Microscopic Theory of $\Gamma_3$ Quadrupole Ordering in Pr Compounds on the Basis of a $j$-$j$ Coupling Scheme

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Toward the understanding of incommensurate $\Gamma_3$ quadrupole ordering in PrPb$_3$, we develop a microscopic theory of multipole ordering in $f^2$-electron systems from an itinerant picture on the basis of a $j$-$j$ coupling scheme. For this purpose, we introduce the $\Gamma_7$-$\Gamma_8$ Hubbard model on a simple cubic lattice with the effective interactions that induce local $\Gamma_3$ states. By evaluating multipole susceptibility in a random phase approximation, we find that the hybridization between $\Gamma_7$ and $\Gamma_8$ orbitals plays a key role in the emergence of $\Gamma_3$ quadrupole ordering. We also emphasize that $\Gamma_3$ quadrupole ordering can be understood from the concept of multipole nesting, in which the Fermi surface region with large $\Gamma_3$ orbital density should be nested on the area with a significant $\Gamma_7$ component when the positions of the Fermi surfaces are shifted by the ordering vector. This concept can be intuitively understood from the fact that local $\Gamma_3$ doublets are mainly composed of two singlets between $\Gamma_8$ and $\Gamma_7$ orbitals. Finally, we discuss the possible relevance of the present theory to the experimental results of PrPb$_3$ and point out some future problems in this direction of research.

1. Introduction

In recent decades, multipole ordering in $f$-electron systems has attracted continuous attention in the research field of condensed matter physics.\textsuperscript{1-20} In general, a multipole is considered to be a spin-orbital complex degree of freedom emerging in a system in which spin and orbital degrees of freedom are tightly coupled with each other due to a strong spin-orbit interaction. A description of multipole degrees of freedom has been provided on the basis of the Stevens’ operator-equivalent technique.\textsuperscript{21} Among the $f$-electron systems, rare-earth and actinide compounds with multiple $f$ electrons per ion exhibit diverse multipole phenomena. In particular, for the case of $n = 2$, where $n$ denotes the local $f$-electron number, intriguing phenomena originating from non-Kramers degeneracy have been discussed for a long time. A typical example is considered to be the two-channel Kondo effect, which is expected to occur in U and Pr ions with the $\Gamma_3$ ground state.\textsuperscript{6,7} Another example is the modulated antiferro $\Gamma_3$ $O^0_2$ quadrupole ordering observed in PrPb$_3$ with the AuCu$_3$-type simple cubic structure.\textsuperscript{8,9} In this paper, we are interested in the mechanism of this peculiar quadrupole ordering.

For the investigation of multipole ordering in Pr compounds, one may think that it is enough to employ an $LS$ coupling scheme since, in general, $4f$ electrons of Pr$^{3+}$ are considered to be almost localized. However, for PrPb$_3$, the situation does not seem to be so simple. Before the确认ation of the modulated ordering, the possibility of the antiferro quadrupole ordering has been discussed.\textsuperscript{10,11} Then, the sinusoidal quadrupole ordering has been observed,\textsuperscript{8,9} but it seems to be difficult to explain it on the basis of a localized picture. Furthermore, in PrPb$_3$, the Fermi surfaces have been clearly observed in a de Haas-van Alphen (dHvA) experiment,\textsuperscript{12} suggesting that it is necessary to consider the quadrupole ordering from an itinerant picture. However, it seems to be a difficult task to treat multipole ordering from a microscopic viewpoint in $f^2$-electron systems. In fact, the mechanism of the modulated antiferro quadrupole ordering in PrPb$_3$ has not been clarified yet, although more than ten years has passed since the discovery of the peculiar quadrupole ordering.

For the explanation of multipole ordering concerning multiple $f$ electrons, it seems to be necessary to consider alternative theoretical research complementary to the $LS$ coupling scheme. Thus, we believe that it is meaningful to develop a microscopic theory for multipole ordering from an itinerant picture on the basis of a $j$-$j$ coupling scheme.\textsuperscript{13-15} In fact, recently, several groups have advanced the theoretical investigation on the multipole ordering in $f$-electron systems from the microscopic viewpoint by performing first-principles calculations.\textsuperscript{16-22} For the multipole order in CeB$_6$, in which theoretical research based on the $LS$ coupling scheme has been carried out for a long time, but recently, analysis from the itinerant picture has been performed.\textsuperscript{23} For the analysis of multipole ordering on the basis of the $j$-$j$ coupling scheme, we define the multipole operator as the spin-charge density in the form of a one-body operator.\textsuperscript{13-15} Since the $f$-electron state with angular momentum $\ell = 3$ contains seven orbitals, it is desirable to adopt a seven-orbital Hamiltonian as a realistic $f$-electron model, if possible. However, such a seven-orbital model is too complicated to be a prototype to develop the microscopic theory of multipole ordering. We also encounter difficulties in interpreting the calculation results, even though we can perform the calculations in the seven-orbital model.\textsuperscript{15}

Then, we attempt to effectively reduce the number of relevant orbitals. When we consider the local $f$-electron states on the basis of the $j$-$j$ coupling scheme,\textsuperscript{24} we notice that the $\Gamma_3$ ground states are mainly composed of two singlets among $\Gamma_7$ and $\Gamma_8$ electrons.\textsuperscript{25-30} Note that the double degeneracy originates from the orbital degrees of freedom in $\Gamma_8$ electrons. This is consistent with the fact that $\Gamma_3$ is included in the direct products of $\Gamma_7$ and $\Gamma_8$. Thus, we discuss the $\Gamma_3$ quadrupole ordering in $f^2$-electron systems on the basis of a $\Gamma_7$-$\Gamma_8$ three-orbital Hamiltonian.\textsuperscript{26,30} We evaluate the multipole susceptibility of the model in a random phase approximation (RPA) and attempt to clarify the mechanism of the emergence of incommensurate quadrupole order from a microscopic viewpoint.

In this paper, we construct the $\Gamma_7$-$\Gamma_8$ three-orbital model
for the $f^2$-electron system from the itinerant picture. Then, we introduce the effective interactions that stabilize the local $\Gamma_3$ ground state for the case of $n = 2$. We perform the RPA calculations for the multipole susceptibilities to discuss the condition for the appearance of quadrupole order. We emphasize that the hybridization between $\Gamma_7$ and $\Gamma_8$ orbitals is important for the emergence of the $\Gamma_3$ quadrupole ordering. We also propose a concept of multipole nesting. Namely, the Fermi surface region with large $\Gamma_8$ orbital density is nested on the area with a significant $\Gamma_7$ component when we shift the positions of Fermi surfaces by the ordering vector. This is consistent with the fact that local $\Gamma_3$ doublets are mainly composed of two singlets between $\Gamma_7$ and $\Gamma_8$ orbitals. Finally, we discuss the possible relevance of the present results to the incommensurate quadrupole ordering observed in PrPb$_3$ with some comments on future problems.

The paper is organized as follows. In Sect. 2, the model Hamiltonian with effective interactions among $f$ electrons is introduced. After explaining the multipole operators, we provide the formulation to evaluate multipole susceptibilities in the RPA. In Sect. 3, our calculation results on the multipole susceptibilities are shown. We clarify the key quantity, $\Gamma_7$-$\Gamma_8$ hybridization, for the emergence of the quadrupole ordering. We attempt to unveil the microscopic mechanism of incommensurate quadrupole ordering by focusing on the Fermi surface nesting property as well as the orbital density distribution on the Fermi surfaces. In Sect. 4, we provide several comments on the quadrupole ordering in the present scenario in comparison with the experimental results observed for PrPb$_3$. Finally, we summarize this paper. Throughout this paper, $\hbar = k_B = 1$.

2. Model and Formulation

2.1 Model Hamiltonian

To consider the multipole ordering from a microscopic viewpoint on the basis of the itinerant picture, we set the model Hamiltonian as

$$H = H_{\text{kin}} + H_{\text{loc}},$$

where $H_{\text{kin}}$ and $H_{\text{loc}}$ denote the kinetic and local terms for $f$ electrons, respectively.

First let us discuss in detail how to construct the local term $H_{\text{loc}}$. To consider the electronic properties of $f$-electron compounds, the best way is to treat the seven-orbital model, including Coulomb interactions, spin-orbit coupling, and crystalline electric field (CEF) potentials. For instance, the Kondo phenomena have been discussed in detail on the basis of the seven-orbital Anderson model hybridized with several conduction bands. Then, two-channel Kondo effects was found not only in the Pr ion but also in Nd and other rare-earth systems in an unbiased manner.\(^{31,32}\)

Concerning the multipole ordering, the seven-orbital Hubbard model has also been analyzed with the use of the RPA for the evaluation of multipole susceptibility. Such calculations have actually been performed,\(^{15}\) but it was difficult to clarify the mechanism of the multipole ordering from a microscopic viewpoint, mainly due to the complexity originating from the large number of orbitals. Thus, it is desirable to reduce the number of relevant orbitals to obtain the effective Hamiltonian for the purpose of grasping the essential point concerning the appearance of multipole ordering.

A basic strategy to construct such an effective model is to exploit a $j$-$j$ coupling scheme.\(^{26}\) As schematically shown in Fig. 1, we first include the effect of spin-orbit coupling in the one-$f$-electron state characterized by the orbital $\ell = 3$ and spin $s = 1/2$, leading to an octet with a total angular momentum $j = 7/2$ and a sextet with $j = 5/2$. Since the energy of the sextet is lower than that of the octet, we consider the states of the $j = 5/2$ sextet to construct the effective model for rare-earth and actinide compounds for $n \leq 6$. We accommodate $f$ electrons in the level scheme of the one-$f$-electron states and include the effect of Coulomb interactions among them.

Since we consider the cubic system in this paper, it is convenient to use the cubic irreducible representations. As shown in Fig. 1, under the cubic CEF potentials, the $j = 5/2$ sextet is further split into a $\Gamma_7$ doublet and $\Gamma_8$ quartet. To distinguish the states in the $\Gamma_8$ quartet and $\Gamma_7$ doublet, we introduce three pseudo-orbitals $\tau (=a, b, \text{and} c)$, while pseudospin $\sigma (=\uparrow\text{and} \downarrow)$ is introduced to distinguish the Kramers degeneracy. For the description of the model Hamiltonian, it is useful to define the second-quantized operator $f_{i\tau\sigma}$ with pseudospin $\sigma$ and pseudo-orbital $\tau$ at site $i$, expressed as

$$f_{i\tau\sigma} = \sum_\mu A_{i\tau\sigma,\mu} a_{i\mu},$$

where $a_{i\mu}$ denotes the annihilation operator of an $f$ electron in the $j = 5/2$ sextet with the $z$-component $\mu$ at site $i$ and $A$ indicates the coefficient connecting $f$ and $a$ operators. For $\Gamma_{8a}$ and $\Gamma_{8b}$ electrons, $f$ operators are explicitly given by

$$f_{ia\tau\uparrow} = \sqrt{\frac{5}{6}} a_{i\downarrow} - \frac{\sqrt{1}}{\sqrt{6}} a_{i\uparrow \downarrow},$$

$$f_{ia\tau\downarrow} = \sqrt{\frac{5}{6}} a_{i\uparrow} + \frac{\sqrt{1}}{\sqrt{6}} a_{i\downarrow \downarrow},$$

and

$$f_{ib\tau\uparrow} = a_{i\tau\downarrow},$$

$$f_{ib\tau\downarrow} = a_{i\tau\uparrow},$$

respectively.

For an $\Gamma_7$ electron ($\tau = c$), we obtain

$$f_{ic\tau\uparrow} = \sqrt{\frac{1}{6}} a_{i\downarrow} - \frac{\sqrt{5}}{\sqrt{6}} a_{i\uparrow \downarrow},$$

$$f_{ic\tau\downarrow} = \sqrt{\frac{1}{6}} a_{i\uparrow} + \frac{\sqrt{5}}{\sqrt{6}} a_{i\downarrow \downarrow}.$$
For the standard time-reversal operator $K = -i\sigma_y K$, where $K$ denotes an operator taking the complex conjugate, we can easily show the relation $K f_{i\tau\sigma} = \sigma f_{i\tau-\sigma}$, which is the same definition for a real spin.\(^{24}\)

Now we consider the local term, which should be composed of the CEF potential and Coulomb interaction terms. However, we include only the latter term in this paper for the reason which we will explain later. The Coulomb interaction term is given in the second-quantized form as

$$H_{\text{loc}} = \sum_{\alpha, \lambda, \tau, \sigma} I_{1234} f_{i4}^\dagger f_{i2} f_{i3} f_{i4},$$

where $I$ indicates the Coulomb interactions and we use shorthand notation such as $1 = \{\tau_1, \sigma_1\}$. Hereafter we use this notation when there is no possibility of confusion.

Concerning the matrix elements of $I$, there are several methods to evaluate these values. A straightforward way to obtain $I$ is to estimate the Coulomb integrals with the use of $f$-electron wavefunctions in the limit of large spin-orbit coupling $\lambda$.\(^{24}\) This has the merit that we can obtain all the matrix elements analytically, while we encounter a serious problem which we will explain later. The Coulomb interaction term is stabilized since we are more interested in the mechanism of the sixth-order CEF potentials, expressed by the terms of $B^0_{\alpha, \beta}$.\(^{33}\)

A simple way to include the effect of $B^0_{\alpha, \beta}$ is to perform the perturbation expansion in terms of $1/\lambda$ to take into account the effect of the $j = 7/2$ octet in which the $B^0_{\alpha, \beta}$ terms are correctly included.\(^{39}\) Another method is to include the effect of $B^0_{\alpha, \beta}$ through the two-body potential for the $j = 5/2$ sextet.\(^{32}\)

Finally, it is also possible to more systematically obtain the effective interactions to reproduce the low-energy spectrum of the seven-orbital model by maximizing the overlap integrals between the states of the seven-orbital model and those of the three-orbital model.\(^{28}\)

In this paper, basically we follow the last method, but we do not pay special attention to the reproduction of the low-energy spectrum of the seven-orbital model. Rather, we simply consider the situation in which the local $\Gamma_3$ ground state is stabilized since we are more interested in the mechanism of the $\Gamma_3$ quadrupole order. An outline of how to determine the effective interaction is as follows. When we consider local $f^2$ states in the present three-orbital model, there are 15 eigenstates in total, originating from a nonet ($J = 2$), quintet ($J = 4$), and singlet ($J = 0$),\(^{24}\) where $J$ denotes the total angular momentum of the $f^2$ multiplet when we suppress the CEF potentials. Note that the nonet of $J = 4$ is the ground-state multiplet due to Hund’s rules. When we include the cubic CEF potentials, the nonet of $J = 4$ is further split into four groups: a $\Gamma_1$ singlet, $\Gamma_3$ doublet, $\Gamma_4$ triplet, and $\Gamma_5$ triplet. Under the cubic CEF potentials, the quintet of $J = 2$ is split into a $\Gamma_3$ doublet and $\Gamma_5$ triplet. Namely, the 15 $f^2$ states are classified into two $\Gamma_1$ singlets, two $\Gamma_3$ doublets, one $\Gamma_4$ triplet, and two $\Gamma_5$ triplets. Since the states belonging to the same symmetry are mixed, in general, the interaction term is expressed as

$$H_{\text{int}} = \sum_{i, \gamma, \rho, \rho'} V^\Gamma_{\rho\rho'} \langle f^i, \Gamma_\gamma | \langle f^i, \Gamma^\rho_\gamma |$$

where $V^\Gamma_{\rho\rho'}$ indicates the effective interaction, $|f^i, \Gamma^\rho_\gamma \rangle$ denotes the $f^2$ state at site $i$, $\Gamma$ and $\gamma$ characterize the irreducible representation, and $p$ ($= 1$ and 2) denotes the index used to distinguish the same irreducible representation. Note also that $V^\Gamma_{\rho\rho'}$ does not depend on $\gamma$.

Let us exhibit all the $f^2$ states in the following. First, for the $\Gamma_1$ singlet states, we obtain

$$|f^i, \Gamma^{(1)}_1 \rangle = \sqrt{\frac{1}{6}} (f^i_{1\alpha\uparrow} f^i_{1\alpha\downarrow} + f^i_{1\beta\uparrow} f^i_{1\beta\downarrow} - 2 f^i_{1\sigma\uparrow} f^i_{1\sigma\downarrow} |0\rangle,\quad (8)

\begin{align*}
|f^i, \Gamma^{(2)}_1 \rangle &= \sqrt{\frac{1}{3}} (f^i_{1\alpha\uparrow} f^i_{1\alpha\downarrow} + f^i_{1\beta\uparrow} f^i_{1\beta\downarrow} + f^i_{1\gamma\uparrow} f^i_{1\gamma\downarrow} |0\rangle,\quad (9)
\end{align*}

and

\begin{align*}
|f^i, \Gamma^{(1)}_3 \rangle &= \sqrt{\frac{1}{2}} (f^i_{3\alpha\uparrow} f^i_{3\alpha\downarrow} - f^i_{3\beta\uparrow} f^i_{3\beta\downarrow} |0\rangle,\quad (9)
|f^i, \Gamma^{(2)}_3 \rangle &= \sqrt{\frac{1}{2}} (f^i_{3\alpha\downarrow} f^i_{3\alpha\uparrow} - f^i_{3\beta\downarrow} f^i_{3\beta\uparrow} |0\rangle,\quad (10)
\end{align*}

and

\begin{align*}
|f^i, \Gamma^{(2)}_3 \rangle &= \sqrt{\frac{1}{2}} (f^i_{3\gamma\uparrow} f^i_{3\gamma\downarrow} - f^i_{3\sigma\uparrow} f^i_{3\sigma\downarrow} |0\rangle,
\end{align*}

respectively. As schematically shown in Fig. 2, $\Gamma^{(1)}_3$ and $\Gamma^{(1)}_3$ are given by the singlets between $\Gamma_7$ and $\Gamma_8$ orbitals, while $\Gamma^{(2)}_3$ and $\Gamma^{(2)}_3$ denote the singlets in $\Gamma_8$ orbitals. Namely, the index $\alpha$ and $\beta$ used to distinguish the non-Kramers $\Gamma_3$ doublets just correspond to $a$ and $b$ orbitals, respectively. Note that the main components of the $\Gamma_3$ states from $J = 4$ ($J = 2$) are $\Gamma^{(1)}_3$ and $\Gamma^{(2)}_3$, $\Gamma^{(1)}_3$, and $\Gamma^{(2)}_3$, $\Gamma^{(2)}_3$, and $\Gamma^{(2)}_3$.

For the $\Gamma_4$ triplet state, we introduce $\gamma = \xi, \eta, \zeta$ to distinguish the double degeneracy, although it is not necessary
to introduce \( p\) since only one \( \Gamma_4\) is found. Then, we obtain
\[
|f_{i}^{T}, \Gamma_{4}\rangle = \left(-\sqrt{\frac{3}{2}} f_{i}^{\downarrow} f_{i}^{\uparrow} + f_{i}^{\downarrow} f_{i}^{\uparrow}\right]|0\rangle,
\]
\[
|f_{i}^{T}, \Gamma_{4y}\rangle = \left(\frac{1}{2} f_{i}^{\downarrow} f_{i}^{\uparrow} + \frac{1}{2} f_{i}^{\downarrow} f_{i}^{\uparrow}\right)|0\rangle,
\]
\[
|f_{i}^{T}, \Gamma_{4z}\rangle = \left(-\frac{1}{2} f_{i}^{\downarrow} f_{i}^{\uparrow} - \sqrt{\frac{3}{2}} f_{i}^{\downarrow} f_{i}^{\uparrow}\right)|0\rangle.
\]
Finally, for the \( \Gamma_3\) triplet, we again introduce \( \gamma = \xi, \eta, \) and \( \zeta \) to distinguish the triple degeneracy. Since we obtain two \( \Gamma_3\), it is necessary to prepare \( p \) in this case. Then, we obtain
\[
|f_{i}^{T}, \Gamma_{3}\rangle = \left(\frac{1}{2} f_{i}^{\downarrow} f_{i}^{\uparrow} + \frac{1}{2} f_{i}^{\downarrow} f_{i}^{\uparrow}\right)|0\rangle,
\]
\[
|f_{i}^{T}, \Gamma_{3y}\rangle = \left(\frac{1}{2} f_{i}^{\downarrow} f_{i}^{\uparrow} + \frac{1}{2} f_{i}^{\downarrow} f_{i}^{\uparrow}\right)|0\rangle,
\]
and
\[
|f_{i}^{T}, \Gamma_{3z}\rangle = \left(-\frac{1}{2} f_{i}^{\downarrow} f_{i}^{\uparrow} - \frac{1}{2} f_{i}^{\downarrow} f_{i}^{\uparrow}\right)|0\rangle.
\]

In the present form of the effective interactions, it is necessary to set 10 parameters for \( V_{PP}^{T}\). Namely, there are seven diagonal parameters, \( V_{11}^{T}, V_{12}^{T}, V_{13}^{T}, V_{14}^{T}, V_{15}^{T}, V_{16}^{T}, \) and \( V_{17}^{T}\), for the hopping between \( \Gamma_7\) and \( \Gamma_8\); \( V_{12}^{T}\), \( V_{13}^{T}\), \( V_{14}^{T}\), and \( V_{17}^{T}\), for the hopping between \( \Gamma_7\) and \( \Gamma_8\); \( V_{18}^{T}\), \( V_{19}^{T}\), \( V_{20}^{T}\), \( V_{21}^{T}\), \( V_{22}^{T}\), and \( V_{23}^{T}\). For simplicity, we define \( v_1 = V_{12}^{T}, v_2 = V_{13}^{T}, v_5 = V_{18}^{T}, \) and \( v_6 = V_{19}^{T}.\) In this paper, \( v_3 \) is a control parameter used to discuss the quadrupole ordering.

Now we explain the reason why we suppress the one-electron CEF potential term \( H_{CEF}\) in this paper. Since we use \( \Gamma_7\) and \( \Gamma_8\) bases in the present model, the one-electron potential term is given by \( H_{CEF} = \sum_{i}^{N} 2 \rho_{\alpha i} - \rho_{\alpha i} - \rho_{\alpha i}\), where \( \rho_{\alpha i} = \sum_{J} f_{i}^{\alpha} f_{i}^{\beta} f_{i}^{\gamma} f_{i}^{\delta} \), \( b_i \) is the fourth-order CEF parameter.\(^{33}\) Concerning the experimental finding for the level scheme, we refer to the result for CePb, which is the \( f_1 \) component with the same lattice structure as that of PbPb. For CePb, it has been found that \( \Gamma_7\) is the ground state and \( \Gamma_8\) is the excited state,\(^{35}\) indicating that \( b_i\) is positive. Thus, for PbPb, it is recommended to accommodate two \( f \) electrons in this level scheme in the \( j-j \) coupling scheme. However, this CEF potential term works toward the destruction of the \( \Gamma_7\) state, which consists of \( \Gamma_7\) and \( \Gamma_8\) electrons. We emphasize that our purpose here is to search for the condition for the appearance of \( \Gamma_3\) quadrupole ordering in the \( f^2\)-electron systems. Thus, we suppress \( H_{CEF}\) from the outset in this paper by taking \( b_4 = 0 \), although we are interested in the effect of the one-electron CEF potential on the \( \Gamma_3\) quadrupole order.

Now we consider the kinetic term. As emphasized above, in this paper, we discuss the mechanism of the multipole ordering from the itinerant picture in \( f\)-electron systems. For this purpose, we include the hopping of \( f \) electrons, although we do not seriously consider the heavy-mass enhancement due to the hybridization between localized and conduction electrons. Then, the kinetic term \( H_{kin}\) is expressed as
\[
H_{kin} = \sum_{k<\tau<\sigma} \varepsilon_{k<\tau<\sigma} f^\dagger_{k<\tau<\sigma} f_{k<\tau<\sigma},
\]
where \( f^\dagger_{k<\tau<\sigma}\) denotes the Fourier transform of \( f_{k<\tau<\sigma}\). By considering only the hopping between nearest-neighbor sites, we obtain the one-\( f\)-electron energy \( \varepsilon_{k<\tau<\sigma}\) in a matrix form as
\[
\varepsilon_{k<\tau<\sigma} = \begin{pmatrix}
\tau \s, \tau' \s & \tau \s, \tau' \s
\end{pmatrix} = \begin{pmatrix}
\tau \s, \tau' \s & \tau \s, \tau' \s
\end{pmatrix} = \begin{pmatrix}
\tau \s, \tau' \s & \tau \s, \tau' \s
\end{pmatrix}.
\]

Finally, we provide a comment on another effective model. In this paper, we analyze the three-orbital model, which is composed of \( \Gamma_7\) and \( \Gamma_8\) orbitals. Since the non-Kramers \( \Gamma_4\) doublets in the \( f^2\) state are expressed by two local singlets between \( \Gamma_7\) and \( \Gamma_8\) orbitals, the \( \Gamma_7\)-\( \Gamma_8\) three-orbital model is suitable for the discussion of the multipole ordering in PrPb from a microscopic viewpoint. The \( \Gamma_8\) two-orbital Hamiltonian is frequently used as the minimal model to discuss the multipole ordering in \( f\)-electron systems,\(^{28,39-45}\) but the \( \Gamma_3\) states composed of a pair of \( \Gamma_1\) electrons are not the main component of the \( f^2\) states of the Pr ion. Thus, we adopt the \( \Gamma_7\)-\( \Gamma_8\) three-orbital model in this paper.

### 2.2 Multipole susceptibility in the RPA

Now we explain the procedure to calculate the multipole susceptibility in the RPA. First, we define the multipole operator in the one-electron-density form by using the cubic tensor operator \( T^{(K)}_{\tau}(q)\),\(^{13-15}\) where \( q\) is momentum, \( \Gamma\) and \( \gamma\) indicate the irreducible representation for the cubic point group, and \( k\) denotes the rank of the multipole. In the second-quantized form, the cubic tensor operators are given by
\[
T^{(K)}_{\tau,q}(q) = \sum_{\tau,q,q,q'} T^{(K)}_{\tau,q,q,q'} f^\dagger_{\tau,q} f_{\tau,q'} q',
\]
where we use the shorthand notation \( K = \{k, \Gamma\gamma\} \) and the coefficient \( T^{(K)}_{\tau,q,q,q'} \) is given by
\[
T^{(K)}_{\tau,q,q,q'} = \sum_{\mu,\mu',\nu} G^{(K)}_{\gamma\gamma,q,q} O^{(K)}_{\gamma\gamma,\mu,\mu',\nu}.\]

Here \( q \) runs between \( -k \) and \( k \), \( G^{(K)}_{\gamma\gamma,q,q} \) is the transformation matrix between spherical and cubic harmonics, and \( O^{(K)}_{\gamma\gamma,\mu,\mu',\nu} \) denotes the spherical tensor operator defined in the space of \( j = 5/2\). The matrix element of \( O^{(K)}_{\gamma\gamma,\mu,\mu',\nu} \) is explicitly calculated.
by the Wigner-Eckart theorem as\(^{26}\)
\[
O_{q,j}(k) = \frac{\langle j | O(k) | j \rangle}{\sqrt{2j + 1}} (j \mu | j \mu' \rangle q),
\]
where \(j = 5/2, (j \mu | j \mu' \rangle q)\) indicates the Clebsch-Gordan coefficient, and \(\langle j | O(k) | j \rangle\) is the reduced matrix element for the spherical tensor operator, given by
\[
\langle j | O(k) | j \rangle = \frac{1}{2^j} \sqrt{\frac{(2j + k + 1)!}{(2j - 1)!}}.
\]

Table I. Irreducible representations for multipoles up to rank 5. Here we use the shorthand notations explained in the main text. Note that at rank 5, two \(\Gamma_{4u}\) triplets appear, which are distinguished as \(4u_1\) and \(4u_2\).

| rank | irreducible representations |
|------|----------------------------|
| 0    | 1g                         |
| 1    | 4u                         |
| 2    | 3g, 5g                     |
| 3    | 2u, 4u, 5u                 |
| 4    | 1g, 3g, 4g, 5g             |
| 5    | 3u, 4u, 5u                 |

Note that we define multipole operators from rank 0 to rank 5 in the present model, since the highest rank is given by \(2j\).

Concerning the correspondence to Mulliken notation, note which are simply expressed as “3g” and “5g”, respectively.

Thus, we introduce the multipole operator \(X_q\) by the linear combination of the cubic tensor operators, given by
\[
X_q = \sum_{k, \Gamma_q} P_k(q) T^{(K)}_{\Gamma_q}(q),
\]
where \(P_k(q)\) indicates the coefficient of the multipole operator in rank \(k\) and irreducible representation \(\Gamma_q\).

Next it is necessary to consider a way to determine the coefficient \(P\).\(^{15}\) For this purpose, we evaluate the multipole susceptibility in the static limit. In the linear response theory, the multipole susceptibility is defined by
\[
\chi(q) = \int_0^{1/T} d\tau X_q(\tau) X_{-q}(0),
\]
where \(T\) is the temperature, \(X_q(\tau) = e^{i\omega \tau} X_q e^{-i\omega \tau}\), and \(\langle \cdots \rangle\) indicates the thermal average by using \(H\). From Eqs. (21) and (22), we obtain the multipole susceptibility as
\[
\chi(q) = \sum_{k, k'} P_k \chi_{k k'}(q) P_{k'},
\]
where the susceptibility matrix is given by
\[
\chi_{k k'}(q) = \sum_{l=4}^{1} \chi_{l,34}(q) T^{(K)}_{l,34}(q).
\]

Note that we use the shorthand notations. We also note that \(T^{(k)}_{i,i} = T^{(k)}_{1,i}\), where the asterisk denotes the complex conjugate. Then, \(\chi\) and \(P\) should be determined by the maximum eigenvalue \(\chi_{\text{max}}\) and the corresponding normalized eigenstate of the susceptibility matrix equation, respectively.

To calculate the multipole susceptibility, in this paper, we resort to the RPA on the basis of the perturbation expansion in terms of the Coulomb interactions. In the RPA, the susceptibility is expressed in a compact matrix form as\(^{28}\)
\[
\chi^{(0)}(q) = -T \sum_{n, k} G_{n, k}^{(0)}(k, i \omega_n) G_{n, k}^{(0)}(k + q, i \omega_n).
\]

Here \(\omega_n = \pi T(n + 1)\) is the fermion Matsubara frequency with integer \(n\) and \(G_{n, k}^{(0)}\) is the one-electron Green’s function defined from \(H_{\text{kin}}\). Note that \(G_{n, k}^{(0)} = \delta_{\nu, \nu'} G_{n, k}^{(0)}(\nu, \nu')\).

For actual calculations of \(\chi^{(0)}(q)\), it is convenient to first diagonalize \(H_{\text{kin}}\) as
\[
H_{\text{kin}} = \sum_{k, \nu, \sigma} E_{k \nu} f_{k, \nu, \sigma} f_{k, \nu, \sigma}^{\dagger},
\]
where \(\nu\) denotes the index used to distinguish the band, \(E_{k \nu}\) is the band energy, and the relation between \(f\) and \(\tilde{f}\) is expressed as
\[
f_{k, \nu, \sigma} = \sum_{\nu'} U_{\nu, \nu'}(k) f_{k, \nu', \sigma},
\]
Then, the bare susceptibility is given by
\[
\chi_{12,34}^{(0)}(q) = \sum_{k, \nu, \nu'} U_{\nu, \nu'}(k) U_{\nu, \nu}(k) \chi_{12,34}(q + k + q) U_{\nu, \nu}(k + q),
\]
where \(\chi_{\nu, \nu'}(q)\) is given by
\[
\chi_{\nu, \nu'}(q) = f(E_{k + q, \nu'}) - f(E_{k, \nu}) \frac{E_{k + q, \nu'}}{E_{k, \nu}} f(E_{k + q, \nu'}),
\]
and \(f\) is the Fermi distribution function.

For the momentum \(q\) in multipole susceptibility, we divide the first Brillouin zone into \(32 \times 32 \times 32\) meshes. Namely, the unit of \(q\) in the present calculation is \(\pi/16\). To efficiently perform the \(k\) integration in the bare susceptibility Eq. (29), we exploit the Gauss-Legendre quadrature with due care. First we divide the first Brillouin zone into \(16 \times 16 \times 16\) meshes. Then, in each cube, we adopt 8-point Gauss-Legendre quadrature along the \(k_x, k_y,\) and \(k_z\) directions. In this numerical calculation, we can arrive at low temperatures such as \(T/|t_s| = 0.01\).
Note that the multipole state among the different irreducible representations is specified by the multipole susceptibility, but the multipoles belonging to the same irreducible representation cannot be distinguished in the present calculations of $\chi_{\text{max}}$. In this paper, the kind of multipole in the same irreducible representation is deduced from the main component in the eigenvector of the corresponding eigenvalue $\chi_{\text{max}}$ at $v_3 = \varepsilon v_3^0$, where $\varepsilon$ takes a value between 0.9 and 0.98 depending on the hopping parameters.

In Figs. 3(a) and 3(b), we show the phase diagrams for the ordered multipole states for $v_3 > 0$ and $v_3 < 0$, respectively, on the $t_{78}$-$t_7$ plane for $t_8 = -1.0$ and $s_8 = -0.2$. The 3g multipole states are classified into $O^2_2$, $O^4_3$, rank 4$\alpha$, and rank 4$\beta$ from the main component in the eigenvector of the corresponding eigenvalue $\chi_{\text{max}}$ at $v_3 = \varepsilon v_3^0$. Here we focus on this kind of multipole, while we suppress the information on the ordering vector, which will be separately discussed later. Note that in the present calculations, $v_3 = 0$ does not mean the non-interacting case since there are finite other interactions. In fact, in Figs. 3(a) and 3(b), we find gray regions near $t_{78} = t_7 = 0$, in which the RPA susceptibilities already diverge even at $v_3 = 0$ due to the flat-like $\Gamma_1$ band. We are not interested in the gray regions since the magnetic phase is stabilized by an effective interaction other than $v_3$.

In Fig. 3(a), as well as for the gray region, we find three regions as one magnetic state and two quadrupole states, $O^2_2$ and $O^4_3$. For $t_{78} < 0$, we mainly obtain the 3g state, but it is found that 85% of this 3g state is rank 2 and 15% is rank 4. Thus, this state is characterized by the 3g quadrupole $O^2_2$ or $O^4_3$. Note that the winner of the competition between $O^2_2$ and $O^4_3$ is not determined only by the local conditions, since the local ground states provide the same contribution to $O^2_2$ and $O^4_3$. For $t_{78} \geq 0$, magnetic 4u states appear, which are a mixture of dipoles, octupoles, and dotoriactopoles. We remark that the magnetic multipole state always appears in the present model at $t_{78} = 0$.

On the other hand, as shown in Fig. 3(b), for $v_3 < 0$, two 3g hexadecapole states are stabilized in the region of $t_{78} > 0$. In this case, 95% of the 3g state is rank 4 and 5% is rank 2, indicating that the amounts of ranks 2 and 4 are almost reversed in comparison with the 3g states for $v_3 > 0$. Note that “rank 4$\alpha$” and “rank 4$\beta$” in Fig. 3(b) indicate hexadecapoles belonging to the same group as $O^2_2 (\Gamma_{3\alpha})$ and $O^4_3 (\Gamma_{3\beta})$, respectively. For $t_{78} \leq 0$, we again find that 4u magnetic multipole states appear. We suppress the information on the ordering vector $Q$ in these diagrams, where $Q$ is defined as the momentum at which the maximum quadrupole susceptibility appears. At this stage, we simply comment that $Q$ is different even in the same multipole state, depending on the hopping amplitudes.

At $t_{78} = 0$, we find that the magnetic multipole states always appear irrespective of the sign of $v_3$. This is consistent with a previous result.\(^{30}\) Namely, the magnetic ground state in the RPA has also been obtained in the three-orbital model including only nearest-neighbor hopping ($f f o$) and the negative Hund’s rule interaction between $\Gamma_7$ and $\Gamma_8$ electrons. Note that $t_7 = t_{78} = 0$ when we consider only ($f f o$).

Here readers may consider that the above results look strange. Namely, the electric multipole states are not always stabilized, in spite of the choice of the interaction parameters with the local 3g doublet ground state without any dipole moments. In our calculations, we confirm that the stabilized
multipole state is found to be one of 3g, 4u, and 5u as long as we change \( v_3 \) as the control parameter. Note that the 5u octupole appears only in limited parameter regions (not shown here) and the competition between 3g and 4u usually occurs in the present calculations. The ordered multipole moments and corresponding \( Q \) also depend on the hopping parameters and other local parameters. We notice that the multipole diagrams for \( v_3 > 0 \) and \( v_3 < 0 \) are almost symmetric about the line of \( t_{78} = 0 \). This tendency is also found when we change hopping parameters \( t_8 \) and \( s_8 \). For the stabilization of the 3g quadrupole states, the condition of \( t_{78} \neq 0 \) is considered to be important.

We find that in the non-interacting case, \( \max(\chi^{4u}_{\max}, \chi^{5u}_{\max}) = \max(\chi^{3g}_{\max}, \chi^{3g}_{\max}) \), where \( \chi^{3g}_{\max} \) indicates the maximum eigenvalue of the susceptibility for the multipole \( \Gamma \) and \( \max(A, B) \) indicates the larger value of \( A \) and \( B \). The 4u-5u competition as well as the 1g-3g competition in the non-interacting case depends on the hopping amplitudes. With increasing \( |v_3| \) for both \( v_3 > 0 \) and \( v_3 < 0 \), we observe the enhancement of \( \chi^{3g}_{\max} \) or \( \chi^{4u}_{\max} \).

To understand the competition between magnetic and electric states, we discuss the low-order terms of the RPA susceptibility, which provide significant contributions to the difference between magnetic and electric multipole susceptibilities. It is possible to roughly sketch the phase diagram by the evaluation of such perturbation expansion terms, although the winner of the competition between 3g and 4u is finally determined by the RPA calculations.

We analyze the dependence on \( \sigma \) and \( \tau \) of the RPA susceptibility by evaluating \( \chi_{12,34}(q) \) in Eq. (24) for the RPA susceptibility Eq. (25). After some numerical calculations, we find that the terms shown in Figs. 4(a)-4(c) induce a significant difference between magnetic and electric (\( \Gamma_{1n} \)) susceptibilities. To estimate the contribution of each Feynman diagram, we consider the first- and second-order terms of \( \Gamma_{\text{RPA}} \) in terms of the effective interaction \( v_3 \). When we consider the non-interacting case, the contributions of these Feynman diagrams vanish due to the conservation of pseudospin as long as we take into account only the hopping between nearest-neighbor sites. Namely, the enhancement of such Feynman diagrams strongly depends on the structure of the four-point vertex \( \Gamma_{\text{RPA}} \) in the RPA.

In Fig. 4(d), we show the first-order term \( \Gamma_{\text{RPA}} \) with respect to \( v_3 \). Here we remark that the local \( \Gamma_3 \) states are composed of two local singlets, as shown in Fig. 2. Note that \( v_3 \) is the off-diagonal term between Figs. 2(a) and 2(b) since we consider the \( \Gamma_3 \) (\( O^2_{1} \)) state. In Fig. 4(d), the \( \Gamma_7 \) state appears just once in the scattering process, leading to the contribution of \( G_{\alpha \alpha}G_{\alpha \alpha}G_{\alpha \alpha}v_3 \) for Fig. 4(a), \( G_{\alpha \alpha}G_{\alpha \alpha}G_{\alpha \alpha}v_3 \) for Fig. 4(b), and \( G_{\alpha \alpha}G_{\alpha \alpha}v_3 \) for Fig. 4(c), where \( G_{\alpha \alpha}, G_{\alpha \alpha}, G_{\alpha \alpha} \) denote the Green’s function between \( \alpha \). Next we consider the second-order terms with respect to \( v_3 \), as shown in Fig. 4(e). Since the bubble includes the Green’s functions between different pseudospins, the second-order terms simply vanish.

When we repeat the above discussion for higher-order terms with respect to \( v_3 \), we find that \( \Gamma_{\text{RPA}} \) never includes the terms of even order of \( v_3 \). Thus, concerning the \( v_3 \) dependence, the contributions of Figs. 4(a)-4(c) are expressed by an odd function of \( v_3 \). Concering the \( t_{78} \) dependence, when we expand the Green’s function \( G_{\alpha \alpha} \) in terms of \( t_{78} \), we notice that \( G_{\alpha \alpha} \) is an odd function of \( t_{78} \). Thus, the contributions from Figs. 4(a) and 4(b) are given by an odd function of \( t_{78} \), while that from Fig. 4(c) is considered to be an even function of \( t_{78} \). Then, only for \( t_{78} \approx 0 \), the contributions of these Feynman diagrams are almost suppressed, even though we change the other hopping parameters \( t_8, s_8 \), and \( t_7 \). The mechanism can be intuitively understood as follows.

Since the susceptibilities in Figs. 4(a) and 4(b) are considered to be an odd function of \( t_{78} \), they are suppressed for the case of \( t_{78} = 0 \). Thus, only the Feynman diagram in Fig. 4(c) remains since it includes a term independent of \( t_{78} \). Since other effective interactions such as \( v_1 \) and \( v_2 \) are found to enhance the magnetic multipole, the enhancement of the electric multipoles shown by the Feynman diagram in Fig. 4(c) is too small to stabilize them, indicating that the susceptibility of the magnetic multipole is always larger than that of the electric multipole at \( t_{78} = 0 \). Namely, for the stabilization of the 3g quadrupole state, the condition of \( t_{78} \neq 0 \) is found to be necessary.

From the discussion on the \( t_{78} \) and \( v_3 \) dependences of the susceptibilities, it is also possible to qualitatively explain the symmetric behavior of the multipole phase diagrams shown in Figs. 3(a) and 3(b) about the line of \( t_{78} = 0 \). For \( t_{78} < 0 \) and \( v_3 > 0 \), the susceptibilities in Figs. 4(a)-4(c) enhance the \( O^2_{1} \) quadrupole and suppress the 4u multipole, leading to the stabilization of the \( O^2_{1} \) state. On the other hand, for the case of \( v_3 < 0 \), the \( O^2_{1} \) quadrupole should be suppressed since these terms are odd functions of \( v_3 \). Thus, the 4u multipole is stabilized, in sharp contrast to the case of \( v_3 > 0 \). The appearance of the 3g hexadecapole and 4u multipole in the region of \( t_{78} > 0 \) can also be understood by the dependence of each term on \( t_{78} \) and \( v_3 \) in addition to the form of the matrix elements of hexadecapole moments.

### 3.2 Fermi surface structure and multipole nesting

In this subsection, we discuss the ordering vector \( Q \) of the quadrupole susceptibility when the 3g state is stabilized. Here we point out an important result. As shown in Fig. 5, \( Q \) of the RPA susceptibility is the same as that of the non-interacting susceptibility if the quadrupole state is stabilized. Note that we do not mention the comparison between 3g and 4u multipole states. In the following, we explain this claim in detail.

In Fig. 5, we show Eq. (24) for the RPA susceptibility.
Fig. 5. (Color online) (a) $O^2$ bare susceptibility, (b) $O^2_{\text{RPA}}$ susceptibility, (c) $O^2$ bare susceptibility, and (d) $O^2_{\text{RPA}}$ susceptibility on the $q_x q_z$ plane with $q_x = \pi$ for $t_8 = -1.0$, $s_8 = -0.2$, $t_7 = 0.4$, and $t_{78} = -1.0$. In the RPA calculation, the $O^2$ quadrupole state is found to be stabilized for these parameters. To depict (b) and (d), we set $v_3 = 4.0$.

In Eq. (25) and the bare susceptibility Eq. (26) with $K = K' = \{2, 3g\alpha\}$. In Figs. 5(a) and 5(b), we show the $O^2$ bare and RPA susceptibilities, respectively, on the $q_x q_z$ plane with $q_x = \pi$ for $t_8 = -1.0$, $s_8 = -0.2$, $t_7 = 0.4$, and $t_{78} = -1.0$. For these parameters, we obtain the $O^2$ quadrupole state and $Q = (\pi, \pi, 5\pi/8)$ in the present RPA calculation. In actual calculations, we find that $1/\chi_{\text{max}}$ becomes zero at $v_3 = 4.3$. Then, we depict Fig. 5(b) for $v_3 = 4.0$. We emphasize that the peak position of the bare susceptibility in Fig. 5(a) is the same as $Q = (\pi, \pi, 5\pi/8)$.

In Figs. 5(c) and 5(d), we show the $O^2$ bare and RPA susceptibilities, respectively, for the same parameters as in Figs. 5(a) and 5(b). Namely, these are the results in the $O^2$ quadrupole state. The peak position is found to be $Q = (\pi, 5\pi/8, \pi)$ for both the bare and RPA susceptibilities. Since the $O^2$ quadrupole ordered state is stabilized, the magnitude of the RPA susceptibility in Fig. 5(d) is smaller than that in Fig. 5(b). It is stressed that the magnitude of the bare susceptibility in Fig. 5(c) is also smaller than that in Fig. 5(a). We notice that this tendency is always observed as long as we consider the quadrupole ordered state in the present research. Namely, it is possible to deduce the kind of quadrupole and the ordering vector $Q$ in the non-interacting case.

From the analysis of the bare and RPA susceptibilities in the quadrupole state, we notice that the incommensurability of the quadrupole ordering is determined by the Fermi surface structure in the non-interacting case, at least in the RPA. Concerning the effect beyond the RPA, we provide a comment later. Then, hereafter we concentrate on the relation between the Fermi surface structure and the bare susceptibility.

In Fig. 6, we depict the Fermi surfaces for $t_8 = -1.0$, $s_8 = -0.2$, $t_7 = 0.4$, and $t_{78} = -1.0$. The electron Fermi surface in Fig. 6(a) is depicted at the center of the $\Gamma$ point and is mainly composed of $\Gamma_8$ electrons. On the other hand, in Fig. 6(b), we show the hole Fermi surface at the center of the R point, which is composed of $\Gamma_7$ electrons. Our Fermi surface structure is similar to the result of the band-structure calculations, except for the small-size Fermi surface, which is not observed for the present parameters. When we evaluate $n_7$ and $n_8$, which are the average electron numbers in the $\Gamma_7$ and $\Gamma_8$ orbitals per ion, respectively, we obtain $n_7 = 0.79$ and $n_8 = 1.21$ in the present case. These values seem to be consistent with those expected from the local $\Gamma_7$ singlets, although there are deviations from $n_7 = n_8 = 1$ due to the difference in the inelastic properties of $\Gamma_7$ and $\Gamma_8$ electrons.

When we recall the susceptibility of the one-band model, $Q$ is basically determined from the nesting condition of the Fermi surface. We imagine that the nesting is still important for the determination of $Q$ of multipole susceptibility in the multiband systems, but it is difficult to conclude the importance of the nesting only from Fig. 6. Thus, we analyze the bare susceptibility in more detail.

For this purpose, we perform the multipole decomposition of the bare susceptibility as in the case of Eq. (24). After some algebraic calculations, we obtain

$$\chi_{K,K'}^{(0)}(q) = \sum_k \chi_{K,K'}^{(0)}(k, q),$$

(31)

where $\chi_{K,K'}^{(0)}(k, q)$ is given by

$$\chi_{K,K'}^{(0)}(k, q) = \sum_{\nu\sigma, \nu'\sigma'} L_{\nu\sigma, \nu'\sigma'}^{(K)}(k, q) L_{\nu\sigma, \nu'\sigma'}^{(K)*}(k, q) \times \chi_{\nu,\sigma}(k, q),$$

(32)

and $L$ is defined as

$$L_{\nu\sigma, \nu'\sigma'}^{(K)}(k, q) = \sum_{\tau, \tau'} T_{\tau, \tau, \nu', \sigma'}^{(K)} U_{\tau, \nu}(k) U_{\tau, \nu'}(k + q).$$

(33)

In Fig. 7, we show the results for $t_8 = -1.0$, $s_8 = -0.2$, $t_7 = 0.4$, and $t_{78} = -1.0$. In this case, we have already found that $Q = (\pi, \pi, 5\pi/8)$ in the $O^2$ susceptibility. Then, we focus on the $k$ dependence of $\chi_{K,K'}^{(0)}(k, Q)$ in Eq. (31) for $K = K' = \{2, 3g\alpha\}$. Since it is difficult to depict all the results in the first Brillouin zone, we exhibit $\chi_{K,K'}^{(0)}(k, Q)$ on the $k_x k_y$ plane for $k_z = 3\pi/10$ in Fig. 7(a). Note that the value of $k_z$ is chosen for convenience. The spot-like bright regions denote large contributions to the susceptibility, but only from this result, we cannot understand the reason why such regions appear. Then, we show the orbital densities on the curves defined by $E_{k\nu} = \mu$ and $E_{k+q\nu'} = \mu$ in Figs. 7(b) and 7(c), respectively. We clearly observe that the $\Gamma_8$ and $\Gamma_7$ densities become significantly large on the curves defined by $E_{k\nu} = \mu$ and $E_{k+q\nu'} = \mu$, respectively.

In Fig. 7(d), we consider the nesting between the two curves $E_{k\nu} = \mu$ and $E_{k+q\nu'} = \mu$ with significant orbital densities. Then, we notice the existence of segments on the
curves that satisfy the condition of $E_{k\nu} = E_{k+Q\nu'}$, leading to the same positions as the spot-like bright regions in Fig. 7(a). We emphasize the importance of the nesting between the curve of $E_{k\nu} = \mu$ with large $\Gamma_{8a}$ density and that of $E_{k+Q\nu'} = \mu$ with large $\Gamma_7$ density. Namely, for the stabilization of the $O^0_2$ quadrupole order, it is necessary to obtain the nesting between the Fermi surfaces with $\Gamma_{8a}$ and $\Gamma_7$ densities. Thus, we call it multipole nesting in this paper.

For different hopping parameters, the $O^0_2$ quadrupole state is found in Fig. 3(a). We can depict figures similar to Fig. 7, but here we only explain the difference from Fig. 7 without showing the figures. In the $O^0_2$ quadrupole state, we observe the multipole nesting between $\Gamma_{8b}$ and $\Gamma_7$ orbital densities. In addition, we also find multipole nesting between $\Gamma_{8a}$ and $\Gamma_{8b}$ orbital densities in this case. As shown in Eq. (10), the local $\Gamma_{3/3}$ doublet is composed of a pair of singlets, but after some algebraic calculations, the singlet between $\Gamma_{8b}$ and $\Gamma_7$ orbitals is found to be the main component of the local $\Gamma_{3/3}$ doublet. Another singlet between $\Gamma_{8a}$ and $\Gamma_{8b}$ gives a minor contribution. This local singlet structure seems to be consistent with the above explanation for the multipole nesting in the $O^0_2$ quadrupole state.

We provide a comment on the appearance of the 4u magnetic state for $t_{78} \neq 0$. If the multipole nesting properties for both $O^0_2$ and $O^0_2$ are found to be weak, the largest susceptibility among the electric multipoles is the 1g hexadecapole in the non-interacting system. In this situation, the susceptibilities of the quadrupole become smaller than that of the magnetic multipole. Thus, in such a case, the 4u magnetic multipole state is stabilized for $t_{78} \neq 0$.

From the present calculation results, we propose that the $O^0_2$ ($O^0_2$) quadrupole ordering is regarded as the quadrupole density wave state composed of $\Gamma_{8a}$ ($\Gamma_{8b}$) and $\Gamma_7$ electrons. To stabilize this state, it is necessary to have nesting between the segments on the Fermi surface with large $\Gamma_8$ and $\Gamma_7$ densities. This is the most important result of this paper.

4. Discussion and Summary

In this paper, we introduced the $\Gamma_7$-$\Gamma_8$ model Hamiltonian with the effective interactions that induce the local $\Gamma_3$ ground states for $n = 2$. Then, we estimated the multipole susceptibilities in the RPA to reveal the condition for the emergence of $\Gamma_3$ quadrupole ordering. We clarified that the $\Gamma_3$ quadrupole order can be understood from the concept of multipole nesting, in which the Fermi surface region with large $\Gamma_8$ orbital density should be nested on the area with a significant $\Gamma_7$ component when we shift the positions of the Fermi surfaces with the ordering vector $Q$. This result suggests that the $\Gamma_3$ quadrupole ordering can be understood from the combination of the $\Gamma_7$ and $\Gamma_8$ electrons in the momentum space, corresponding to the local $\Gamma_3$ doublets composed of two singlets between $\Gamma_7$ and $\Gamma_8$ orbitals. In the present work, we proposed that the quadrupole ordering is regarded as the quadrupole density wave state from the itinerant picture. We believe that our scenario works for the understanding of the $\Gamma_3$ quadrupole order in PrPb$_3$. First we remark that Fermi surfaces have been observed in PrPb$_3$ in a dHvA experiment. This fact seems to support the starting point of our present approach from the itinerant picture for $f$ electrons. Note, however, that the band-structure calculations were carried out for LaPb$_3$, not for PrPb$_3$, probably due to the difficulty in the treatment of non-Kramers $\Gamma_3$ states from the itinerant picture. Thus, the contribution of $f$ electrons to the Fermi surfaces seems to be unclear, but we simply assume that a 4f-electron admixture should appear, more or less, in the Fermi surfaces. We consider that our present model is constructed for such itinerant $f$ electrons through the hybridization with conduction electrons.

Next we emphasize that the incommensurate quadrupole order in PrPb$_3$ is considered to be the sinusoidal wave state. It is difficult to reproduce such a state from the localized picture. However, in the itinerant picture, as emphasized in this paper, it is possible to regard it as the quadrupole density wave state. Also from this viewpoint, we believe that the present approach works for PrPb$_3$.

However, there are some problems in the present approach. One is the incommensurability of the quadrupole order. The ordering vector of the peculiar incommensurate quadrupole state has been found to be $Q_0 = (\pi, \pi \pm \delta, 0)$ and $(\pi \pm \delta, \pi, 0)$ with $\delta = \pi/4$. Unfortunately, in the present calculations including only the nearest-neighbor hopping, we did not reproduce the quadrupole ordering with $Q_0$. When we include the next-nearest-neighbor hopping and further neighbors, it may be possible to obtain the quadrupole ordering with $Q_0$, but in the present paper, we did not make such an effort for the
parameter tuning for the reason below.

Another problem relates to the choice of local interactions. In this paper, to obtain the $\Gamma_3$ quadrupole ordering, we restricted ourselves only to the situation in which the local $\Gamma_3$ state is stabilized by the effective interactions chosen by hand. We recognize that it is necessary to further investigate the condition for the effective interactions to obtain the $\Gamma_3$ quadrupole ordering from the itinerant picture with realistic parameters.

We emphasize that our purpose is to explore a route to the $\Gamma_3$ quadrupole order from the itinerant picture. Thus, we did not thoroughly perform the parameter search for the hopping amplitudes and local interactions within the present model. Such effort may be a future task, but it is more desirable to perform the first-principles calculations to estimate the effective hopping amplitudes and local interactions with the use of the Wannier basis functions.\(^{17}\) In the thus obtained three-orbital model, it is highly recommend to perform the present calculations for the multipole susceptibility in the RPA. We believe that this is the next step in this direction of research, when we attempt to further develop the present theory for the quadrupole ordering in $f^2$-electron systems.

Here we briefly discuss the effect of $H_{CEF}$. Since it destabilizes the local $\Gamma_3$ states composed of $\Gamma_7$ and $\Gamma_8$ singlets, we ignored this term in this paper, but it may be interesting to consider the quantum critical behavior induced by CEF potentials in the $\Gamma_3$ quadrupole ordering. It may be interesting to observe unconventional superconductivity induced by quadrupole fluctuations near such a critical point. This is another future issue.

Finally, we provide a brief comment on the determination of $Q$ from the interaction viewpoint. We evaluated the multipole susceptibility in the RPA in the present paper and arrived at the picture of multipole nesting for the microscopic understanding of $\Gamma_3$ quadrupole ordering. For the ordering vector $Q$, within the RPA, we found that $Q$ in the RPA susceptibility is the same as that in the bare susceptibility. This statement was found to be valid when we investigated the present model by using other effective interactions. It is difficult to prove it mathematically, but we believe that $Q$ of the quadrupole order is determined in the non-interacting case as long as we consider the quasi-particle picture on the basis of the Fermi liquid theory. In the perturbation expansion, it is possible to discuss the peak of susceptibility including the effect of the vertex corrections beyond the RPA.\(^{17}\) This point is another future problem.

In summary, we discussed the $\Gamma_3$ quadrupole ordering in $f^2$-electron systems from the microscopic viewpoint. We emphasized the point that the $\Gamma_3$ quadrupole order in $f^2$-electron systems can be understood from the multipole nesting, in which the Fermi surface region with large $\Gamma_8$ orbital density is nested on the area with a significant $\Gamma_7$ component when we shift the positions of the Fermi surfaces with the ordering vector. This is the conceptual finding of the present paper, although we have not perfectly explained the $\Gamma_3$ quadrupole order in PrPb$_3$. The ordering vector will also be explained within the present scheme, for instance, by evaluating hopping and interaction parameters using first-principles calculations, which is a future task.

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