\sigma}^{} U_{\tau\rho\pi\tau} c_{i\rho\pi\sigma} + U' \sum_{i}^{} \rho_{a\rho b} + J \sum_{i,\tau \neq \tau'}^{} c^\dagger_{i\tau\sigma} c_{i\tau' \sigma} + c^\dagger_{i\tau\sigma} c_{i\tau' \sigma},$$

where $a$ and $b$, respectively, denote the vectors connecting nearest- and next-nearest neighbor sites. $\tau_x$ and $\tau_z$ are Pauli matrices. The energy level shift has been neglected here for simplicity. The intra-orbital Coulomb interactions are given by $U_1 = E_0 - 3E_2 + E_1$ and $U_2 = E_0 + 5E_2 + E_1$ for the 1 and 2 orbitals, respectively, and the inter-orbital Coulomb interaction is denoted by $U' = E_0 - 5E_2$. The Hund’s coupling and the pair-hopping interactions are given by $J = 10E_2$ and $J' = E_1$, respectively.

Three comments on $H_7$ are in order. (1) There is no transverse component in the Hund’s coupling term. (2) $U_1 \neq U_2$ since the 1 and 2 orbitals belong to different symmetries. (3) For the case of $n=1$, both $J$ and $J'$ are sometimes neglected for simplicity, since they become irrelevant in the large-$U'$ limit. When we are interested in the strongly correlated region, it is possible to safely set $E_1 = E_2 = 0$ for the case of $n=1$, leading to $U_1 = U_2 = U' = E_0$. 

FIG. 3: Schematic view of a two-dimensional lattice composed of Ce and In ions for CeMIn$_5$ (M=Ir, Rh, and Co).
III. ANALYSIS AND RESULTS

In the previous section, we have discussed in detail the construction of a microscopic model for \( f \)-electron systems based on the \( j-j \) coupling scheme. For practical purposes, we have also prepared a couple of simplified models corresponding to an actual crystal structure. Those models can be analyzed with several techniques from both an analytical and a numerical viewpoint. It is impossible to show here the results for all models. In this section, we show exact diagonalization results for \( H_s \) as a typical example of an orbital degenerate system.

A. Measured quantities

Before proceeding to the exhibition of calculated results, let us discuss the quantities we would measure in a model including orbital degree of freedom. First of all, in order to see the spin and charge structure, it is quite natural to measure the spin and charge correlation functions, defined as

\[
S(q) = \sum_{ij} e^{i\mathbf{q} \cdot (\mathbf{i} - \mathbf{j})} \langle s_i \overline{s}_j \rangle, \quad (60)
\]

and

\[
C(q) = \sum_{ij} e^{i\mathbf{q} \cdot (\mathbf{i} - \mathbf{j})} \langle \rho_i \overline{\rho}_j \rangle, \quad (61)
\]

respectively, where \( s_i \equiv \sum_\sigma (\rho_{i\uparrow} - \rho_{i\downarrow})/2 \) and \( \rho_i = \sum_\sigma \rho_{i\sigma} \). On the other hand, in order to see the orbital structure, it is quite useful to calculate the orbital correlation function, given by

\[
O_{\tau'\tau}(q) = \sum_{ij} e^{i\mathbf{q} \cdot (\mathbf{i} - \mathbf{j})} \langle \rho_{i\tau} \overline{\rho}_{j\tau'} \rangle. \quad (62)
\]

As is easily understood from the above equations, even if the orbital degree of freedom is further included in the model Hamiltonian, there is no ambiguity in the definitions for spin and charge correlations, given by sums in terms of an orbital index. For the orbital correlations, we also consider as an orbital-dependent charge correlation, which can be defined without any difficulty.

However, when we attempt to discuss the superconducting pair correlation, we immediately encounter some serious problems. Namely, it is necessary to determine the form factors for the pairing states in both momentum and orbital space. Note that even in the single-orbital Hubbard model, it is necessary to determine the momentum dependence, but in general, our task can be reduced through the help of a group-theoretical analysis. In the orbital degenerate model, the extra task of determining the form factor in orbital space is also imposed upon us. Especially in the present realistic models, in which the orbital degree of freedom does \textit{not} provide a good quantum number, the situation seems to be very severe at first glance, since we cannot resort to a group-theoretical analysis for the orbital dependence of the form factor.

In order to overcome this problem, we carefully reconsider it based on the concept of off-diagonal long-range order. Let us define the pair correlation as

\[
P_{\pm} = \langle \Phi_\pm \Phi_\pm \rangle, \quad (63)
\]

where the subscript \(- (+)\) denotes spin singlet (triplet) pairing and \( \Phi_\pm \) is a pair operator, given in general by

\[
\Phi_\pm = \sum_{i\alpha \mu \mu'} (c_{i\mu\uparrow} c_{i+\mathbf{q}\mu'\downarrow} \pm c_{i\mu\downarrow} c_{i+\mathbf{q}\mu'\uparrow}) / \sqrt{2}. \quad (64)
\]

Since a pair with zero total momentum is considered here, \( \varphi_{\pm \mu \mu'} \) depends only on \( \mathbf{a} \), which is the vector connecting the sites. Note also that the orbital dependence of \( \varphi_{\pm \mu \mu'} \) is not solely determined by symmetry considerations.

We can easily show that the pair correlation is written in the form

\[
P_{\pm} = \sum_{\alpha \beta \mu \mu', \nu \nu'} \varphi_{\pm \mu \mu'} p_{\alpha \mu \beta \nu} \varphi_{\beta \nu \nu'}, \quad (65)
\]

where the matrix element \( p_{\alpha \mu \beta \nu} \) is written as

\[
p_{\alpha \mu \beta \nu} = \sum_{ij} \langle (c_{ij\uparrow} c_{i+\mathbf{q} \mu' \downarrow})^\dagger (c_j^{\dagger} c_{j+\mathbf{q} \nu' \uparrow}) \rangle \]
\[
+ \langle (c_{ij\downarrow} c_{i+\mathbf{q} \mu' \uparrow})^\dagger (c_j^{\dagger} c_{j+\mathbf{q} \nu' \downarrow}) \rangle \]
\[
+ \langle (c_{ij\uparrow} c_{i+\mathbf{q} \mu' \downarrow}) (c_j^{\dagger} c_{j+\mathbf{q} \nu' \uparrow}) \rangle \]
\[
+ \langle (c_{ij\downarrow} c_{i+\mathbf{q} \mu' \uparrow}) (c_j^{\dagger} c_{j+\mathbf{q} \nu' \downarrow}) \rangle \rangle / 2. \quad (66)
\]

Here it is necessary to recall the concept of off-diagonal long-range order. Namely, the occurrence of superconductivity is detected when the largest eigenvalue of the pair correlation matrix becomes the order of \( N \), where \( N \) is the number of electrons. Thus, in a small cluster calculation, the possible superconducting pair state should be defined by the eigenstate with the maximum eigenvalue \( \rho_{\text{max}} \) of the matrix \( P \). Of course, in order to prove the existence of off-diagonal long-range order, we need to show that \( \rho_{\text{max}} \) becomes the order of \( N \) with increasing the cluster size. However, at some cluster size, a possible pairing state is determined without ambiguity by the eigenstate with \( \rho_{\text{max}} \).

A prescription to define the pair operator is briefly summarized. First, we determine the pair correlation matrix \( p_{\pm \mu \mu', \nu \nu'} \). Then we diagonalize it, and the form factor \( \varphi_{\pm \mu \mu'} \) will be defined by the eigenstate corresponding to the maximum eigenvalue of the pair correlation matrix.

B. Symmetry of the orbital dependent Cooper-pair

In the previous subsection, we have discussed a way to define the pair operator in orbital degenerate systems.
Here we further consider the symmetry of the Cooper pair in orbital space from a general point of view. Anomalous Green’s functions for spin triplet and singlet pairs are, respectively, defined by

$$F_{\mu \nu}^a(k, \tau) = -[\langle c_{k\mu}^\dagger(\tau)c_{-k\nu} \rangle + \langle c_{k\mu}(\tau)c_{-k\nu}^\dagger \rangle], \quad (67)$$

and

$$F_{\mu \nu}^s(k, \tau) = -[\langle c_{k\mu}^\dagger(\tau)c_{-k\nu} \rangle - \langle c_{k\mu}(\tau)c_{-k\nu}^\dagger \rangle], \quad (68)$$

where $c_{k\mu}(\tau) = e^{iHt}c_{k\mu}e^{-iHt}$ and $\tau$ denotes imaginary time. Due to cyclic invariance of the trace, we obtain the following relations:

$$F_{\mu \nu}^s(-k, \tau) = -F_{\nu \mu}^s(k, \beta - \tau),$$

$$F_{\mu \nu}^s(-k, \tau) = F_{\nu \mu}^s(k, \beta - \tau), \quad (69)$$

where $\beta$ is the inverse temperature. Further, after Fourier transformation, we obtain

$$F_{\mu \nu}^s(-k, i\omega_n) = F_{\nu \mu}^s(k, -i\omega_n),$$

$$F_{\mu \nu}^t(-k, i\omega_n) = -F_{\nu \mu}^t(k, -i\omega_n), \quad (70)$$

where $\omega_n$ is the fermion Matsubara frequency, given by $\omega_n = \pi T(2n + 1)$ with $n$ an integer. These are the basic relations representing the symmetry of Cooper pairs in orbital degenerate systems.

Except for differences in the spin states such as singlet and triplet, “parity” is the only extra good quantum number to specify the pairing state, since there is no conservation law regarding orbital degrees of freedom. Thus, we can produce even- and odd-parity states, satisfying

$$P F_{\mu \nu}^s(k, i\omega_n) = \pm F_{\mu \nu}^s(k, i\omega_n), \quad (71)$$

where $P$ indicates the operator to change $k$ to $-k$. It is easy to understand that $F_{\mu \nu}^s$ is given by linear combinations of $F_{\mu \nu}^s(k, i\omega_n)$ and $F_{\nu \mu}^s(k, -i\omega_n)$. Although we cannot define $F_{\mu \nu}^t$ uniquely, it is convenient to consider combinations of odd and even functions both for orbital exchange and sign-change in frequency. If we introduce two orbitals “a” and “b”, then after some simple algebra, we obtain

$$F_{\mu \nu}^s(k, i\omega_n) = \sum_{i=1}^{4} A_i^\pm F_{\mu \nu}^{i\pm}(k, i\omega_n), \quad (72)$$

where $A_i^\pm$ is an arbitrary number and $F_{\mu \nu}^{i\pm}(k, i\omega_n)$ is given by

$$F_{1}^{\pm}(k, i\omega_n) = F_{\mu \nu}^{a\pm}(k, i\omega_n) \pm F_{\mu \nu}^{b\pm}(k, -i\omega_n),$$

$$F_{2}^{\pm}(k, i\omega_n) = F_{\mu \nu}^{ab}(k, i\omega_n) \pm F_{\mu \nu}^{ba}(k, -i\omega_n),$$

$$F_{3}^{\pm}(k, i\omega_n) = F_{\mu \nu}^{a\pm}(k, i\omega_n) + F_{\mu \nu}^{b\pm}(k, -i\omega_n) + F_{\mu \nu}^{ab}(k, i\omega_n) - F_{\mu \nu}^{ba}(k, -i\omega_n),$$

$$F_{4}^{\pm}(k, i\omega_n) = F_{\mu \nu}^{ab}(k, i\omega_n) \mp F_{\mu \nu}^{ab}(k, -i\omega_n).$$

Since the present Hamiltonian is not invariant with orbital exchange the terms “orbital symmetric” and “orbital antisymmetric” cannot be used as a label to specify the state. However, it is convenient to categorize $F_{i}^{\pm}(k, i\omega_n)$ as follows: The $F_{1}^{\pm}(k, i\omega_n)$ ($i = 1 \sim 3$) are orbital-symmetric and even function of frequency, while the $F_{1}^{-}(k, i\omega_n)$ ($i = 1 \sim 3$) are orbital-symmetric and odd function of frequency. On the other hand, $F_{4}^{\pm}(k, i\omega_n)$ is orbital-antisymmetric and an odd function of frequency, while $F_{4}^{-}(k, i\omega_n)$ is orbital-antisymmetric and an even function of frequency.

If we consider the zero-frequency limit, we can simply drop the odd functions of frequency. Namely, the even-parity pair is expressed as a combination of orbital-symmetric functions, while the odd-parity solution is just given by $F_{4}^{-}(k, i\omega_n)$, the orbital-antisymmetric part. Note, however, that this is just an accident due to the vanishing of odd-functions of frequency. We must not consider that the orbital state provides a good label to specify the pairing symmetry, although it is a convenient way to classify the pair state. Again, it is stressed that spin state and parity are labels used to specify the pairing symmetry.

For the case of spin triplet, it is easy to repeat the same discussion as that for spin singlet. Note that in the zero-frequency limit, the odd-parity solution is given by the combination of orbital-symmetric parts, while the even-parity function is expressed only by the orbital-antisymmetric part.

Up to now we have discussed the general situation in which the system is not invariant under the exchange of orbitals. We believe that this is quite natural since in actual materials, the shapes of orbitals are different from one another. However, it is possible to consider a fictitious Hamiltonian which is invariant under orbital exchange. In such a situation, the words “orbital symmetric” and “orbital antisymmetric” recover physical meanings which distinguish the pairing states. Namely, we can further classify anomalous Green’s functions as

$$F_{\mu \nu}^{s}(k, i\omega_n) = \sum_{i=1}^{3} A_i^{+} F_{\mu \nu}^{i}(k, i\omega_n),$$

$$F_{\mu \nu}^{t}(k, i\omega_n) = F_{\mu \nu}^{4}(k, i\omega_n),$$

$$F_{\mu \nu}^{s}(k, i\omega_n) = \sum_{i=1}^{3} A_i^{-} F_{\mu \nu}^{i}(k, i\omega_n),$$

$$F_{\mu \nu}^{s}(k, i\omega_n) = F_{\mu \nu}^{4}(k, i\omega_n), \quad (74)$$

where the subscripts + and − denotes parity even and odd, while “s” and “a” indicate the orbital-symmetric and orbital antisymmetric, respectively. In this case, the frequency dependence is automatically classified: Even-function for +s and −a and odd-function for +a and −s.

Finally, it is again stressed that when we consider pair correlation in the static limit, at first glance, orbital symmetric and antisymmetric parts seem to be separated, but such a separation is spurious owing to the speciality of the static limit.

### C. Numerical Results

Next we show results obtained using exact diagonalization techniques for an 8-site tilted cluster. Since we
In Fig. 4(c), we can see an orbital disordered (OD) phase where orbital fluctuations are suppressed in the Mott insulator. As observed in Ref. 13, this phase is characterized by a paramagnetic (PM) phase, while for $|\epsilon|>0.5$, $S(\pi, \pi)$ becomes abruptly dominant, strongly suggesting an antiferromagnetic (AF) phase. This abrupt change is due to level crossing, but it is instructive to see the charge and orbital correlations. In Fig. 4(b), we show charge correlation, exhibiting again an abrupt change around $\epsilon \approx 0.5$. A decrease of charge correlation is the signature of a metal-insulator transition, since the charge fluctuations are suppressed in the Mott insulator. As observed in Fig. 4(c), we can see an orbital disordered (OD) phase for $\epsilon <0.5$ and a ferro-orbital (FO) phase for $\epsilon >0.5$. By monitoring the change in spin correlations, we can draw the ground-state phase diagram for $n=1$, as shown in Fig. 4(d). We see OD/PM phase for small $U$ and FO/AF phase for large $U$ region.

In Fig. 4(e), we show the eigenvalues of the pair correlation matrices for spin singlet and triplet states as a function of $\epsilon$. The state with the largest eigenvalue is a singlet, while a triplet appears as the second largest eigenvalue state. Even if we introduce a finite value of $J$, unfortunately, this triplet state is not the largest eigenvalue state, at least within the present 8-site calculation. However, in the previous analysis using the random phase approximation, the appearance of a triplet state has been suggested in the small $\epsilon$ region. It may be related to the present result having the triplet state as the second largest eigenvalue state.

In Fig. 4(f), the pair amplitudes for the largest eigenvalue state is shown in momentum space. Since we are measuring the static pair correlation, we can observe here an “orbital symmetric” state with “aa”, “bb”, and “ab+ba”, while the “orbital antisymmetric” part such as “ab−ba” is not mixed. As discussed in the previous subsection, it is just an accident due to the static limit, and the orbital symmetric state is not separated in general. Next we focus on the momentum dependence of each component. As seen in Fig. 4(f), the “aa” and “bb” parts of the pair amplitude exhibit $B_{1g}$, while “ab+ba” seems to belong to $A_{1g}$. If we recall that “a” and “b” each correspond to $e_g$ orbitals, then they have different signs for $\pi$/4 rotation in space. Thus, there exists a discrepancy in the symmetry between (“aa”, “bb”) and “ab+ba” components, although the total symmetry should be $B_{1g}$ in this case.

We have obtained a simultaneous onset of spin and orbital ordering, which can be interpreted as a transition between PM and AFM phases controlled by the suppression of orbital fluctuations. Moreover, just around the transition regime between PM and AFM phases, we can expect the appearance of d-wave superconductivity induced by AFM spin fluctuations, which has been identified as the $B_{1g}$ pairing state with the largest eigenvalue. In fact, the present model has been analyzed using the random phase approximation, leading to a transition between PM and d-wave superconducting phases with an increase of $\epsilon$. If we further increase $\epsilon$, eventually the system becomes an AFM insulating phase, and this successive transition agrees with the present results. Here it is stressed that the orbital degree of freedom plays a key role to control the ground-state properties. We believe that this viewpoint is applicable to the appearance of d-wave superconductivity in CeMIn$_5$, although the quantitative features should be discussed in detail using the $\Gamma_7$ model.

Next we consider the case of $n=1.5$ for the same $\Gamma_8$ model. For $\epsilon=0$, we depict the phase diagram in the $(U',J)$ plane, as shown in Fig. 5(a). Note that the region with $J>U'$ is unphysical and here we just ignore it. We see the appearance of the ferromagnetic (FM) phase, which is stabilized due to the strong Hund’s rule coupling. The interesting point is the pair amplitude inside the FM phase, as shown in Fig. 5(b). The momentum dependence of the largest eigenvalue state is characterized by even parity. As naively expected, due to the Hund’s rule
coupling, a local triplet is formed, but in order to gain kinetic energy, this pair should be spatially extended, as shown in Fig. 5(b). Note here that this is $A_{1g}$-like, since it is an even-parity state. Since we are now considering the pairing state in the strong coupling region, there is no reason to exclude the triplet state with even parity, which is not directly connected to the usual odd-parity triplet state. This is not surprising, since local triplet pair must have even parity, provided that one ion with $f$-orbitals is included in the unit cell. Thus, quite generally, we can conclude that the odd-parity triplet pair is not stabilized in the local Hund’s rule coupling, at least in the Bravais lattice, which is consistent with the previous discussion.

As for the mechanism of the attractive interaction in the pair inside the FM phase, it should be considered to be orbital fluctuations, since spin fluctuations are dead in the fully spin-polarized state. This point is intriguing due to a possible connection with the coexistence of superconductivity and ferromagnetism in UGe$_2$. Of course, in order to confirm such an exotic type of superconductivity, it would be necessary to consider the problem in the bulk limit using, for instance, the Green’s function method. This case will be discussed elsewhere.

Finally, we note that due care should be paid to the correspondence between pseudo-spin and total angular momentum $J$, when we intend to make a comparison with actual materials. In experiments on $f$-electron compounds, for instance, the external magnetic field couples to $J$, not to the pseudo-spin. Thus, when we attempt to calculate physical quantities observed in actuality, it is necessary to consider the response of $J$. The present analysis based on the pseudo-spin model is useful to see qualitative tendencies, while a quantitative discussion is left for future development.

**IV. SUMMARY AND DISCUSSION**

We have constructed a microscopic model Hamiltonian for $f$-electron systems based on the $j$-$j$ coupling scheme: The Coulomb matrix elements have been expressed in terms of the Racah parameters, and the CEF terms for the two-electron case have been determined by those for $J=5/2$. The validity of this $j$-$j$ coupling picture has been carefully discussed in the present paper. The $f$-electron hopping amplitudes are obtained using Slater’s two-center integral. Two types of simplified models have also been presented: One is a Hamiltonian including $\Gamma_8$ and the other for $\Gamma_7$ levels. These are believed to be useful for further investigations of superconductivity and magnetism in $f$-electron systems.

In this paper the $\Gamma_8$ model has been analyzed using the exact diagonalization method. We have measured several kinds of correlation functions and developed a prescription to define the pairing state in multi-orbital systems. Furthermore, the symmetry of the orbital dependent Cooper pair has been carefully discussed. In the analysis of the $\Gamma_8$ model, it has been suggested that unconventional superconductivity should appear around the phase boundary between metallic OD-PM and insulating FO-AFM phases. In addition, we have found evidence for triplet superconductivity in the ferromagnetic phase, induced by strong Hund’s rule coupling. With the present method of defining the pairing state, it has been found that the triplet pairing state is not localized, but extended spatially to gain kinetic energy.

Based on the $j$-$j$ coupling scheme, it is easy to consider the case of several $f$ electrons per site. Although we have not shown any results in this paper for the case of $n=2$, corresponding to the $U^{4+}$ ion (see Fig. 6), we have obtained that the ground-state is an AFM insulator, which is driven by AFM superexchange coupling between neighboring $S=1$ spins formed by the local Hund’s rule coupling. When we introduce a level splitting into this AFM insulating state, we have found robustness for this phase, compared with the transition around $\varepsilon=0.5$ for the case of $n=1$. For UMGa$_5$, if the uranium ions are considered to take U$^{3+}$, again it is naively deduced to have an AFM ground state, if the local spin is formed by Hund’s rule coupling, as shown in Fig. 6. However, without any calculations, it is impossible to determine whether it is a metallic or insulating state, although in experiments, metallic AFM phase has
been suggested. This is left as a future problem.

As introduced in Sec. 1, PuCoGa₅ amazingly exhibits superconductivity with \( T_c = 18.5 \text{K} \). In order to understand this high \( T_c \), first of all, we generally consider that the spatial extent of the 5\( f \) wavefunction is large compared to that of 4\( f \) electrons, leading to a larger hybridization among conduction and 5\( f \) electrons. Namely, the basic energy scale (or effective bandwidth of the quasiparticles) in the Pu-compound should be larger than that of Ce-materials. Here we envision a scenario similar to the high-\( T_c \) cuprates: If superconductivity in those “115” materials is considered to originate from an electronic mechanism, \( T_c \) should be increased as the energy scale is enhanced. It may be useful to point out a possible analogy with high-\( T_c \) materials, but we emphasize that as a separate important issue the active role of orbitals, which discussed intensively in this paper. It has been deduced from the local moment behavior that the plutonium valence is Pu\(^{3+}\), indicating that five \( f \)-electrons are accommodated. In our \( j-j \) coupling picture with pseudo-spin representation, we can put five electrons in the sextet of \( j=5/2 \), as shown in Fig. 6, which is just the hole version of CeMln₅. Thus, the appearance of superconductivity itself may be understood without any calculations on the basis of our \( j-j \) coupling picture. As explained above, the drastic changes of \( T_c \) in the “115” materials may be understood, based on the difference in the energy scale for 4\( f \) and 5\( f \) electrons, but we believe that another key issue related to this problem would be the shape of the orbitals. A difference between the electron and hole pictures should exist stemming from the shape of the active orbital, as easily deduced from Fig. 6. If such differences among orbitals, i.e., level schemes relating to the CEF effect, will be clarified in those materials, it may be possible to obtain a unified view to understand unconventional superconductivity and novel magnetism in “115” materials including CeMln₅, UMGa₅, and PuCoGa₅. This point will be further investigated based on the present model.

As repeatedly mentioned in this paper, there remain several open questions in the electronic properties of \( f \)-electron materials. We believe that the microscopic models presented and discussed in this paper will be useful to advance our understanding of unconventional superconductivity and novel magnetism in \( f \)-electron systems.

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