Multipole interactions of $\Gamma_3$ non-Kramers doublet systems on cubic lattices

Katsunori Kubo$^1$ and Takashi Hotta$^2$

$^1$Advanced Science Research Center, Japan Atomic Energy Agency, Tokai, Ibaraki 319-1195, Japan
$^2$Department of Physics, Tokyo Metropolitan University, Hachioji, Tokyo 192-0397, Japan
E-mail: kubo.katsunori@jaea.go.jp

Abstract. We investigate the multipole interactions between adjacent $f^2$ ions with the $\Gamma_3$ crystalline electric field (CEF) ground state. In this study, we consider only the $\Gamma_8$ states as the one-electron states. We construct the $\Gamma_3$ doublet state of the electrons in the $\Gamma_8$ states, and indeed, it can become the CEF ground state of a simple model Hamiltonian. To derive the multipole interactions, we apply the second-order perturbation theory with respect to the intersite hopping. We obtain no multipole interaction for a simple cubic lattice and octupole interactions for bcc and fcc lattices. We discuss the similarities and differences in the multipole interactions among the models with the local $\Gamma_3$ CEF states.

1. Introduction

In $f$-electron systems, multipole physics has been studied, in particular, on the $\Gamma_8$ systems such as $\text{NpO}_2$ [1–5] and $\text{Ce}_x\text{La}_{1-x}\text{B}_6$ [6–12]. The $\Gamma_8$ quartet has sufficient degrees of freedom to possess higher-order multipoles such as octupoles and it is regarded as an ideal system for the multipole physics.

However, such large degeneracy is not a necessary condition to possess higher-order multipoles. If the crystalline electric field (CEF) ground state does not have the dipole but is not a singlet, this state inevitably has higher-order multipoles. Indeed, the $\Gamma_3$ non-Kramers doublet does not have the dipole but has quadrupole and octupole moments. In addition, the absence of the dipole moment is an advantage of the $\Gamma_3$ systems for multipole physics since we can focus only on the higher-order multipole moments.

Previously, we have investigated the multipole interactions between the $\Gamma_3$ ions by using a model in which the $f^2$-$\Gamma_3$ states are constructed as pseudospin singlets between the $\Gamma_7$ and $\Gamma_8$ orbitals of the total angular momentum $j = 5/2$ [13] [Fig.1(b)]. Then, we have found that the quadrupole interaction is dominant in the simple cubic (sc) lattice and the octupole interactions are dominant in the bcc and fcc lattices. These features depending on the lattice structure are similar to the multipole interactions in the $f^1$-$\Gamma_8$ system [4].

In this study, to clarify the influence of the choice of the model, we use another method for constructing the $f^2$-$\Gamma_3$ state. We construct the $f^2$-$\Gamma_3$ doublet state of the electrons only in the $\Gamma_8$ state [Fig.1(a)]. To derive the multipole interactions, we apply the second-order perturbation theory with respect to the intersite hopping. In general, the $f^2$-$\Gamma_3$ states composed of $j = 5/2$ electrons are superpositions of the $f^2$-$\Gamma_3$ states of the present study and of the previous study.
Figure 1. Electron configurations of the $f^2$-$\Gamma_3$ states (a) in the present study and (b) in the previous study [13]. The bold lines denote spin singlets.

Thus, if we obtain a common result between these studies, it will not depend on the details of the model.

2. Model and method

The $\Gamma_8$ states at site $r$ are given by

$$c_{r\sigma\uparrow}^\dagger |0\rangle \equiv \left( \frac{1}{\sqrt{6}} \left( \sqrt{5}a_{r5/2}^\dagger + a_{r-3/2}^\dagger \right) \right) |0\rangle,$$  \hspace{1cm} (1a)

$$c_{r\sigma\downarrow}^\dagger |0\rangle \equiv \left( \frac{1}{\sqrt{6}} \left( \sqrt{5}a_{r-5/2}^\dagger + a_{r3/2}^\dagger \right) \right) |0\rangle,$$  \hspace{1cm} (1b)

$$c_{r\beta\uparrow}^\dagger |0\rangle \equiv a_{r1/2}^\dagger |0\rangle,$$  \hspace{1cm} (1c)

$$c_{r\beta\downarrow}^\dagger |0\rangle \equiv a_{r-1/2}^\dagger |0\rangle,$$  \hspace{1cm} (1d)

where $a_{rj}^\dagger$ is the creation operator of the electron with the $z$-component $j_z$ of the total momentum $j = 5/2$ at $r$ and $|0\rangle$ denotes the vacuum state. $\sigma = \uparrow$ or $\downarrow$ denotes the Kramers degeneracy of the one-electron states. While it is not a real spin, we call it spin in this paper.

The model Hamiltonian is

$$H = H_{\text{kin}} + H_{\text{loc}},$$  \hspace{1cm} (2)

where $H_{\text{kin}}$ is the kinetic energy term composed of the nearest-neighbor hopping of the $\Gamma_8$ electrons. $H_{\text{loc}}$ denotes the onsite interactions:

$$H_{\text{loc}} = U \sum_{rr'} n_{rr\uparrow} n_{rr\downarrow} + U' \sum_{rr'\sigma} n_{rr\sigma} n_{rr'\sigma} + J \sum_{r\sigma\sigma'} c_{r\sigma\uparrow} c_{r\sigma\uparrow}^\dagger c_{r\sigma\downarrow}^\dagger c_{r\sigma\downarrow} + J' \sum_{r \neq r' \tau} c_{r\tau\uparrow}^\dagger c_{r\tau\downarrow}^\dagger c_{r'\tau\downarrow} c_{r'\tau\uparrow}^\dagger,$$  \hspace{1cm} (3)

where $n_{rr\sigma} = c_{r\sigma\uparrow}^\dagger c_{r\sigma\downarrow}$ and $n_{rr\tau} = \sum_{\sigma} n_{rr\sigma}$. When we consider only the Coulomb interaction between the electrons, $U$ is the intraorbital Coulomb interaction, $U'$ is the interorbital Coulomb interaction, $J$ is the exchange interaction, and $J'$ is the pair hopping interaction. In the present study, however, they should be regarded as effective interactions including the effects of the excited $j = 7/2$ states. Through the $j = 7/2$ states, the effects of the sixth-order terms of the CEF, which are indispensable to stabilize the $f^2$-$\Gamma_3$, can be taken into account [14].

Among the eigenstates of $H_{\text{loc}}$ of the $f^2$ states, we focus on the following singlets:

$$|z(r)\rangle = \left( \frac{1}{\sqrt{2}} (c_{r\sigma\uparrow}^\dagger c_{r\sigma\downarrow} - c_{r\beta\uparrow}^\dagger c_{r\beta\downarrow}^\dagger) \right) |0\rangle,$$  \hspace{1cm} (4)
with energy \( U - J' \) and

\[
|x(r)\rangle = \frac{1}{\sqrt{2}} (c_{r\alpha}^\dagger c_{r\beta}^\dagger - c_{r\alpha}^\dagger c_{r\beta}^\dagger) |0\rangle,
\]

(5)

with energy \( U' + J \). They are degenerate due to the relation \( U = U' + J + J' \), which holds under the cubic symmetry. These two states constitute a basis of the \( \Gamma_3 \) representation. If the effective interactions satisfy \( J < 0 \) and \( J' > 0 \), the \( f^2 \) ground state is the \( \Gamma_3 \) state given above.

We assume these conditions in the following, but the situation of \( J < 0 \) and \( J' > 0 \) is realized, if we appropriately include the effects of the sixth-order CEF terms into the effective interactions between the \( \Gamma_8 \) electrons.

For the formulation of the multipole interactions, it is convenient to rewrite the \( \Gamma_3 \) states as

\[
|\mu(r)\rangle = \sum_{\tau,\tau',\sigma,\sigma'} B^\mu_{\tau\sigma,\tau'\sigma'} c_{\tau\sigma}^\dagger c_{\tau'\sigma'}^\dagger |0\rangle,
\]

(6)

where

\[
B^\mu_{\tau\sigma,\tau'\sigma'} = \frac{i}{2\sqrt{2}} \sigma^\mu_{\tau\tau'} \sigma^\nu_{\sigma\sigma'}. \tag{7}
\]

\( \sigma^\mu \) is the \( \mu \)-component of the Pauli matrices.

To derive the multipole interactions, we consider the intermediate \( f^1-f^3 \) configurations of the nearest-neighbor sites. The intermediate \( f^1 \) state is the \( \Gamma_8 \) state given by Eq. (1). The intermediate \( f^3 \) state is the one-hole state in the \( \Gamma_8 \) orbitals and obviously follows the \( \Gamma_8 \) symmetry. The energy of the \( f^3 \) state is \( U + 2U' - J \). Note that, within the second-order perturbation theory with respect to the hopping, there is no other intermediate states in the present model.

The kinetic energy term of the Hamiltonian is given by

\[
H_{\text{kin}} = \sum_{r,\xi,\tau,\sigma,\tau',\sigma'} c_{r+\xi,\tau,\sigma,\tau',\sigma'}^\dagger \xi c_{r,\tau,\sigma,\tau',\sigma'} = \sum_{r,\xi,\nu,\nu'} c_{r+\xi,\nu,\nu'}^\dagger \xi c_{r,\nu,\nu'}, \tag{8}
\]

where \( \xi \) denotes the vector connecting the nearest-neighbor sites. Here, we have introduced an abbreviation \( \nu = (\tau, \sigma) \). Since \( H_{\text{kin}} \) is Hermitian, \( \xi_{\nu,\nu'} = i^{-\xi} \).

Concerning the hopping integrals, we consider only the \( \sigma \) bonding \((\{f\})\) as in the previous study [13]. The hopping integrals were derived in Ref. [15] for the sc lattice and in Ref. [4] for the bcc and fcc lattices. To write out the hopping integral \( t^\xi \) for each lattice, it is convenient to introduce the following \( 4 \times 4 \) matrices:

\[
\tilde{1}_{\tau,\tau'\sigma,\sigma'} = \delta_{\tau,\tau'} \delta_{\sigma,\sigma'}, \tag{9a}
\]

\[
\tilde{\tau}_{\tau,\tau'\sigma,\sigma'} = \sigma_{\tau,\tau'} \delta_{\sigma,\sigma'}, \tag{9b}
\]

\[
\tilde{\sigma}_{\tau,\tau'\sigma,\sigma'} = \delta_{\tau,\tau'} \sigma_{\sigma,\sigma'}, \tag{9c}
\]

\[
\tilde{\eta}^\pm = (\pm \sqrt{3} \tilde{\tau}^z - \tilde{\tau}^z)/2. \tag{9d}
\]

Then, the hopping integrals for the sc lattice are written as

\[
t^{(1,0,0)} = [\tilde{1} - \tilde{\eta}^+] t_1, \tag{10a}
\]

\[
t^{(0,1,0)} = [\tilde{1} - \tilde{\eta}^-] t_1, \tag{10b}
\]

\[
t^{(0,0,1)} = [\tilde{1} - \tilde{\tau}^z] t_1, \tag{10c}
\]
where we have set the lattice constant as unity and $t_1=3(f/f\sigma)/14$. For the bcc lattice,

$\tau^{(1/2, 1/2, 1/2)} = [\hat{1} + \tau^y (\sigma^x + \sigma^y + \sigma^z) / \sqrt{3} ] t_2,$ (11a)

$\tau^{(-1/2, 1/2, 1/2)} = [\hat{1} + \tau^y (-\sigma^x + \sigma^y - \sigma^z) / \sqrt{3} ] t_2,$ (11b)

$\tau^{(1/2,-1, 1/2, 1/2)} = [\hat{1} + \tau^y (-\sigma^x + \sigma^y - \sigma^z) / \sqrt{3} ] t_2,$ (11c)

$\tau^{(1/2, 1/2, -1/2)} = [\hat{1} + \tau^y (\sigma^x + \sigma^y + \sigma^z) / \sqrt{3} ] t_2,$ (11d)

with $t_2=2(f/f\sigma)/21$. For the fcc lattice,

$\tau^{(0,1/2, 1/2)} = [\hat{1} + (\hat{1} + 4\sqrt{3}\tau^y \hat{\sigma}^x)] t_3,$ (12a)

$\tau^{(1/2, 0, 1/2)} = [\hat{1} + (\hat{1} - 4\sqrt{3}\tau^y \hat{\sigma}^x)] t_3,$ (12b)

$\tau^{(1/2, 1/2, 0)} = [\hat{1} + (\hat{1} - 4\sqrt{3}\tau^y \hat{\sigma}^x)] t_3,$ (12c)

$\tau^{(0,1/2, -1/2)} = [\hat{1} + (\hat{1} + 4\sqrt{3}\tau^y \hat{\sigma}^x)] t_3,$ (12d)

$\tau^{(-1/2, 0, 1/2)} = [\hat{1} + (\hat{1} - 4\sqrt{3}\tau^y \hat{\sigma}^x)] t_3,$ (12e)

$\tau^{(1/2, -1/2, 0)} = [\hat{1} + (\hat{1} + 4\sqrt{3}\tau^y \hat{\sigma}^x)] t_3,$ (12f)

with $t_3=(f/f\sigma)/8$. For the other directions such as $(1, 0, 0)$, we can use the relation $t-\tau\hat{H} = \tau\hat{H}$.

By employing the second-order perturbation theory with respect to $H_{kin}$, we derive the effective Hamiltonian. In general, it is given by

$$H^{(eff)} = \sum_{a,b} \sum_{m=0} \langle 0, a | H_{kin} | m, u \rangle \langle m, u | H_{kin} | 0, b \rangle / (E_0 - E_m).$$ (13)

Here, $|0, a\rangle$ is a ground state without $H_{kin}$ with the energy $E_0$ and $|m, u\rangle$ is an $m$-th excited state with the energy $E_m$. However, as noted above, we have only one excited level in the intermediate states, and the effective Hamiltonian can be rewritten as

$$H^{(eff)} = -\frac{1}{\Delta E} \sum_{a,b} \langle 0, a | H_{kin}^2 | 0, b \rangle / (E_0 - E_m).$$ (14)

where

$$\Delta E = E_1 - E_0 = (U + 2U' - J) - 2(U' + J) = U - 3J.$$ (15)

If $\Delta E < 0$, the $f^2$ state is unstable. Thus, we assume a positive $\Delta E$. Then, the matrix elements of the effective interaction between ions at $r_1$ and $r_2$ is now evaluated by simply calculating the matrix elements of $H_{kin}^2$ between the ground states:

$$H^{(eff)}_{\mu_1 \mu_2; \mu'_1 \mu'_2} (r_1, r_2) = -\langle \mu_1 (r_1) \mu_2 (r_2) | H_{kin}^2 | \mu'_1 (r_1) \mu'_2 (r_2) \rangle / \Delta E$$

$$= -32 \text{Re} \left( B^{02} t^{r_2-r_1} B^{01} B^{01} t^{r_1-r_2} B^{02} \right) / \Delta E,$$ (16)

where Re denotes the real part and Tr is the trace of the matrix.

The obtained effective Hamiltonian can be rewritten in terms of the multipole operators for the $f^2$-$\Gamma_3$ state defined by

$$O^{0}_{2r} = \sum_{\mu, \mu'} |\mu(r)\rangle \sigma^{z}_{\mu \mu'} \langle \mu'(r)|,$$ (17a)

$$O^{2}_{2r} = \sum_{\mu, \mu'} |\mu(r)\rangle \sigma^{z}_{\mu \mu'} \langle \mu'(r)|,$$ (17b)

$$T_{xyzr} = \sum_{\mu, \mu'} |\mu(r)\rangle \sigma^{y}_{\mu \mu'} \langle \mu'(r)|.$$ (17c)
$O^0_{2r}$ and $O^2_{2r}$ are the quadrupole moments with $\Gamma_{3g}$ symmetry and $T_{xyzr}$ is the octupole moment with $\Gamma_{2u}$ symmetry.

3. Results
For the sc lattice, we obtain no multipole interaction, that is, the second-order perturbation results in only an overall shift of energy. This result suggests that the present model is too simple to deal with the multipole interactions at least for the sc lattice, and the $\Gamma_7$ orbital should be included as in the previous study [13].

For the bcc lattice, we obtain only the following octupole interaction:

$$H^{(\text{eff})} = 16 \sum_q \cos(q_x/2) \cos(q_y/2) T_{xyzq} T_{xyz-q},$$

(18)

in the unit of $t_2^2/\Delta E$. $T_{xyzq}$ is the Fourier transform of $T_{xyzr}$. We have not obtained the quadrupole interaction. Even in the previous study, we have obtained only the octupole interaction, and thus, we expect that the dominance of the octupole interaction on the bcc lattice does not depend on the details of the model.

For the fcc lattice, we again obtain only the octupole interaction:

$$H^{(\text{eff})} = \frac{384}{49} \sum_q \left[ \cos(q_x/2) \cos(q_y/2) + \cos(q_y/2) \cos(q_z/2) + \cos(q_z/2) \cos(q_x/2) \right] T_{xyzq} T_{xyz-q},$$

(19)

in the unit of $t_3^2/\Delta E$. In the previous study, we have obtained a weak but finite quadrupole interaction. Thus, the appearance of the quadrupole interaction, in addition to the octupole interaction, depends on the model to construct the $f^2-\Gamma_3$ state. However, even in the previous study, the quadrupole interaction is much weaker than the octupole interaction, and the dominance of the octupole interaction on the fcc lattice might not depend on the details of the model.

4. Summary and discussion
We have studied a simple model for the $f^2-\Gamma_3$ systems by considering only the $\Gamma_8$ orbitals as the one-electron states. We obtain no multipole interaction for the sc lattice and the octupole interactions for the bcc and fcc lattices. The dominance of the octupole interaction in the bcc and fcc lattices and the absence of the octupole interaction in the sc lattice are common between the present model and a model including the $\Gamma_7$ orbital in the one-electron states to construct the $f^2-\Gamma_3$ state [13]. Thus, these features will not be altered by changing the details of the model.

However, the absence of the multipole interactions in the sc lattice indicates that the present model including only the $\Gamma_8$ orbitals is too simple. In this regard, we should include at least the $\Gamma_7$ orbital to study the multipole physics of the $f^2-\Gamma_3$ systems from a microscopic viewpoint as in the previous study [13]. In a single ion model considering all the 14 $f$-orbitals with a realistic parameter set to obtain a $\Gamma_3$ ground state for $f^2$, we obtain the $\Gamma_6$ ground state when we accommodate three electrons [14]. Indeed, we obtain the $f^3-\Gamma_6$ CEF ground state in the previous model, but the $f^3$ states are $\Gamma_8$ in the present model. This problem on the $f^3$ states also indicates the importance of the $\Gamma_7$ orbital.

Note that we have implicitly assumed an insulating state to derive the multipole interactions. For a metallic state, it might be necessary to consider the conduction band explicitly and derive the multipole interactions as the Ruderman-Kittel-Kasuya-Yosida (RKKY) interactions. It is a future problem whether the multipole interactions as the RKKY interactions are much different or not.
Finally, from our studies, we notice that it is interesting to search the \( \Gamma_3 \) systems on the bcc lattices for the octupole ordering. The diamond structure is also a candidate to realize octupole ordering since the nearest-neighbor ions locate along [111] direction and so on as in the bcc lattice and we obtain only the octupole interaction in our models.

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