Multipole State of Heavy Lanthanide Filled Skutterudites

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We discuss multipole properties of filled skutterudites containing heavy lanthanide Ln from a microscopic viewpoint on the basis of a seven-orbital Anderson model. For Ln=Gd, in contrast to naive expectation, quadrupole moments remain in addition to main dipole ones. For Ln=Ho, we find an exotic state governed by octupole moment. For Ln=Tb and Tm, no significant multipole moments appear at low temperatures, while for Ln=Dy, Er, and Yb, dipole and higher-order multipoles are dominant. We briefly discuss possible relevance of these multipole states with actual materials.

KEYWORDS: multipole, filled skutterudites, heavy lanthanide, numerical renormalization group method

Recently, filled skutterudite compounds \(\text{LnT}_4X_{12}\) with lanthanide \(\text{Ln}\), transition metal atom \(T\), and pnictogen \(X\) have attracted much attention in the research field of condensed matter physics due to large varieties of exotic phenomena concerning magnetism and superconductivity.\(^1\)\(^-\)\(^2\) Since these compounds crystallize in the cubic structure with high symmetry of \(T_h\) point group,\(^3\) \(f\)-orbital degeneracy remains in general. Due to the strong spin-orbit coupling of \(f\) electrons, spin-orbital complex degrees of freedom, i.e., multipoles, become active in filled skutterudite compounds, which is a characteristic issue of this material group.

In fact, recent experiments in cooperation with phenomenological theory have revealed that multipoles appear ubiquitously in filled skutterudites. For instance, a rich phase diagram of \(\text{PrOs}_4\text{Sb}_{12}\) including field-induced quadrupole order has been unveiled.\(^4\)\(^-\)\(^6\) In \(\text{NdFe}_4\text{P}_{12}\), a significant role of quadrupole at low temperatures has been suggested from the measurement of elastic constant.\(^7\) In \(\text{SmRu}_4\text{P}_{12}\), a possibility of octupole order has been proposed from experimental results.\(^8\)\(^-\)\(^11\) Recently, antiferro \(\Gamma_1\)-type order\(^1\)\(^2\) has been actively discussed experimentally and theoretically for \(\text{PrRu}_4\text{P}_{12}\)\(^{13,14}\) and \(\text{PrFe}_4\text{P}_{12}\)\(^{15,17}\).

In such current circumstances, it is one of challenging issues to clarify microscopic aspects of multipole degrees of freedom in \(f\)-electron systems. The present author and collaborators have developed a microscopic theory for multipole-related phenomena on the basis of a \(j-j\) coupling scheme.\(^18\) In particular, possible multipole states for light lanthanide filled skutterudites have been discussed by analyzing multipole susceptibility in detail.\(^19\)\(^-\)\(^25\)

However, multipole phenomena in heavy lanthanide systems have not been understood satisfactorily, mainly due to the difficulty in the theoretical treatment of multipoles in lanthanides with large total angular momentum. Experimentally, due to the development of crystal growth technique under high pressure, heavy lanthanide filled skutterudite compounds have been synthesized\(^26\)\(^-\)\(^28\) and research activities to clarify multipoles in such materials will be advanced. It is required to make more effort in the theoretical side to develop a microscopic theory for multipole state of heavy lanthanide systems.

In this Letter, first we define multipole operators of \(f\) electrons. Then, we analyze multipole susceptibility of a seven-orbital Anderson model by using a numerical renormalization group technique. It is found that quadrupole moments appear even for \(\text{Ln=Gd}\) and an exotic phase governed by octupole moment is suggested for \(\text{Ln=Ho}\). We find no significant multipole moments at low temperatures for \(\text{Ln=Tb}\) and \(\text{Tm}\), while dipole and higher-order multipole moments are dominant for \(\text{Ln=Dy}\), \(\text{Er}\), and \(\text{Yb}\). We discuss these multipole states in comparison with available experimental results.

The seven-orbital Anderson model is given by

\[
H = \sum_{k,\sigma} \varepsilon_k c_{k\sigma}^\dagger c_{k\sigma} + \sum_{k,\sigma,m} (V_m c_{k\sigma}^\dagger f_{m\sigma} + h.c.)
+ \sum_{m,m',\sigma,\sigma'} (B_{m,m'}(\delta_{\sigma\sigma'} + \lambda_{m,m',\sigma,\sigma'}) f_{m\sigma}^\dagger f_{m'\sigma'}
+ \sum_{m,m'\sigma,\sigma'} I_{m_1,m_2,m_3,m_4} f_{m_1\sigma}^\dagger f_{m_2\sigma'}^\dagger f_{m_3\sigma'} f_{m_4\sigma},
\]

where \(\varepsilon_k\) denotes conduction electron dispersion, \(c_{k\sigma}\) indicates the annihilation operator for conduction electron with momentum \(k\) and spin \(\sigma\), \(\sigma=\pm 1\) \((-1\) for up (down) spin), \(f_{m\sigma}\) is the annihilation operator for \(f\) electron with spin \(\sigma\) and \(z\)-component \(m\) of angular momentum \(\ell=3\), \(V_m\) is the hybridization between conduction and \(f\) electrons, \(B_{m,m'}\) is a crystalline electric field (CEF) potential for \(f\) electrons, \(\delta_{\sigma\sigma'}\) is the Kronecker’s delta, \(\lambda\) is the spin-orbit coupling, \(\delta_{m,\pm 1,m,\pm 1}=\pm \sqrt{2}-m(m+1)/2\), and zero for the other cases. The Coulomb integral \(I\) is expressed by the combination of Slater-Condon parameters, \(F^0\), \(F^2\), \(F^4\), and \(F^6\).\(^{29}\)

For filled skutterudites, the main conduction band is given by \(a_u\), constructed from \(p\)-orbitals of pnictogen.\(^{30}\) Note that the hybridization occurs between the states with the same symmetry. Since the \(a_u\) conduction band has \(xyz\) symmetry, we set \(V_2=-V_2=V\) and zero for other \(m\). For the \(T_h\) point group, \(B_{m,m'}\) is given by three CEF parameters, \(B_2^0\), \(B_2^2\), and \(B_2^4\), expressed as \(B_2^0=V x/15\), \(B_2^2=W (1-|x|)/180\), and \(B_2^4=W y/24.31,32\) Here \(x\) and \(y\) specify the CEF scheme, while \(W\) determines the energy scale of the CEF potential. In order to adjust the local \(f\)-electron number \(n\), we appropriately change the chemical potential.

Let us set the parameters of the model. Details of the determination of the parameters will be discussed elsewhere. Concerning Slater-Condon parameters, we set \(F^0=10\text{ eV}\) by hand. Others are determined so as to reproduce excitation spectra of \(\text{Pr}^{3+}\) ion.\(^{33}\) Here we show only the results: \(F^2=8.75\text{ eV}, F^4=6.60\text{ eV}, \text{and } F^6=4.44\text{ eV}\). We use these values for all
lanthanides. On the other hand, we use experimental value of \( \lambda = 0.180 \) eV (Gd), 0.212 eV (Tb), 0.240 eV (Dy), 0.265 eV (Ho), 0.295 eV (Er), 0.326 eV (Tm), and 0.356 eV (Yb).\(^{34}\) The hybridization is fixed as \( V = 0.05 \) eV and a half of the bandwidth of \( a_u \) conduction band is set as 1 eV. Concerning CEF parameters, we set \( W = -0.4 \) meV, \( y = 0.3 \), and \( z = 0.3 \) so as to reproduce quasi-quartet CEF scheme of PrOs\(_4\)Sb\(_{12}\).\(^{35-37}\)

Here we provide a comment on the local CEF state. Due to the lack of space, we do not show the CEF energy schemes for \( n = 7 \sim 13 \), but they are almost the same as those obtained in Ref. 20, even though we have used different parameters there. Namely, the CEF energy schemes are not changed drastically, as long as we use realistic Coulomb interaction and spin-orbit coupling. As for the CEF ground state, except for \( n = 10 \), it is not easily converted when we slightly change the value of \( x \) around at \( x = 0.3 \). Thus, we set \( x = 0.3 \) as a typical value for \( n = 7 \sim 9 \) and 11 \sim 13. For \( n = 10 \), it has been found that \( \Gamma_{25}^+ \) doublet and \( \Gamma_4^+ \) triplet states are almost degenerate in the wide range of the values of \( x \).\(^{20}\) Namely, it is necessary to discuss carefully the case of \( n = 10 \).

Now we define the multipole operator \( \hat{X} \) for \( f \) electron. In general, \( \hat{X} \) is expressed as

\[
\hat{X} = \sum_{k, \gamma} p^{(k)}_{\gamma} \hat{T}^{(k)}_{\gamma},
\]

where \( k \) is a rank of multipole, \( \gamma \) is a label to express \( O_h \) irreducible representation, and \( \hat{T}^{(k)}_{\gamma} \) is cubic tensor operator, given by \( \hat{T}^{(k)}_{\gamma} = \sum_q G_{\gamma,q}^{(k)} \hat{T}_q^{(k)} \). Here an integer \( q \) runs between \( -k \) and \( k \), \( \hat{T}_q^{(k)} \) is spherical tensor operator, and \( G_{\gamma,q}^{(k)} \) is the transformation matrix between spherical and cubic harmonics. The coefficient \( \lambda^{(k)}_{\gamma} \) will be discussed later.

In this paper, we define multipole as spin-orbital density in the form of one-body operator from the viewpoint of multipole expansion of electron density in magnetism. Then, the spherical tensor operator \( \hat{T}^{(k)}_q \) for \( f \) electron is given in the second-quantized form as

\[
\hat{T}^{(k)}_q = \sum_{m, m', \sigma} T_{m, m', \sigma}^{(k,q)} \hat{f}_{m, \sigma}^\dagger \hat{f}_{m', \sigma'},
\]

where \( T_{m, m', \sigma}^{(k,q)} \) can be calculated by using the Wigner-Eckart theorem\(^{38}\)

\[
T_{m, m', \sigma}^{(k,q)} = \sum_{\mu, \mu'} \frac{(j|T^{(k)}_q|j)}{\sqrt{2j+1}} (j\mu|j\mu'|kq) \\
\times \langle j\mu|(m\sigma \quad 2) (j\mu'|m'\sigma') \rangle.
\]

Here \( \ell = 3, s = 1/2 \), \( j = \ell \pm s \), \( \mu \) is the \( z \)-component of \( j \), \( (j\mu|j\mu'|j\mu'') \) denotes the Clebsch-Gordan coefficient, and \( (j|T^{(k)}_q|j) \) is the reduced matrix element for spherical tensor operator, given by \( (j|T^{(k)}_q|j) = \sqrt{(2j+k+1)!/(2j-k)!} k^{3/2} \).\(^{38}\) Note that \( k \leq 2j \) and the highest rank of \( f \)-electron multipole is 7 in the present definition.

We note that it is not necessary to take double summations concerning \( j \) in eq. (4), since the matrix representation of total angular momentum \( J = j + s \) is block-diagonalized in the \( (j, \mu) \)-basis. We have checked that the same results as eq. (4) are obtained when we calculate higher-order multipole operators by following the symmetrized expression of multiple products of \( J \),\(^{38,40,42}\) given in the \( (m, \sigma) \)-basis as \( J_{m, m', \sigma} = \delta_{m, m'} L_{m, m'} + S_{\sigma, \sigma} \delta_{m, m'} \). Here \( L \) denotes angular momentum operator for \( \ell = 3 \) and \( S \) indicates spin operator, given by \( S = \sigma/2 \) with Pauli matrix \( \sigma \).

Let us now determine the coefficient \( p^{(k)}_{\gamma} \). In order to discuss the multipole state, it is necessary to evaluate the multipole susceptibility in the linear response theory.\(^{21}\) However, multipoles belonging to the same symmetry are mixed in general, even if the rank is different. In addition, multipoles are also mixed due to the CEF effect. Thus, we determine \( p^{(k)}_{\gamma} \) by the normalized eigenstate of susceptibility matrix

\[
\chi_{\ell k \gamma, k' \gamma'} = \frac{1}{Z} \sum_{i,j} e^{-E_i/T} - e^{-E_j/T} \langle i|\hat{T}^{(k)}_{\gamma} - p^{(k)}_{\gamma}|j \rangle \times \langle j|\hat{T}^{(k')}_{\gamma'} - p^{(k')}_{\gamma'}|i \rangle,
\]

where \( E_i \) is the eigenenergy for the \( i \)-th eigenstate \( |i \rangle \) of \( H \), \( T \) is a temperature, \( p^{(k)}_{\gamma} = \sum_i e^{-E_i/T} |\langle i|\hat{T}^{(k)}_{\gamma}|i \rangle|^2 / Z \), and \( Z \) is the partition function given by \( Z = \sum_i e^{-E_i/T} \). Note that the multipole susceptibility is given by the eigenvalue of the susceptibility matrix.

In order to evaluate the susceptibility matrix, here we employ a numerical renormalization group (NRG) method,\(^{42}\) in which momentum space is logarithmically discretized to include efficiently the conduction electrons near the Fermi energy. In actual calculations, we introduce a cut-off \( \Lambda \) for the logarithmic discretization of the conduction band. Due to the limitation of computer resources, we keep \( M \) low-energy states. In this paper, we set \( \Lambda = 5 \) and \( M = 4500 \). Note that the temperature \( T \) is defined as \( T = \Lambda^{1/2}(N-1)/2 \) in the NRG calculation, where \( N \) is the number of the renormalization step. Here five comments are in order. (i) In this paper, we call higher multipoles by following the numerical terms of IUPAC,\(^{33} \) i.e., 16=hexadeca, 32=dotriaconta, 64=tetrahexaconta, and 128=octacosahecta. (ii) We express the irreducible representation of the CEF state by Bethe notation in this paper, but for multipoles, we use short-hand notations by the combination of the number of irreducible representation and the parity of time reversal symmetry, \( g \) for gerade and \( u \) for ungerade. (iii) For \( \Gamma_2 \) symmetry, \( \Gamma_1 \) and \( \Gamma_2 \) of \( O_h \) are mixed. We remark that \( \Gamma_4 \) and \( \Gamma_5 \) of \( O_h \) are also mixed.\(^3\) Thus, we obtain six independent multipole components as 1g2g, 2u, 3g, 3u, 4g+5g, and 4u+5u for filled skutterudites. Note that 1u does not appear within rank 7. (iv) We normalize each multipole operator so as to satisfy the orthonormal condition \( \text{Tr} (\hat{T}^{(k)}_{\gamma} \hat{T}^{(k')}_{\gamma'}) = \delta_{kk'} \delta_{\gamma\gamma'} \),\(^{44}\) when we express the multipole moment as eq. (2). (v) The susceptibility for 4u multipole moment does not mean magnetic susceptibility, which is evaluated by the response of magnetic moment \( L + 2S \), i.e., \( J + S \).\(^{19,20}\)

Now we discuss the numerical results. In Fig. 1(a), we show the results for \( n = 7 \) (Gd\(^{3+} \) ion). Note that we depict only the largest eigenvalue state of each symmetry group. The CEF ground state is well described by \( L = 0 \) and \( J + S = 7/2 \), but it is almost independent of \( x \), since the CEF potentials for \( L = 0 \) provide only the energy shift. The dominant multipole component is 4u dipole and the contributions from higher multipoles are negligibly small. We find that the secondary components are 3g and 5g quadrupoles. Around at \( T = 10^{-7} \), there
the dominant component is 4u dipole, while for very large $x$ we fully occupy $\Gamma_1^+$. Quite recently, it has been observed in GdRu$_2$P$_{12}$, $T_N$ is found to be 20K, but another anomaly is observed at $T_1=10^5$ K. It may be interesting to discuss $T_1$ in the context of antiferro hexadecapole and tetrahexacantapole order.

In Fig. 1(c), the results for $n=9$ (Dy$^{3+}$ ion) are depicted. In this case, the CEF ground state is $\Gamma_5^-$ doublet and the excited state is $\Gamma_{6^-}$ quartet with excitation energy of 2.7 meV. The dominant multipole is always the mixture of 4u and 5u. The main component is dipole, but we find significant contribution from octacosahectapole.

Next we focus on the case of $n=10$ (Ho$^{3+}$ ion). At $x=0.3$, the CEF ground state is $\Gamma_1^+$ triplet, but the first excited state is $\Gamma_{23}^+$ doublet with very small excitation energy such as $10^{-5}$ eV. Thus, Ho-based filled skutterudite is considered to be in the quasi-quintet situation. In Fig. 2(a), we show the results for $n=10$ and $x=0.3$. We observe several kinds of multipoles, but the dominant one is always given by the mixture of 4u and 5u from dipole, octupole, dotriacontapole, and octacosahectapole.

As mentioned above, the CEF ground state is fragile for $n=10$. If we slightly decrease $x$, the ground state is easily changed. Then, we evaluate multipole susceptibility for $x=0.25$ with $\Gamma_{24}^+$ doublet ground state, as shown in Fig. 2(b). The multipole states at high temperatures are similar to those in Fig. 2(a), but at low temperatures, we find 2u multipole state, expressed as $\rho_2^{(3)}=0.955$ and $\rho_2^{(7)}=0.297$. Namely, the main component is 2u octupole, but there is contribution of 2u octacosahectapole. From the elastic constant measurement for
HoFe$_4$P$_{12}$, some anomalous features have been discussed. It may be interesting to reexamine experimental results from the viewpoint of 2u octupole state. Let us move onto the cases of $n=11, 12, and 13$. In Fig. 3(a), we show the results for $n=11$ (Er$^{3+}$ ion). For $n=11$, the CEF ground state is $\Gamma^+_5$ doublet and the excited state is $\Gamma_{67}$ quartet. The excitation energy is 5.6 meV. We find that the dominant multipole state is given by 4u+5u, but main components are 4u dipole and 4u octacosahectapole. The admixture is almost independent of temperature.

In Fig. 3(b), the results for $n=12$ (Tm$^{3+}$ ion) are depicted. The CEF ground state at $x=0.3$ is $\Gamma^+_1$ singlet, while the excited state is $\Gamma^+_4$ triplet with the excitation energy of 5.9 meV. In the high-temperature region, several kinds of multipoles appear, but when we decrease temperature, there appear no significant multipole moments, as in the case of $n=8$. Again we mention that a possibility of antiferro $1g+2g$ ordering cannot be excluded.

In Fig. 3(c), we depict the results for $n=13$ (Yb$^{3+}$ ion). The CEF ground and excited states are both $\Gamma^-_5$ doublets with the excitation energy of 5.1 meV. When temperature is decreased, there appears the dominant mixed multipole of 4u and 5u with significant components of dipole, octupole, dotriacontapole, and octacosahectapole. Among them, large contributions come from dotriacontapole and octacosahectapole. Finally, let us briefly discuss the Kondo effect. First we note that the so-called underscreening Kondo effect can occur in the present model, since we include only the single $a_u$ conduction band hybridized with some of seven $f$ orbitals. In fact, we have found the partial screening for $n=7$, but for other values of $n$, we did not observe the Kondo behavior in the low temperature range, since the Kondo temperature becomes much smaller than the CEF splitting. However, if $V$ is increased, we expect to find the Kondo behavior for $n=7$. When we perform the calculations for $V=0.5$, we actually observe that the residual 4u moment is eventually screened even in the present temperature range for $n=7$. Note, however, that the Kondo behavior can be found only for unrealistic large value of $V$ in the present model. In order to discuss appropriately the Kondo effect in filled skutterudites, it is highly required to include not only $a_u$ but also $e_u$ conduction bands. It is one of future problems.

In summary, we have discussed possible multipole states of filled skutterudites including heavy lanthanide ion Ln$^{3+}$. For Ln=Gd, we have found the effect of quadrupole moments due to the deviation from the $LS$ coupling scheme. For Ln=Ho, the CEF ground state is quasi-quintet with $\Gamma^+_3$ doublet and $\Gamma^+_1$ triplet. When we slightly change the CEF potential, the exotic state dominated by 2u octupole moment has been found. For Ln=Tb and Tm, the CEF ground state is $\Gamma^+_1$ singlet and we have found no significant multipole moments at low temperatures, although we cannot exclude a possibility of antiferro $1g+2g$ ordering. For Ln=Dy, Er, and Yb, the CEF ground state is $\Gamma^-_5$ doublet, and the dominant moment is the mixture of 4u and 5u. We believe that the present results stimulate further study of multipole phenomena in heavy lanthanide filled skutterudites.

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