Octupolar ordering of $\Gamma_8$ ions in magnetic field

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Abstract

We study $f$-electron lattice models which are capable of supporting octupolar, as well as dipolar and quadrupolar order. Analyzing the properties of the $\Gamma_8$ ground state quartet, we find that (111)-type combinations of the $\Gamma_5$ octupoles $T_{\beta}^{111} = T_{x}^{\beta} + T_{y}^{\beta} + T_{z}^{\beta}$ are the best candidates for octupolar order parameters. Octupolar ordering induces $\Gamma_5$-type quadrupoles as secondary order parameter. Octupolar order is to some extent assisted, but in its basic nature unchanged, by allowing for the presence of quadrupolar interactions. In the absence of an external magnetic field, equivalent results hold for antiferro-octupolar ordering on the fcc lattice. In this sense, the choice of our model is motivated by the recent suggestion of octupolar ordering in NpO$_2$.

The bulk of our paper is devoted to a study of the effect of an external magnetic field on ferro-octupolar ordering. We found that octupolar order survives up to a critical magnetic field if the field is lying in specific directions, while for general field directions, the underlying symmetry of the model is destroyed and therefore the phase transition suppressed even in weak fields. Field-induced multipoles and field-induced couplings between various order parameters are discussed on the basis of a group theoretical analysis of the Helmholtz potential. We also studied the effect of octupolar ordering on the non-linear magnetic susceptibility which satisfies novel Ehrenfest-type relations at continuous octupolar transitions.

1 Introduction

The nature of the 25K phase transition of NpO$_2$ is a long-standing mystery. The developments up to 1999 are reviewed in [1]. NpO$_2$ is a semiconductor with well-localized $5f^3$ shells, thus in principle relatively easy to understand in terms of crystal field theory and superexchange interactions. However, it was concluded that the phase transition at 25K cannot be modeled by any combination of dipolar and quadrupolar ordering phenomena. This leaves us with the possibility that the primary order parameter is one of the octupolar moments [2]. Recent experimental evidence is successfully interpreted by postulating that
the primary order parameters are $\Gamma_5$ octupoles, and that the transition is accompanied by the induced order of $\Gamma_5$ quadrupoles [3,4].

In comparison to well-studied quadrupolar phenomena, the physics of models supporting octupolar order is less explored [5]. Motivated by recent suggestions that certain actinide and rare earth compounds undergo octupolar ordering transitions [2,3,6], we study a lattice of $f$-shells with $\Gamma_8$ quartet ground states, assuming symmetry-allowed octupole–octupole and quadrupole–quadrupole interactions. Our choice of model is motivated by certain features of NpO$_2$ (and to a lesser extent, by Ce$_{1-x}$La$_x$B$_6$) physics, but we could not claim that we are offering a model for NpO$_2$. In particular, we consider only spatially uniform solutions though it is known that NpO$_2$ has antiferro-octupolar order following the four-sublattice triple-$\vec{q}$ pattern characteristic of the fcc lattice [4]. Nevertheless, our study of hypothetical ferro-octupolar ordering, in addition to having interest on its own, offers some insight into the physics of actual NpO$_2$. Some of the features of NpO$_2$ follow from the point group symmetry of the local Hilbert space, and from the mere fact of having symmetry breaking by $\Gamma_5$-type octupolar order; we are able to account for these. We are, however, missing the interesting consequences of antiferro-octupolar intersite interactions, and $Q \neq (0,0,0)$ space group symmetry. We plan to return to these questions in a sequel to our present work.

Analyzing the possible order parameters carried by the $\Gamma_8$ ground state set, we find that the best choice of the local order parameter is the 111-type combination of $\Gamma_5$ octupoles. In contrast to the case of CeB$_6$ (which can also be modeled as an array of $\Gamma_8$ shells), the fourfold degeneracy is lifted in a single continuous transition. We find that the primary ordering of octupolar moments induces 111-type quadrupoles even in the absence of quadrupole–quadrupole interactions. However, allowing for a non-vanishing $\Gamma_5$-type quadrupole–quadrupole interaction assists the octupolar ordering. These features are common to our hypothetical ferro-octupolar ordering model, and the actual antiferro-octupolar ordering of NpO$_2$. This holds in the absence of external (magnetic or strain) fields. However, our main interest lies in the study of field effects.

The effect of external magnetic fields on ferro-octupolar transitions is analyzed in detail. Since octupolar ordering is a mechanism for the spontaneous breaking of time reversal invariance, and the application of a magnetic field removes this invariance, it might have been guessed that the ground state degeneracy is completely lifted in a magnetic field, and consequently no octupolar symmetry breaking is possible. Such is indeed the case for fields applied in general (non-symmetrical) directions: the phase transition is smeared out by arbitrarily weak fields. However, we found that for magnetic fields lying in certain planes, or pointing along specific directions, there is a remaining ground state degeneracy which is removed by a continuous symmetry-breaking transition (or a sequence of two transitions). The critical temperature is gradually suppressed by increasing the field, eventually vanishing at a critical magnetic field. In simple terms, the explanation is the following: Magnetic fields will, in general, induce octupolar moments as a higher order polarization effect. However, for special field directions, the field is not able to induce at least one of
the $\Gamma_5$ octupole moments. Then this moment can be generated by intersite interaction only, and it will become non-zero below a critical temperature.

We stress that this latter part of our work rests on the assumption of uniform order, and we have not attempted to to apply similar considerations to the antiferro-octupolar phase. The essential difficulty is that an external magnetic field will, in general, turn the octupole moments from their original direction, and therefore the symmetrical zero-field triple-$\vec{q}$ structure is expected to undergo a complicated distortion which is difficult to analyze.

There is a great variety of multipolar moments induced by the concerted action of pre-existing uniform octupolar order and an external magnetic field. The existence of such polarization effects can be deduced from general symmetry analysis (Section 4, and particularly Sections 5.1 and 5.3); herein we follow and extend the approach by [7, 8, 9]. Illustrative examples are provided by mean field calculations.

1.1 Short review of NpO$_2$

The experimental results on NpO$_2$ are known from Refs. [1, 2, 3, 4]. We quote only the findings which are pertinent to our model study.

Actinide dioxides have the CaF$_2$ crystal structure at room temperature. The sublattice of the metal ions is an fcc lattice. Np$^{4+}$ ions have the configuration $5f^3$, the corresponding Hund’s rule ground state set belongs to $J = 9/2$. The tenfold degenerate free-ion manifold is split by the cubic crystal field, yielding a $|\Gamma_6\rangle$ doublet and the $|\Gamma^{(1)}_8\rangle$ and $|\Gamma^{(2)}_8\rangle$ quartets. Neutron spectroscopy has shown that the ground state quartet $|\Gamma^{(2)}_8\rangle$ is well separated from the first excited state (the other quartet) [10].

$5f^3$ states have both non-Kramers and Kramers degeneracy; the latter might have been expected to be lifted by magnetic ordering. There is, in fact, an apparently continuous phase transition at $T_0 = 25K$, which was first observed as a large $\lambda$-anomaly in the heat capacity [11]. The linear susceptibility rises to a small cusp at $T_0$, and stays almost constant below $T_0$ [12, 2]. The observations were, at first, ascribed to antiferromagnetic ordering. However, diffraction experiments failed to detect magnetic order [13], and Mössbauer effect has put the upper bound of $0.01\mu_B$ on the ordered moment. Thus we can exclude dipolar ordering, and have to consider the possibilities of multipolar order.

A $\Gamma_8$ ground state quartet can carry a variety of local order parameters: in addition to the $\Gamma_4$ dipoles, also $\Gamma_3$ and $\Gamma_5$ quadrupoles, and $\Gamma_2$, $\Gamma_4$, and $\Gamma_5$-type octupoles [7]. The nature of intersite interactions decides which of these will actually undergo an ordering transition. Though magnetic ordering is the commonly expected outcome, there is no rule to guarantee that dipolar ordering is the leading instability. In fact, for light rare earths (and also for light actinides) quadrupolar ordering often pre-empts, or preceeds, dipolar order. However, the possibility that octupolar order comes first, is quite novel [6].

The possibility of an explanation in terms of quadrupolar ordering has been examined with great care [1, 2, 3, 4]. The ordering pattern has to conform to
the observed fact that the \( T < T_0 \) phase preserves cubic symmetry, but this requirement can be satisfied by the triple-\( \vec{q} \) order of \( \Gamma_5 \) quadrupoles \[3\]. Indeed, resonant X-ray scattering finds long-range order of the \( \Gamma_5 \) electric quadrupole moments. However, the unquestionable appearance of quadrupolar order cannot be the whole story. Quadrupolar ordering alone could not resolve the Kramers degeneracy \[15\], and thus there should remain low-\( T \) magnetic moments giving rise to a Curie susceptibility; this is contrary to observations. Furthermore, muon spin relaxation shows that local magnetic fields, with a pattern suggestive of magnetic octupoles, appear below \( T_0 \) \[3\].

Though there are cases (as in CeB\(_6\)) when the Kramers and non-Kramers degeneracies of the \( \Gamma_8 \) quartet are lifted in separate phase transitions, this is not the case for NpO\(_2\): quadrupolar and octupolar moments appear simultaneously. This alone suffices to show that they must be coupled, i.e., the octupolar moments must also be of \( \Gamma_5 \) symmetry \[16\]. Still, the question may be posed whether the transition is primarily octupolar or quadrupolar. We confirm the proposal made in \[3\], and \[4\]: the primary order parameter is the octupole moment, and its ordering induces quadrupolar moments of the same symmetry. NpO\(_2\) has antiferro-octupolar order. However, systems with a uniform polarization of octupolar moments may, in principle, exist and their study is logically the first step in studying the nature of octupolar order, and its coupling to other kinds of order, and to external fields. Incidentally, we find that there is a phenomenological similarity between our findings and the observed behavior of NpO\(_2\) (and also Ce\(_{1-x}\)La\(_x\)B\(_6\)), the reason being that for \( \Gamma_8 \) Hilbert spaces, the \( \Gamma_5 \) octupolar states are non-magnetic, and magnetic susceptibility arises only due to transitions between octupolar levels. The mechanism relies only on the existence of an octupolar effective field, and it is basically the same for ferro- and antiferro-type alignments. Naturally, the details of polarization phenomena depend on the kind of octupolar long range order, and we hope to return to the case of antiferro-octupolar order in a future work.

In the absence of an external magnetic field, the thermodynamics of ferro- and antiferro-octupolar ordering is quite similar, as is also the case for more straightforward kinds of ordering. Our \( H = 0 \) self-consistency equation for the uniform polarization is the same as the one for either of the sublattice polarizations in the triple-\( \vec{q} \) structure. Also the results for non-vanishing quadrupolar interactions are transferable since the coupled quadrupolar order is of the same \( \Gamma_5 \) symmetry, and therefore the four-sublattice structure remains the same. For either ferro-octupolar, or triple-\( \vec{q} \) antiferro-octupolar order we find that i) octupole–octupole coupling alone is sufficient to select a unique ground state; ii) the ground state carries also quadrupolar moment; iii) allowing for an additional quadrupole-quadrupole interaction does not change the character of the low-\( T \) phase until the quadrupole-quadrupole interaction exceeds a threshold value; beyond that, a purely quadrupolar transition is followed by octupolar ordering.
2 Octupolar moments in the $\Gamma_8$ quartet state

Neutron diffraction measurements indicate that the ground state is one of the two $\Gamma_8$ quartets. Since the same irrep occurs twice, symmetry alone cannot tell us the basis functions: their detailed form depends on the crystal field potential. Exploiting the fact that the crystal field splittings are large, we neglect the higher-lying levels, and describe the phase transition within the ground state set. Since thus the sequence and separation of levels is of little consequence, we have arbitrarily chosen one of the quartets obtained by assuming a purely fourth-order potential $\mathcal{H}_{\text{cryst}} = \mathcal{O}_4^0 + 5\mathcal{O}_4^4$ as the ground state. We believe that this assumption has no influence on the main features of our results [17]. The general form of the basis states is (numerical coefficients will be given in Appendix A):

$$\begin{align*}
\Gamma^1_8 &= \alpha |\frac{7}{2}\rangle + \beta |\frac{1}{2}\rangle + \gamma |\frac{-1}{2}\rangle \\
\Gamma^2_8 &= \gamma |\frac{9}{2}\rangle + \beta |\frac{1}{2}\rangle + \alpha |\frac{-7}{2}\rangle \\
\Gamma^3_8 &= \delta |\frac{5}{2}\rangle + \epsilon |\frac{-3}{2}\rangle \\
\Gamma^4_8 &= \epsilon |\frac{3}{2}\rangle + \delta |\frac{-5}{2}\rangle \\
\end{align*}$$

It is apparent that the $\Gamma_8$ quartet is composed of two time-reversed pairs, thus it has twofold Kramers, and also twofold non-Kramers, degeneracy. The above choice of the basis emphasizes the presence of $J_z$ dipole and $\mathcal{O}_2^0 = \frac{1}{4}(3J_z^2 - J(J + 1))$ quadrupole moments, but of course it is not unique. In fact, the decomposition

$$\Gamma_8 \otimes \Gamma_8 = \Gamma_{1g} \oplus \Gamma_{4u} \oplus \Gamma_{3g} \oplus \Gamma_{5g} \oplus \Gamma_{2u} \oplus \Gamma_{4u} \oplus \Gamma_{5u}$$

[where $g$ ($u$) indicates invariance (change of sign) under time reversal] shows that the subspace carries 15 different kinds of moments: three dipolar $\Gamma_4$, two quadrupolar $\Gamma_3$, three quadrupolar $\Gamma_5$, and seven kinds ($\Gamma_2$, $\Gamma_4$, and $\Gamma_5$) of octupolar moments [7]. Within the subspace [7], we can rotate so as to get non-vanishing expectation values of any of the 15 potential order parameters. Or in other words, if there is an effective field $-\mathcal{R}/\langle\mathcal{R}\rangle$ (where $\mathcal{R}$ may be any of the fifteen components), then the fourfold ground state degeneracy will be at least partially lifted.

In general, intersite interactions affect all 15 moments. Lacking a microscopic mechanism of Np–Np interactions in NpO$_2$, we have to assume some form of the interaction, and argue from the consequences.

Restricting our attention to octupolar ordering, we have to choose between $\Gamma_2$, $\Gamma_4$, and $\Gamma_5$. The possibility of $\Gamma_2$ octupolar ordering was first suggested
by Santini and Amoretti \[2\]. In a later work, this choice was discarded because there would be no coupling to quadrupoles \[3\]. We may also add that Γ2 ordering would still leave us with a twofold degenerate ground state. We can also exclude the Γ4 type octupolar moments, because symmetry allows their mixing with the magnetic dipoles, and dipole moments are excluded by experiments.

This leaves us with the possibility of the ordering of Γ5-type octupole moments \[7\]

\[
\begin{align*}
T^\beta_x &= \frac{1}{3}(\overline{J_x J_y^2} - \overline{J_y J_x^2}) \\
T^\beta_y &= \frac{1}{3}(\overline{J_y J_z^2} - \overline{J_z J_y^2}) \\
T^\beta_z &= \frac{1}{3}(\overline{J_z J_x^2} - \overline{J_x J_z^2})
\end{align*}
\]

where the bars on the angular momentum operators mean the symmetrized combinations of operators \(\overline{J_x J_y^2} = J_x J_y J_x J_y + J_x J_y J_x J_y + J_x J_y J_x J_y\), etc. Acting as a field, either of \(T^\beta_x\), \(T^\beta_y\), or \(T^\beta_z\) splits the Γ8 quartet into two doublets. The doublets carry magnetic moments. Thus assuming, say, \(T^\beta_x\)-type ordering would still leave us with a residual degeneracy which should be lifted by a separate magnetic (dipolar) phase transition.

Figure 1: Left: The direction dependence of the magnitude of the octupolar moment \(T(\vartheta, \phi)\) (see equation (4)). Right: The spectrum of \(T(\vartheta, \phi)\) in the \([1\overline{1}0]\) plane (\(\phi = \pi/4\)).

However, we may choose a different orthogonal set of Γ5 octupole operators as order parameters. Fig. 1 (right) shows the spectrum of octupoles \[18\]

\[
T(\vartheta, \phi) = \sin \vartheta (\cos \phi T^\beta_x + \sin \phi T^\beta_y) + \cos \vartheta T^\beta_z
\]

for \(\phi = \pi/4\). It appears that the ground state is always a singlet except for the special points \(\vartheta = 0\) and \(\vartheta = \pi\) (i.e., \(T^\beta_z\) which we discussed above). Furthermore, the overall width of the spectrum varies with \(\vartheta\), reaching its maximum at
\[ \vartheta = \arccos \left( \frac{1}{\sqrt{3}} \right), \] or equivalent positions. Thus within the \( \Gamma_8 \) subspace, the three-dimensional pseudovector of \( \Gamma_5 \) octupoles is “longest” in the (111) direction, or in equivalent directions. At any \((\vartheta, \phi)\) the maximum of the absolute value of the eigenvalues is taken as the magnitude of the octupole moment (note that the spectrum is symmetrical about 0). This is the quantity shown in Fig. 4 (left). We see sixteen maxima. However, it is easy to check that the plotrange for \((\vartheta, \phi)\) gives two points for every direction, therefore the number of maxima is only eight. The directions (111), (\(\bar{1}11\)), (1\(\bar{1}1\)), and (11\(\bar{1}\)) are equivalent by cubic symmetry, and for each direction, the octupole moment may be of either sign (Fig. 4 (right)).

Thinking of the ordering as caused by an octupole-octupole interaction with cubic symmetry [19]

\[ H_{oc} = -J_{oc} \sum_{i,j} (T^\beta_{i,x} T^\beta_{j,x} + T^\beta_{i,y} T^\beta_{j,y} + T^\beta_{i,z} T^\beta_{j,z}) \] (5)

it is plausible that it will occur in one of the (111) directions. We may think of it as the cubic crystal field giving rise to an octupolar single-ion anisotropy with the (111) directions as easy axes. Thus our candidates for order parameters are

\[
\begin{align*}
T^\beta_{111} &= T^\beta_x + T^\beta_y + T^\beta_z \\
T^\beta_{1\bar{1}1} &= T^\beta_x - T^\beta_y - T^\beta_z \\
T^\beta_{\bar{1}11} &= -T^\beta_x + T^\beta_y - T^\beta_z \\
T^\beta_{\bar{1}\bar{1}\bar{1}} &= -T^\beta_x - T^\beta_y + T^\beta_z .
\end{align*}
\] (6)

The four minima seen in Fig. 4 belong to \( \pm T^\beta_{111} \) and \( \pm T^\beta_{1\bar{1}1} \) [20]. We have checked that the ground state of either of these operators carries a \( \Gamma_5 \)-type quadrupolar moment, but no magnetic dipole moment.

We note that these single-ion properties would be useful for modelling NpO\(_2\); however, the interionic interactions may still be chosen as either ferro-octupolar or antiferro-octupolar. Let us furthermore point it out that the four equivalent states [19] are ideally suited for constructing a four-sublattice ground state for nearest-neighbor antiferro-octupolar coupling on an fcc lattice. This would correspond to the experimentally motivated suggested of triple-\(q\) order by Caciuffo et al. [4]. The triple-\(q\) octupolar ordering can then induce the observed triple-\(q\) structure of the \( \Gamma_5 \) quadrupoles

\[ O_{111} = O_{xy} + O_{yz} + O_{zx} , \] (7)

e tc., as a secondary order parameter. In the absence of a magnetic field, our mean field results are formally valid for either the ferro- or antiferro-octupolar case, while as far as field effects are concerned, we stick definitely to the former case. We have to refrain from making detailed comments on NpO\(_2\) until we completed work on the magnetic properties.
Denoting the ground state of $T_{111}$ by $|\phi_0\rangle$, we quote the numerical values from Appendix B:

$$
\langle \phi_0 | T_{111}^\beta | \phi_0 \rangle = A = -15.683
$$

$$
\langle \phi_0 | O_{111} | \phi_0 \rangle = B = 8.019
$$

$$
\langle \phi_0 | J_z | \phi_0 \rangle = \langle \phi_0 | J_y | \phi_0 \rangle = \langle \phi_0 | J_z | \phi_0 \rangle = 0
$$

and

$$
\langle \phi_0 | O_{xy} | \phi_0 \rangle = \langle \phi_0 | O_{yz} | \phi_0 \rangle = \langle \phi_0 | O_{xz} | \phi_0 \rangle.
$$

One may be wondering whether the $\Gamma_5$ quadrupoles by themselves would like a different orientation than the one forced upon them by the octupoles. This is not the case: a calculation shows that the length of the pseudovector $(O_{xy}, O_{yz}, O_{zx})$ is the same in all directions. There is no single-ion anisotropy for the $\Gamma_5$ quadrupoles; picking the (111) solution is exclusively the octupoles’ doing.

3 The octupolar–quadrupolar model

We assume the presence of $\Gamma_5$-type quadrupolar and octupolar interactions

$$
\mathcal{H} = \mathcal{H}_{oc} + \mathcal{H}_{quad}
$$

where $\mathcal{H}_{oc}$ was given in (5) and analogously

$$
\mathcal{H}_{quad} = -J_{quad} \sum_{i,j} (O_{i,xy} O_{j,xy} + O_{i,yz} O_{j,yz} + O_{i,zx} O_{j,zx}).
$$

For the sake of simplicity, we assume $J_{quad}/J_{oc} \geq 0$.

For ferro-octupolar coupling ($J_{oc} > 0$), we may assume uniform (111) order. The mean-field single-site Hamiltonian is of the form

$$
\mathcal{H}_{MF} = -T_{111}^\beta \langle T_{111}^\beta \rangle - j O_{111} \langle O_{111} \rangle
$$

where we have chosen the octupolar effective field amplitude as the energy unit, and $j = J_{quad}/J_{oc}$. Henceforth we assume that all effects arising from lattice geometry, and the detailed form of the interactions are included in $J_{oc}$, $J_{quad}$, and hence also in $j$.

We note that formally the same mean field problem arises by assuming antiferro-octupolar interactions, and postulating four sublattices with local order parameters as defined in (6) and the analogous quadrupolar moments.

The temperature dependence of the order parameters $T = \langle T_{111}^\beta \rangle$ and $q = \langle O_{111} \rangle$ is obtained by the numerical solution of the self-consistency equations derived from diagonalizing (12) in the basis (11). The overall behavior is similar to that found in dipolar–quadrupolar models used in the description of Pr compounds [21, 22]; however, now octupoles play the role of dipoles.
Figure 2: The mean field phase diagram of the zero-field quadrupolar-octupolar model \(^{10}\) in the quadrupolar coupling–temperature plane \((j = J_{\text{quad}}/J_{\text{oc}} \text{ and } t = k_BT/J_{\text{oc}})\). The dashed and continuous lines signify first and second order phase transitions, respectively. Observe the regime of first-order transitions bounded by two tricritical points (marked by black dots).

The dimensionless free energy belonging to \(^{12}\) is

\[
\mathcal{F} = \frac{1}{2}T^2 + \frac{1}{2}j q^2 - t \ln(2 \exp(-B j q/t) \cosh(A T/t) + 2 \exp(B j q/t)) \tag{13}
\]

where \(A\) and \(B\) were introduced in \(^8\), and \(t = k_BT/J_{\text{oc}}\) is the dimensionless temperature.

Octupolar order \((T \neq 0)\) induces quadrupolar moment even in the absence of a quadrupolar coupling, as we can see from setting \(j = 0\) in \(\partial\mathcal{F}/\partial q = 0\)

\[
q = B \frac{\exp(AT/t) + \exp(-AT/t) - 2 \exp(AT/t) + 2 \exp(-AT/t)}{\exp(AT/t) + \exp(-AT/t) + 2} \tag{14}
\]

The \(T \to 0\) limit is expressed in \(^8\). It states that by construction, the \((111)\)-type octupolar eigenstates carry \((111)\)-type quadrupolar moments. The same state of affairs prevails as long as \(T \neq 0\). In the “para” phase above the transition temperature, all moments vanish.

The continuous phase transitions of the model \(^{10}\) can be described by the Landau expansion of the free energy \(^{13}\)

\[
\mathcal{F} \approx \mathcal{F}_0 + \left(\frac{1}{2} - \frac{A^2}{4t}\right) T^2 + \left(\frac{j}{2} - \frac{B^2 j^2}{2t}\right) q^2 + \frac{1}{4} \frac{B j A^2}{t^2} q T^2 + \frac{A^4}{96t^3} T^4 - \frac{B j A^4}{24t^4} q T^4 + \frac{B^4 j^4}{12t^4} q^4 - \frac{B^3 j^3 A^2}{12t^4} q^3 T^2 + ... \tag{15}
\]
where $F_0$ is the non-critical part of the free energy.

Critical temperatures are defined by the change of sign in the coefficient of either of the quadratic terms. Upon lowering the temperature, for small $j$, mixed octupolar–quadrupolar, while for large $j$, pure quadrupolar order sets in first. At intermediate $j$, there is a regime of first order transitions (Fig. 2).

We consider first the weak-$j$ limit. The critical temperature is $t_{oc} = A^2/2$.

At $t_{oc}$, octupolar moment appears as the primary order parameter, but there is also induced quadrupolar order. Minimizing $F$ with respect to $q$, we get

$$q = \frac{BA^2T^2}{4t(jB^2 - t)}.$$  \hspace{1cm} (16)

Thus terms of order $q^2$ and $qT^2$ are effectively of $O(T^4)$. Minimizing with respect to $T$, the critical behavior of the octupolar and quadrupolar moment

$$T \approx \sqrt{\frac{A^2}{2} - t} \sqrt{\frac{6(A^2 - 2B^2j)}{A^2 - 8B^2j}}$$  \hspace{1cm} (17)

$$q \approx -\frac{6B}{A^2 - 8B^2j} \left( \frac{A^2}{2} - t \right)$$  \hspace{1cm} (18)

is characteristic of the mean field solution for primary, and secondary, order parameters.

The coefficient

$$A^4 \frac{4B^2j - t}{96t^3 B^2j - t}$$

of the combined fourth order $O(T^4)$ term of $F$ changes sign at $t = 4B^2j$. Equating this with the critical temperature, we identify the coordinates of the lower tricritical point as $j_{tri,1} = A^2/8B^2 = 0.48$, and $t_{tri,1} \approx 123$. The critical temperature is constant for $j \leq j_{tri,1}$. For $j$ exceeding $j_{tri,1}$ the transition becomes first order. The nature of the coupled orders does not change, but they become more stabilized, and the common transition sets in at higher temperatures (Fig. 2). However, the ground state moments remain independent of the coupling strengths: $q_{T \to 0} = B$, and $T_{T \to 0} = A$. Representative temperature dependences of $T$ and $q$ are shown in Fig. 3.

At large $j$, the first instability is associated with the change of sign of the coefficient of the $q^2$ term: pure quadrupolar order sets in at $t_{quad} = B^2j$. This critical line meets the boundary of first-order transitions at the critical end point $j_{end} \approx 2.75$, $t_{end} \approx 177$ (Fig. 2). For $j > j_{end}$ there are two phase transitions: the onset of pure quadrupolar order is followed by the emergence of mixed octupolar–quadrupolar order at $t_{oc}$. The lower phase transition is of first order up to the second tricritical point $j_{tri,2} \approx 3.75$, $t_{tri,2} \approx 185$. For $j < j_{tri,2}$, the onset of octupolar order is reflected in a discontinuity of $q$ (Fig. 3 right). For $j > j_{tri,2}$, both transitions are continuous.

Deep inside the quadrupolar ordered phase, the development of the octupolar order is essentially unaffected by what the quadrupoles are doing, apart from a
Figure 3: Octupolar ($T$) and quadrupolar ($q$) order parameters as a function of $t = k_B T / J_{oc}$ for $J_{quad} / J_{oc} = 0$ (left), $J_{quad} / J_{oc} = 0.75$ (center), and $J_{quad} / J_{oc} = 3.5$ (right).

weak effect on the transition temperature $t_{oc}$ (note in Fig. 2 that $t_{oc}$ saturates to a constant). Though in this regime, we cannot use Landau expansion to determine $q$, we may assume that it is near its ground state value $B$, and use a low-order expansion in $T$ to obtain in the large-$j$ limit

$$
\lim_{j \to \infty} t_{oc} = \lim_{j \to \infty} \frac{A^2 \exp(Bqj/t_{oc})}{\exp(Bqj/t_{oc}) + \exp(-Bqj/t_{oc})} = A^2 \approx 246. \tag{19}
$$

In familiar phase diagrams of dipolar–quadrupolar models, the mixed order would be completely suppressed at $J_{quad} / J_{dipole} \to \infty$ (see, e.g., Fig. 3 of Ref. [22]). In contrast, we find the finite saturation value (19) as $J_{quad} / J_{oc} \to \infty$. The peculiarity of the situation depicted in Fig. 2 is the endurance of octupolar order even with infinitely strong quadrupolar coupling. The reason, as we understood earlier, is that in the $\Gamma_8$ subspace the $\Gamma_5$ quadrupoles are completely isotropic, thus they can accommodate a reorientation of the basis states without sacrificing any of their rigid order.

Even confining our attention to uniform states, the effects of an external magnetic field are variegated: It may gradually suppress octupolar ordering, without changing its character (111 direction); it may split the transition in two (001 direction); it may change the character of octupolar order but still facilitate a phase transition (11$c$ direction); or it may completely forbid octupolar ordering (non-symmetrical directions). We will understand this in detail in Sections 4 and 5. A straightforward characterization of field effects in terms of the magnetization curve and its derivatives (the susceptibilities) is possible in the $H \parallel (111)$ case only. This is the subject of the next Subsection.

We emphasize that our entire analysis of magnetic field effects is confined to spatially uniform states, and does not cover the cases of supercell ordering, such as the experimentally observable antiferro-octupolar order of NpO$\text{\textsubscript{2}}$. The basic difficulty is that the inter-sublattice angles of various moments may get changed by the field; this effect will be treated in a subsequent work.
3.1 Non-linear susceptibility: the $H \parallel (111)$ case

In certain symmetry directions such as $(111)$, the magnetic field merely acts to suppress uniform octupolar ordering gradually (Fig. 4, left). It appears that the phase boundaries can be scaled onto a common curve by introducing the field-dependent transition temperature

$$\frac{T_{oc}(H)}{T_{oc}(H = 0)} \approx 1 - a_H \cdot H^2 - b_H \cdot H^4 \ldots$$  \hfill (20)

This bears some similarity to the field-induced suppression of antiferro-quadrupolar order in PrFe$_4$P$_{12}$ [22].

Our starting point is the mean-field-decoupled hamiltonian

$$\mathcal{H} = \mathcal{H}_{oc} + \mathcal{H}_{quad} + \mathcal{H}_Z = \mathcal{H}_{oc} + \mathcal{H}_{quad} - \mathbf{H} \cdot \mathbf{J}$$

$$= -T \cdot T^{\beta}_{111} - j q O_{111} - H J_{111}$$  \hfill (21)

where the notations follow [12], $J_{111} = (J_x + J_y + J_z)$, and in the Zeeman term $H$ is the reduced magnetic field.

Multipolar phase transitions, even when non-magnetic, tend to have a strong signature in the non-linear magnetic response. The case of quadrupolar transitions has been extensively studied [23]. To obtain analogous results, we expand the free energy corresponding to (21)

$$\mathcal{F}(T, q, H) = \frac{1}{2} T^2 + \frac{j}{2} q^2$$

$$-t \cdot \ln \left[ 2 \exp \left( -B j q/t \right) \cosh \left( \sqrt{g_H^2 H^2 + A^2 T^2/t} \right) \right]$$

$$+ 2 \exp \left( B j q/t \right) \cosh \left( y_H H/t \right).$$  \hfill (22)
Here \( g_H \) and \( y_H \) are the two parameters of the Zeeman splitting scheme of the \( \Gamma_8 \) subspace (Appendix A). The overall shape of the phase boundary in the \( t-H \) plane is obtained by expanding \( F(T, q, H) \) in powers of \( T \), and identifying the coefficient of the \( T^2 \)-term

\[
c_2(H, t) = \frac{1}{2} - \frac{A^2}{2g_H H} \cdot \frac{\sinh (g_H H/t)}{\cosh (g_H H/t) + \cosh (y_H H/t)}. \tag{23}
\]

Solving \( c_2(H, t) = 0 \) gives a line of continuous transitions in the \( t-H \) plane (Fig. 4, right).

It is interesting that the octupole ordered phase can be suppressed gradually by a magnetic field (Fig 4, left). Dipole ordering and octupole ordering are two independent ways to break time reversal invariance. However, octupolar moments are due to currents with zero total circulation, while dipole moments arise from non-zero integrated circulation. In a finite field \( H \parallel (111) \), the \( 5f^3 \) ion must be able to sustain both kinds of currents simultaneously.

\( F(T, q, H) \) has to be expanded to \( O(H^4) \) in order to derive both the susceptibility \( \chi \), and the non-linear magnetic susceptibility \( \chi_3 \). We do not give the detailed formulas here, but discuss the terms giving rise a quadratic shift of the transition temperature in (20)

\[
F(T, q, H) \approx F(T, q, H = 0) + \frac{g_H^2 - y_H^2}{4t^2} B jq H^2 - \frac{g_H^2}{12t^4} H^2 A^2 B jq T^2 + \frac{g_H^2 + 3y_H^2}{48t^3} A^2 T^2 H^2. \tag{24}
\]

The first term in the second line describes field-induced \( \Gamma_5 \) quadrupoles. The general nature of octupoles would allow the presence of a \( T H \) term; it is the peculiarity of the (111) direction that it does not appear here. We have omitted field-induced terms of the non-critical part of the free energy; they have to be included when calculating the susceptibilities.

Further calculation is analogous to that given for the \( H = 0 \) case. Minimizing with respect to \( q \) gives for the secondary order parameter

\[
q \approx -\frac{B}{4t(t - B^2j)} \cdot \left( A^2 T^2 + (g_H^2 - y_H^2) H^2 \right). \tag{25}
\]

Replacing this back into (24), we can determine the optimum value of the primary order parameter \( T \). Here we quote only the result for the quadratic shift of the transition temperature (cf. Equation (20))

\[
a_H = \frac{1}{6A^4(A^2 - 2B^2j)} \left[ (A^2 - 8B^2j)g_H^2 + 3A^2 y_H^2 \right]. \tag{26}
\]

One of the contributions to \( a_H \) vanishes at the tricritical point \( (j \to A^2/8B^2) \), while the other remains finite.
Figure 5: Linear susceptibility (left), temperature derivative of linear susceptibility (center) and nonlinear susceptibility (right) as a function of temperature for magnetic field parallel to (111) direction ($J_{oc} = 0.02k_B, J_{quad} = 0$).

Representative results for the linear susceptibility $\chi = -\partial^2 F/\partial H^2$, and the third-order susceptibility $\chi_3 = -\partial^4 F/\partial H^4$, are shown in Fig. 5. The octupolar transition appears as a cusp in $\chi$ (Fig. 5 left). The cusp can be also represented as the discontinuity of $\partial \chi/\partial T$ (Fig. 5 middle). The non-linear susceptibility has a discontinuity from positive to negative values (Fig. 5 right). These anomalies are related to each other, and the specific heat discontinuity $\Delta C$, via the Ehrenfest-type equation \[ 24 \]

\[
\frac{a_H}{T} \Delta C + \frac{1}{12a_H} \Delta \chi_3 = \Delta \left( \frac{\partial \chi}{\partial T} \right). \tag{27}
\]

The derivation \[ 25 \] of \[ 27 \] relies only on the fulfillment of \[ 20 \] to order $H^3$. In particular, $b_H$ does not come into \[ 27 \]. The relationship \[ 20 \] is often found for the critical temperature of transitions to non-ferromagnetic phases like antiferromagnets, spin-gapped phases, quadrupolar order, etc. Octupolar ordering belongs to this class of transitions.

Though the example shown in Fig. 5 was for $J_{quad} = 0$, the relationship \[ 27 \] holds everywhere along the lines of continuous phase transitions shown in Fig. 4. As long as we are dealing with ordinary second order transitions, Landau theory would be consistent with all the discontinuities appearing in \[ 27 \] being finite. However, approaching a tricritical point $\Delta C \to \infty$, and \[ 27 \] allows several scenarios. We note from \[ 20 \] that generically $y_H \neq 0$, thus $a_H$ remains finite, and then the simplest expectation is that the divergence of $\Delta C$ is matched by that of $\Delta \partial \chi/\partial T$. Such is indeed the finding for our standard $\Gamma_8$ subspace specified in Appendix A. The same holds for $\Gamma_8$ subspaces derived from a combination of fourth-order and sixth-order crystal field potentials. However, at one particular value of the ratio of the sixth-order and fourth-order terms, the Zeeman spectrum consists of a doublet and two singlets, i.e., the $y_H = 0$ case is realized. For this special model \[ 27 \] $a_H \to 0$ as one approaches the tricritical point, and the field dependence of the transition temperature is purely quartic \[ 20 \]. Here, a peculiar form of the Ehrenfest relation can be derived. $a_H \to 0$ cancels the mean-field divergence of $\Delta C$, and at the same time $\Delta \chi_3 \to 0$. The
discontinuity of \( \partial \chi / \partial T \) is now balanced by that of the fifth-order non-linear susceptibility

\[
\frac{1}{120} \Delta \chi_5 = b_H \Delta \left( \frac{\partial \chi}{\partial T} \right).
\]

(28)

It should be interesting to find a situation where (28) is experimentally testable.

4 Suppression of ferro-octupolar order by magnetic field

Next, we consider the effect of a finite magnetic field of arbitrary orientation on a system of interacting \( \Gamma_5 \) octupoles. Henceforth, our mean field arguments will be based on a simplified version of (21)

\[
\mathcal{H} = \mathcal{H}_{oc} + \mathcal{H}_Z = \mathcal{H}_{oc} - \mathbf{H} \cdot \mathbf{J}
\]

(29)

where \( \mathcal{H}_{oc} \) is taken from (5), and \( J_{\text{quad}} = 0 \). Here, as in Section 3, we will confine our attention to uniform states. An essential extension of our argument would be needed to cover the case of \( \text{NpO}_2 \).

First, let us reconsider the case of a field \( \mathbf{H} \parallel (111) \) (Fig. 4). The nature of the octupolar order parameter is not influenced by the field, only its saturation value, and the transition temperature, are scaled down. Conversely: since there is a \( T = 0 \) phase transition at a critical field \( H_{cr} \) (Fig. 6, left), there must exist (in mean field theory) a finite-\( T \) ordered phase at \( H < H_{cr} \) (Fig. 4, left). Generally, the nature of the field direction dependence of octupolar ordering can be studied by confining our attention to the ground state \( (T=0) \). First, we use mean field theory; later, we give general symmetry arguments.

Let \( E_0 \) be the minimal eigenvalue of the mean field hamiltonian which contains both the external magnetic field, and the octupolar effective field

\[
E_0(\langle \mathcal{T}_H \rangle) = \langle \mathcal{H} \rangle = - \langle \Phi_0 | \mathcal{T}_H | \Phi_0 \rangle - \mathbf{H} \cdot \langle \mathbf{J} \rangle
\]

(30)

where \( |\Phi_0\rangle \) is the interacting ground state, and \( \langle \rangle \) denotes expectation values taken with \( |\Phi_0\rangle \). The energy unit is like in Eqn. (21). We have to minimize

\[
E(\langle \mathcal{T}_H \rangle) = \frac{1}{2} \langle \mathcal{T}_H \rangle^2 + E_0(\langle \mathcal{T}_H \rangle)
\]

(31)

with respect to \( \langle \mathcal{T}_H \rangle \). In general, \( \mathcal{T}_H \) is not pointing in the same direction in the \( \Gamma_5 \) space as the zero-field \( \mathcal{T} = \langle \mathcal{T}_H^0 \rangle \), but neither is it collinear with \( \mathbf{H} \); it has to be chosen in an optimization procedure, observing the symmetry lowering due to the magnetic field.

Fig. 6 shows results obtained by minimizing \( E(\mathcal{T}) \) with respect to \( \mathcal{T} = \langle \mathcal{T}_H^0 \rangle \), our original choice of order parameter. For \( \mathbf{H} \parallel (111) \), the field does not introduce any inequivalence of \( x, y, \) and \( z \), thus the above choice of the order
Figure 6: Left: Field-induced ground state transition from octupolar order to the disordered state for $\mathbf{H} \parallel (111)$. Right: Expectation value of the octupole moment in the ground state as a function of magnetic field for $\mathbf{H} \parallel (123)$. For fields pointing in non-symmetric directions, there is no sharp phase transition.

parameter is optimal, and the second order transition seen in Fig. 6 (left) is genuine.

Fig. 6 (right) shows the self-consistent solution for $\mathcal{T}$ for fields $\mathbf{H} \parallel (123)$. (123) is taken to represent general non-symmetric directions. We find behavior characteristic of smeared-out phase transitions (the marked upward curvature at $H \sim 1.5$ shows where the phase transition might have been; clearly, intersite interactions are important for $H < 1.5$, while their effect is negligible in the high-field tail).

Figure 7: The Landau-type ground state energy expression has symmetric or asymmetric minima depending on whether the field is applied in a symmetry direction ($\mathbf{H} \parallel (111)$, upper curve), or non-symmetry direction ($\mathbf{H} \parallel (123)$, lower curve).

The reason for the discrepancy between the $\mathbf{H} \parallel (111)$ and $\mathbf{H} \parallel (123)$ behav-
ior becomes clear from plotting the Landau-type ground state energy density for different field directions (Fig. 7). For $\mathbf{H} \parallel (111)$, equivalent minima remain at the positions $\pm T_0$, thus the system can pick one of these in a symmetry breaking transition (upper curve). On the other hand, for $\mathbf{H} \parallel (123)$, the two minima are not equivalent, the ground state remains always on the right-hand side. There is no symmetry breaking transition though the $T$-dependence may be non-trivial, showing the shadow of the phase transition which might have happened.

One might object that for $\mathbf{H} \parallel (123)$, $T_x$, $T_y$, and $T_z$ are no longer equivalent, thus the optimal mean field solution should be sought in the form

$$T_\mathbf{H} = r_x T_x + r_y T_y + r_z T_z.$$  \hfill (32)

This is true but we do not have to make the considerable effort of a three-parameter optimization. We will bring general arguments to show that the solution would be like that in Fig. 6 (right), whatever $T_\mathbf{H}$ is chosen. It remains true that for general (non-symmetric) field directions, the ground state of (29) is non-degenerate and therefore no symmetry breaking transition (in particular, no continuous octupolar ordering transition) is possible.

For some symmetry directions which are not equivalent to (111) (e.g., for (001)), the character of the solution is different from either of those shown in Fig. 6. We will discuss these later.

5 Symmetry analysis of field-induced multipoles

5.1 The high-field limit

We learn from Fig. 6 that at sufficiently high fields the ground state is determined by the external field only: either because ordering has been suppressed, or because there was no transition to begin with. The following analysis of the field-induced multipoles does not rely on the mean field approximation, but each of the cases will be illustrated by a mean field calculation.

The octupole operators are third-order polynomials of $J_x$, $J_y$ and $J_z$. The $\Gamma_5$ octupoles can be expressed in terms of dipole and quadrupole operators \[10\]

$$T_x^3 = \left(\frac{1}{3}O_2^0 + \frac{1}{6}O_2^2\right)J_x + \frac{2}{3}(O_{xz}J_z - O_{xy}J_y)$$

$$T_y^3 = \left(-\frac{1}{3}O_2^0 + \frac{1}{6}O_2^2\right)J_y + \frac{2}{3}(O_{xy}J_x - O_{yz}J_z)$$

$$T_z^3 = -\frac{1}{3}O_2^2J_z + \frac{2}{3}(O_{yz}J_y - O_{xx}J_x)$$ \hfill (33)

where the quadrupoles are well-known quadratic expressions

$$O_{2}^{0} = \frac{1}{2}(2J_{z}^{2} - J_{x}^{2} - J_{y}^{2})$$

$$O_{2}^{2} = J_{x}^{2} - J_{y}^{2}$$

$$O_{xy} = \frac{1}{2}(J_{x}J_{y} + J_{y}J_{x})$$

17
\[ O_{yz} = \frac{1}{2} (J_y J_z + J_z J_y) \]
\[ O_{zx} = \frac{1}{2} (J_z J_x + J_x J_z). \]  
(34)

(33) contains exact identities respecting the non-commutative nature of the operators. However, \( T_\beta^z \) etc. are themselves defined as symmetrized expressions (3), so it must be true that the order of the operators on the right-hand side cannot really matter. In fact, there is an arbitrariness in the representation (33): it would be also true that
\[ T_\beta^z = \frac{1}{3} O_{yz} J_y - \frac{1}{3} O_{zx} J_x \]  
(35)
or
\[ T_\beta^z = \frac{2}{3} (O_{yz} J_y - O_{zx} J_x) . \]  
(36)

Similar relationships can be listed for the first two lines of (33). This suggests that the relationships (33) can also be interpreted in terms of \( c \)-numbers, i.e., classical polarization densities [29]. Such considerations are valid for either field-induced, or interaction-induced multipole densities. This enables us to use relationships like (33) in Landau expansions.

First, we discuss field-induced densities. The basic idea is that an external field induces \( \langle J \rangle = (\langle J_x \rangle, \langle J_y \rangle, \langle J_z \rangle) \| H \), and this gives rise to induced quadrupoles \( \langle O_{xy} \rangle = \langle J_x \rangle \langle J_y \rangle \) as a second-order effect, and induced octupoles as a third-order effect, etc. If an octupole component is field-induced, it can no longer play the role of the order parameter of a symmetry breaking transition. The question is, can it happen that certain octupole moments are not induced by the field.

(35) and (36) are still separate operator identities, but they must have the same classical meaning when \( J_x \), etc. are treated as \( c \)-numbers. Indeed from (36)
\[ T_\beta^z = \frac{2}{3} (O_{yz} J_y - O_{zx} J_x) \]  
(37)
which is the same that we would have obtained from (35). Similarly,
\[ T_\beta^x = \frac{2}{3} (O_{yx} J_y - O_{xy} J_x) \]  
(38)
and
\[ T_\beta^y = \frac{2}{3} (O_{zy} J_z - O_{yz} J_y) \]  
(39)

We can also argue in the following manner. Higher-order polarizations in a magnetic field give rise to the following general \( H \)-dependence of the energy
\[ \mathcal{E}(H) \sim \mathcal{E}(H = 0) - \frac{\chi}{2} H^2 - \frac{\chi}{12} H^4 ... \]  
(40)
The lowest order time reversal invariant expression containing $T$ is $TH$, thus
the coupling of octupolar moments to fields may appear in terms from $O(H^4)$
upwards. If it does, the minimal eigenvalue of the mean field energy \( E_0(T) \) will not
be symmetrical under the sign change of octupole moments: \( E_0(T) \neq E_0(-T) \).
Non-equivalent minima like in Fig. 7 (lower curve) mean that there is no sym-
metry to break, a phase transition is not possible. However, for fields in the
special directions discussed above, there is no field-induced $\Gamma_5$ octupole \( \Gamma_5 \),
the $\pm T$ minima of $E_0(T)$ remain equivalent (Fig. 7 upper curve) and sponta-
neous symmetry breaking remains possible. The eventual merging of the two
minima is no longer a question of symmetry, but of field intensity; a sufficiently
strong field will suppress octupolar (or any other) order, and produce a unique
polarized state for any field direction (Fig. 6 right).

In what follows, we calculate the induced $\Gamma_5$ octupoles using (37)–(39) for
several field directions, and discuss the possibility of symmetry bre aking tran-
sitions.

5.1.1 Non-symmetric directions

First let us observe that a field pointing in a general direction will give non-
zero values for $T_x$, $T_y$, and $T_z$. Since the field induces all $\Gamma_5$ octupoles, there
remains no degeneracy to be lifted, no symmetry breaking transition is possible
\[31\]. This corresponds to the situation in the right-hand panel of Fig. 6.

5.1.2 $H \parallel (111)$

Taking now $H \parallel (111)$, we find $T_x = T_y = T_z = 0$, and also \( \Gamma_5 \) = 0.
The field does not induce $\Gamma_5$ octupoles, and therefore a symmetry breaking transition is possible. Furthermore, as we remarked earlier, the $x$, $y$, and $z$ axes play equivalent roles, and therefore the choice of the order parameter $T = \langle T_{111} \rangle$
is correct. The situation corresponds to Fig. 6 (left).

5.1.3 $H \parallel (001)$

Next consider $H \parallel (001)$. Also here we find $T_x = T_y = T_z = 0$ from Eqs. (37)–
(39), and therefore the possibility of continuous phase transitions. However, it
is intuitively clear that the $z$-axis is inequivalent to $x$ and $y$, and therefore the order parameter may be either $T_z$, or some linear combination of $T_x$ and $T_y$.

We have to perform a two-parameter minimization using the suitably modified
form of \[31\]

\[ E_0(\langle T_z \rangle, \langle T_L \rangle) = -J (\langle T_x + T_y \rangle \langle T_L \rangle + T_z \langle T_z \rangle) \] (41)

with $\langle T_x \rangle = \langle T_y \rangle = \langle T_L \rangle$. Like in Fig. 7 we expect that the ground state energy functional has degenerate local minima: at low fields, we find a pair of these
as a function of $\langle T_z \rangle$, and another pair along the $\langle T_x + T_y \rangle$ direction (the latter
choice is arbitrary in the sense that we could also have taken $\langle T_z - T_y \rangle$) (Fig. 8
top left). These two pairs of minima are not symmetry-related, as it is also
Figure 8: The contour plot of the ground state energy functional in the $\langle T_x^\beta + T_y^\beta \rangle - \langle T_z \rangle$ plane for $\mathbf{H} = (0, 0, H)$ magnetic fields $H = 0.2$ (top left), $H = 0.42$ (top right) and $H = 0.8$ (bottom).

shown by the fact that at intermediate fields, only the $\langle T_x + T_y \rangle \neq 0$ minima survive (Fig. 8 top right). At high fields, the ground state is non-degenerate with $\langle T_x + T_y \rangle = \langle T_z \rangle = 0$ (Fig. 8 bottom).

The corresponding sequence of two second-order ground state transitions is shown in Fig. 9 (left). $\langle T_x^\beta + T_y^\beta \rangle > 0$ (or alternatively, $\langle T_x^\beta - T_y^\beta \rangle > 0$) order develops at higher critical field $H_{c_1}$, with $\langle T_z^\beta \rangle = 0$. Upon reducing the field to a lower critical value $H < H_{c_1}$, a second symmetry breaking occurs. In the low-field phase $H < H_{c_1}$, $\langle T_x^\beta + T_y^\beta \rangle \neq 0$ and also $\langle T_z^\beta \rangle \neq 0$. $\langle T_x^\beta \rangle \neq (\langle T_x^\beta \rangle + \langle T_y^\beta \rangle)/2$ as long as $H > 0$; the $T_{111}$ order ($\langle T_x^\beta \rangle = \langle T_y^\beta \rangle = \langle T_z^\beta \rangle$) appears continuously as $H \to 0$.

5.1.4 $H \parallel (11c)$

$\mathbf{H} \parallel (11c)$ ($c \neq 0$) induces $\langle T_x^\beta - T_y^\beta \rangle \neq 0$, leaving $\langle T_x^\beta + T_y^\beta \rangle = 0$ and $\langle T_z^\beta \rangle = 0$. There is a remaining octupolar degeneracy which is is lifted in a single continuous transition, where $\langle T^\beta \rangle \neq 0$, and $\langle T_x^\beta + T_y^\beta \rangle \neq 0$ appear simultaneously (Fig. 9 right). For $c = 0$, (i.e., $\mathbf{H} \parallel (110)$) $\langle T_x^\beta \rangle$, and $\langle T_x^\beta + T_y^\beta \rangle$ can order indepen-
5.1.5 Field direction dependence: Summary

We have discussed field directions which do not subtend a too large angle with (111), thus it holds that the limit $H \to 0$ picks the (111) ground state. For other field directions, the limit $H \to 0$ may give one of the other ground states, e.g. (111) type order (see (6)).

The previously discussed special directions which allowed a symmetry breaking transition, were all lying in the plane with normal vector $-\mathbf{n} = (1, -1, 0)$. Because of the cubic symmetry, the behaviour is the same for magnetic fields lying in planes with normal vectors $-\mathbf{n} = (1, 1, 0)$, $-\mathbf{n} = (1, 0, 1)$, $-\mathbf{n} = (0, 1, -1)$, and $-\mathbf{n} = (0, 1, 1)$, only the ordering phases change correspondingly. These six planes intersect along the directions [111], [111], [111] and [111] (Fig. 10). Any direction outside these planes excludes the possibility of a continuous octupolar transition.

5.2 Field-induced multipoles

We may also regard the problem of field-induced $\Gamma_5$ octupoles as a special case of field-induced multipoles in general \cite{8}. It is best to begin with quadrupoles. When the magnetic field is zero, the $\Gamma_5$-type quadrupolar moments $O_{xy}, O_{zx}, O_{yz}$ are equivalent by cubic symmetry. Switching on an external magnetic field with general direction $\mathbf{H} \parallel -\mathbf{n}$, where $-\mathbf{n} = (\kappa, \lambda, \mu)$, the quadrupolar operator along the $-\mathbf{n}$ direction can be given as

$$Q(-\mathbf{n}) \approx 3(-\mathbf{n} \cdot \mathbf{J})^2 - J(J + 1) = 3\kappa \lambda (J_x J_y + J_y J_x) + 3\kappa \mu (J_x J_z + J_z J_x)
+3\lambda \mu (J_x J_y + J_y J_x) + \kappa^2 J_x^2 + \lambda^2 J_y^2 + \mu^2 J_z^2 - J(J + 1)
= 3\kappa \lambda O_{xy} + 3\kappa \mu O_{zx} + 3\lambda \mu O_{yz} + (\mu^2 - \lambda^2)(J_z^2 - J_y^2)$$
Figure 10: Field directions lying in any of the planes shown allow a continuous octupolar ordering transition. Special rules hold for the lines of intersection, and other high-symmetry directions.

\[
+ (\kappa^2 - \mu^2) (J_x^2 - J_y^2) + (\lambda^2 - \kappa^2) (J_y^2 - J_z^2)
+ (\kappa^2 + \lambda^2 + \mu^2 - 1) J (J + 1).
\] (42)

This means that the \(O_{xy}, O_{xz}\), and \(O_{yz}\) \(\Gamma_5\)-type quadrupolar operators are no longer equivalent, the quadrupolar moment is distorted along the external magnetic field direction. Above, we obtained the components of the quadrupolar operator in the rotated new basis. The \(\Gamma_5\) quadrupole moments \(O_{xy}, O_{xz}, O_{yz}\) are proportional to \(\kappa \lambda \sim H_x H_y, \kappa \mu \sim H_x H_z, \lambda \mu \sim H_y H_z\). The next three quadrupolar terms, which are linear combinations of the two \(\Gamma_3\) quadrupoles, are shown because they appear in the expressions of the \(T^0\) octupoles: \(J_x^2 - J_y^2 \sim H_x^2 - H_y^2, J_y^2 - J_z^2 \sim H_y^2 - H_z^2\), \(J_x^2 - J_y^2 \sim H_x^2 - H_y^2\). The last term is an invariant number.

5.3 Ordering in external magnetic field

Now we consider arbitrary field intensities. At sufficiently low fields, symmetry breaking transitions are possible. However, the magnetic field lowers the symmetry of the system in a peculiar way, and gives rise to couplings between order parameters which would be independent in the absence of a field. The nature of these couplings depends sensitively on field direction.

Our previous discussion was about the ground state energy \(E_0(y, H)\), where \(H\) is the external magnetic field, and \(y\) stands for all other variables. The magnetic moment, or in our case \(J\), is obtained as \(J = -(\partial E_0 / \partial H)_y\).

In what follows, we prefer to use the Helmholtz free energy \(G\) which is related to \(E_0\) by the Legendre transformation \(G = E_0 + J \cdot H\). The magnetic field will be expressed as

\[
H = \frac{\partial G}{\partial J}.
\] (43)
The generalized Helmholtz free energy can be expanded in terms of the components of the symmetry-allowed multipoles \[7\]

\[
G = G(J_x, J_y, J_z; O_x^2, O_y^2, O_z^2, O_{xy}, O_{yz}, O_{zx}, T_x, T_y, T_z, T_{xy}, T_{xz}, T_{yz}, T_x^3, T_y^3, T_z^3)
\]

\[
= \sum_{i,j,\ldots} \mathcal{I}(\Gamma_i \otimes \Gamma_j \ldots)
\]

We have to go over the list of all possible product representations spanned by the order parameter components, and identify the bases for the identity representation \(\Gamma_1\); these are the invariants \(\mathcal{I}(\Gamma_i \otimes \Gamma_j \ldots)\) (assuming that they are also time-reversal invariant).

It is obvious that the present argument is valid only for phases with uniform order. \(q \neq 0\) Fourier components of the multipole densities should be included in a Landau theory of modulated states, such as the antiferro-octupolar phase observed in \(\text{NpO}_2\).

Returning to \(44\): to construct a Landau theory, we would need all the invariants up to some specified order, but to derive \(\mathbf{H}\), it is enough to consider those which contain the components of \(\mathbf{J}\). Their general form is \(\mathcal{I}(\Gamma_i \otimes \Gamma_j \ldots) = \mathbf{J} \cdot \mathbf{V}\), where the components of \(\mathbf{V}\) give the basis of \(\Gamma_{4u}\) (\(g\) and \(u\) refer to parity under time reversal).

We arrange the invariants according to the number of factors in the underlying product representation. For the present purposes, we will call this number the order of the invariant \[32\]. The second order invariants containing \(\mathbf{J}\) are \(\mathbf{J} \cdot \mathbf{J}\) and \(\mathbf{J} \cdot \tilde{\mathbf{T}}^\alpha\). Third order invariants arise from \(\Gamma_4 \otimes \Gamma_5 \otimes \Gamma_5\), \(\Gamma_4 \otimes \Gamma_3 \otimes \Gamma_5\), \(\Gamma_4 \otimes \Gamma_2 \otimes \Gamma_5\), and \(\Gamma_4 \otimes \Gamma_4 \otimes \Gamma_5\). To take the simplest example, consider \(\Gamma_4 \otimes \Gamma_2 \otimes \Gamma_5\), for which

\[
\mathcal{I}(\Gamma_4 \otimes \Gamma_2 \otimes \Gamma_5) = J_x O_{yz} T_{xyz} + J_y O_{zx} T_{xyz} + J_z O_{xy} T_{xyz},
\]

and the corresponding term of \(\mathbf{V}\) is

\[
\mathbf{V}(\Gamma_2 \otimes \Gamma_5) = (O_{yz} T_{xyz}, O_{zx} T_{xyz}, O_{xy} T_{xyz}).
\]

Taking e.g., the \(z\)-component, we find that the magnetic field couples to \(O_{xy} T_{xyz}\). One possible interpretation is that, in the presence of \(\mathbf{H} \parallel (001)\), \(O_{xy}\)-type quadrupolar moment induces the octupole \(T_{xyz}\) \[4\]. Alternatively, \(T_{xyz}\)-type octupole order would induce \(O_{xy}\) quadrupoles.

In our further discussion of third order invariants, we confine our attention to those which have a bearing on the question of \(\Gamma_5\) octupolar order, i.e., one of the factors is \(\Gamma_{5u}\). As for \(\Gamma_4 \otimes \Gamma_4 \otimes \Gamma_5\) invariants, since one of the \(\Gamma_4\) has to give \(\mathbf{J}\), i.e., it is \(\Gamma_{4u}\), the remaining \(\Gamma_4\) must be \(\Gamma_{4g}\). The lowest order \(\Gamma_{4g}\) multipole is a hexadecapole. However, within our \(\Gamma_8\) subspace, hexadecapoles cannot be independent of the first 15 multipoles, thus the formally third order expression would have to be rewritten as a fourth-order invariant. We generally neglect terms of fourth order, and seek to draw conclusions from the genuinely third order terms. These belong to \(\Gamma_{4u} \otimes \Gamma_{5u} \otimes \Gamma_{5g}\) which gives

\[
\mathcal{I}(\Gamma_{4u} \otimes \Gamma_{5u} \otimes \Gamma_{5g}) = J_x (-O_{xy} T_y^\beta + O_{zx} T_z^\beta) + J_y (-O_{yz} T_x^\beta + O_{xy} T_x^\beta)
\]

\[
+ J_z (-O_{zx} T_x^\beta + O_{yz} T_y^\beta),
\]

\[
(47)
\]
and to $\Gamma_4 \otimes \Gamma_5 \otimes \Gamma_3 g$ which gives
\[
\mathcal{I}(\Gamma_4 \otimes \Gamma_5 \otimes \Gamma_3 g) = -\frac{1}{2} J_x (O_2^0 + O_2^3) T_x^\beta + \frac{1}{2} J_y (O_2^0 - O_2^3) T_y^\beta + J_z O_2^0 T_z^\beta.
\] (48)

The invariants (47) and (48) appear with the independent coefficients $w_1$ and $w_2$ in $G$. For the $z$-component of the field we give first a fuller expression derived from a number of low-order invariants
\[
H_z = u_1 J_z + u_2 T_\alpha^\beta + v_1 (J_z O_0^0 + v_2 O_{xy} T_{xyz})
+ w_1 (-O_{zx} T_x^\beta + O_{yz} T_y^\beta) + w_2 O_2^0 T_x^\beta + ...
\] (49)

Terms in the first line are needed to recover the results by [7]. However, we are now only interested in the interplay of $\Gamma_5$ octupoles and fields, therefore we omit from (49) terms not containing $T_\beta^\alpha$

\[
H_z = w_1 (-O_{zx} T_x^\beta + O_{yz} T_y^\beta) + w_2 O_2^0 T_x^\beta.
\] (50)

If quadrupolar interactions induce any of the quadrupolar moments appearing in the above equation, the field will induce $\Gamma_5$ octupoles, thus explicitly breaks the symmetry of the problem. However, in the absence of such interactions, we can turn to the high-field expressions (37)–(39) which give none of these quadrupoles. Therefore, symmetry breaking by octupolar ordering is a possibility.

For fields of other orientation, we need also the following relationships
\[
H_x = w_1 (-O_{xy} T_y^\beta + O_{zx} T_x^\beta) - \frac{w_2}{2} (O_2^0 + O_2^3) T_x^\beta,
\] (51)

and
\[
H_y = w_1 (-O_{yz} T_x^\beta + O_{yx} T_y^\beta) + \frac{w_2}{2} (O_2^0 - O_2^3) T_y^\beta.
\] (52)

For a field in the $(111)$ direction,
\[
H_{111} = w_1 [(O_{xy} - O_{zx}) T_x^\beta + (O_{yz} - O_{yx}) T_y^\beta + (O_{zx} - O_{yz}) T_z^\beta]
+ w_2 \left[ -\frac{1}{2} (O_2^0 + O_2^3) T_x^\beta + \frac{1}{2} (O_2^0 - O_2^3) T_y^\beta + O_2^0 T_z^\beta \right].
\] (53)

Neither of the quadrupolar coefficients seen above are field-induced. Therefore, if there is no quadrupolar interaction to introduce some of them as order parameters, $H \parallel (111)$ fields will allow the same kind of $\Gamma_5$ octupolar ordering as in the absence of a field (remember, though, that the amplitude of the order will be gradually suppressed by the field).

In a $(110)$ field
\[
H_{110} = -\frac{w_2}{2} O_2^0 (T_x^\beta - T_y^\beta)
- \frac{w_2}{2} O_2^3 (T_x^\beta + T_y^\beta) + w_1 (O_{zx} - O_{yz}) T_z^\beta.
\] (54)
The point to note from (37)–(39) is that though \((O_{zx} - O_{yz})\) and \(O_{0z}^2\) are not induced by the field, \(O_{0z}^2\) is, and therefore the octupolar component \((T_{\beta x}^\beta + T_{\beta y}^\beta)\) do not couple to the field. Since these are associated with different terms in the expansion (44), \((T_{\beta x}^\beta + T_{\beta y}^\beta)\) and \(T_{\beta z}^\beta\) may order independently.

Finally, we comment upon the case \(H \parallel (11c)\)

\[
H_{11c} = w_1 [(O_{xy} - cO_{zz}) T_{\beta x}^\beta + (cO_{yz} - O_{xy}) T_{\beta y}^\beta + (O_{zx} - O_{yz}) T_{\beta z}^\beta] + w_2 \left[ \frac{1}{2} (O_{0z}^\beta + O_{2z}^\beta) T_{\beta x}^\beta + \frac{1}{2} (O_{0z}^\beta - O_{2z}^\beta) T_{\beta y}^\beta + cO_{0z}^\beta T_{\beta z}^\beta \right].
\]

Again only \((T_{\beta x}^\beta - T_{\beta y}^\beta)\) is field induced. However, once octupole–octupole interaction gives rise to \(T_{\beta z}^\beta\) order, it induces \(O_{0z}^2\), which in turn induces \((T_{\beta x}^\beta + T_{\beta y}^\beta)\), thus there is a single phase transition (Fig. 9, right).

6 Conclusion

The \(\Gamma_8\) subspace supports a variety of competing order parameters. The fourfold ground state degeneracy can be lifted either in two steps (removing Kramers and non-Kramers degeneracies separately), or in a single phase transition. The latter possibility is realized by the ordering of \(\Gamma_5\) octupoles. We have found that the crystal field gives rise to a peculiar single-ion octupolar anisotropy which makes the choice of \(T_{111}^\beta = T_{\beta x}^\beta + T_{\beta y}^\beta + T_{\beta z}^\beta\) octupoles preferable as order parameter. Though it breaks time reversal invariance, octupolar ordering is non-magnetic in the sense of yielding vanishing dipole moments. On the other hand, the ordering of \(\Gamma_5\) octupoles induces \(\Gamma_5\) quadrupoles as secondary order parameter; this feature allows the simultaneous lifting of Kramers and non-Kramers degeneracies.

Our discussion is mainly about a hypothetical \(\Gamma_5\)-type ferro-octupolar ordering in a lattice of \(\Gamma_8\) shells. The mean-field results presented in Fig. 2 and Fig. 3 are equally valid for ferro-octupolar, and the triple-\(\vec{k}\) antiferro-octupolar, ordering patterns, but our main interest is in magnetic field effects, and our arguments for the case of non-zero magnetic field are restricted to uniform phases.

Magnetic octupoles are not time reversal invariant, thus we might have expected that spontaneous symmetry breaking due to uniform octupolar ordering is necessarily suppressed by magnetic fields. Indeed, for fields of a general orientation, we find that the degeneracy of different octupolar ground states is immediately lifted, and the para-octupolar state prevails at all temperatures. However, the analysis of field-induced multipoles shows that for field directions lying in certain planes, the field does not induce all the \(T^\beta\)-type octupolar moments, and therefore sharp octupolar transitions remain possible up to a certain critical field. The size of the critical field, and the nature of the transition to the high-field dipolar state, depend on the details of field orientation within the symmetry-specified planes.
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[6] The possibility of pure octupolar order was suggested for Phase IV of Ce$_x$La$_{1-x}$B$_6$ (H. Kusunose and Y. Kuramoto: J. Phys. Soc. Japan 70, 1751 (2001)). Some of the features (susceptibility cusp, and apparent lack of dipole order) make Ce$_x$La$_{1-x}$B$_6$ similar to NpO$_2$, but due to its metallic character, its physics is bound to be more complicated than that of the insulator NpO$_2$. We note, however, that the zero field mean field theory developed by Kusunose and Kuramoto is to some extent parallel with ours. However, they did not consider the effect of a magnetic field, which is the main point of interest for us. A very recent work by K. Kubo and Y. Kuramoto (cond-mat/0304689) discusses the effects of octupole ordering on elastic behavior.
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[15] We note that the octupolar scenario is not universally accepted. Relying on quadrupolar order alone, one may invoke singlet formation of $5f^3$ cores with ligand electrons (See A.V. Nikolaev and K.H. Michel: cond-mat/0212521. Similar ideas were advanced earlier by A. Zolnierek, G. Solt, and P. Erdős: J. Phys. Chem. Solids 42, 773 (1981)).
[16] Though as far as the subgroup of proper rotations is concerned, the symmetry of $\Gamma_5$ quadrupoles and $\Gamma_5$ octupoles is the same, they have different parity under time reversal. Their coupling is made possible by the invariant arising from $\Gamma_{5u} \otimes \Gamma_{5u} \otimes \Gamma_{5g}$ (see Sec. 5.3).
[17] In other words, we do not aim at describing those features which would uniquely follow from adopting some specific ratio of the fourth order and sixth order terms of the crystal field potential. It is known that fine-tuning the parameters can give rise to exceptional behavior (G. Solt and P. Erdős: J. Magn. Magn. Mater. 15–18, 57 (1980)). A fit to the measured $\Gamma_8^{(2)} - \Gamma_8^{(1)}$ excitation energy of 49meV is achieved in Ref. [2].
[18] This would be the spectrum of the mean field hamiltonian $\mathcal{T}(\theta, \phi) \langle \mathcal{T}(\theta, \phi) \rangle$ if we set $\langle \mathcal{T}(\theta, \phi) \rangle = 1$.
[19] Individual interaction terms depend on the orientation of the pair, but the sum (5) as a whole respects cubic symmetry.
[20] While for general orientation, the spectrum of $\mathcal{T}$ consists of four singlets, the 111 directions are special by possessing the level scheme singlet-doublet-singlet. We exploit only the fact that the ground state is a singlet.
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[26] It means that (27) is, though often applicable, still system-specific, and not literally an Ehrenfest relation. True Ehrenfest relations [24] are thermodynamic identities, once the assumption about finite discontinuities is made.

[27] A closely related observation was made by Solt and Erdős [13, 17]. In their model, a ground state which appears non-magnetic if the field is applied in a certain direction, can be selected by quadrupolar interaction.

[28] In our present model, the vanishing of $a_H$ at the tricritical point is not generic; however, in some other multipolar models it is. A detailed discussion of various possibilities admitted by the relation (27) will be published elsewhere.

[29] A classical description of multipolar ordering was developed (with application to TmTe) by R. Shiina, H. Shiba, and O. Sakai: J. Phys. Soc. Japan 68, 2105 (1999).

[30] Though octupoles of other symmetries may be induced by the same fields.

[31] There is a general resemblance to the well-known fact that the ferromagnetic Ising model does not have a sharp phase transition in an external magnetic field, basically because the field picks a preferred spin direction, and thus there remains no symmetry to break. More precisely: this rules out a continuous transition only. Suitably constructed models may have a sharp first-order transition. Similarly, our high-field analysis cannot exclude first-order octupolar transitions. However, we found no evidence for these.

[32] This ad hoc meaning is different from identifying the order as the power of $J$ when the familiar expansions are inserted. For instance, we call both $J\cdot J$ and $\bar{T}^\alpha \cdot \bar{T}^\alpha$ second order invariant, though the latter is a sixth-order polynomial in $J_x, J_y, J_z$.

A  Numerical coefficients of cubic crystal field levels in the $\Gamma_8$ basis

$$\alpha = \frac{28 \sqrt{3} + \frac{1}{6} \sqrt{206} \sqrt{14}}{\sqrt{1 + (\frac{28}{3} + \frac{1}{6} \sqrt{206} \sqrt{14})^2 + (\frac{5}{6} \sqrt{14} - \frac{1}{6} \sqrt{206})^2}} = 0.9530$$
The Zeeman splitting parameters appearing in Sec. 3.1 are

$$\beta = \frac{-\frac{5}{6}\sqrt{14} - \frac{1}{6}\sqrt{206}}{\sqrt{1 + \left(\frac{26}{27} + \frac{1}{6}\sqrt{206}\sqrt{14}\right)^2 + \left(-\frac{5}{6}\sqrt{14} - \frac{1}{6}\sqrt{206}\right)^2}} = -0.2980$$

$$\gamma = \frac{1}{\sqrt{1 + \left(\frac{26}{27} + \frac{1}{6}\sqrt{206}\sqrt{14}\right)^2 + \left(-\frac{5}{6}\sqrt{14} - \frac{1}{6}\sqrt{206}\right)^2}} = 0.05409$$

$$\delta = \frac{-\frac{1}{15}\sqrt{14}\sqrt{6} - \frac{1}{30}\sqrt{6}\sqrt{206}}{\sqrt{1 + \left(-\frac{1}{15}\sqrt{14}\sqrt{6} - \frac{1}{30}\sqrt{6}\sqrt{206}\right)^2}} = -0.8721$$

$$\epsilon = \frac{1}{\sqrt{1 + \left(-\frac{1}{15}\sqrt{14}\sqrt{6} - \frac{1}{30}\sqrt{6}\sqrt{206}\right)^2}} = 0.4891$$

The Zeeman splitting parameters appearing in Sec. 3.1 are

$$g_H = \frac{3}{206}\sqrt{129471 + 618\sqrt{206}\sqrt{14}} = 5.736$$

$$y_H = \frac{1}{618}\sqrt{1078719 - 6798\sqrt{206}\sqrt{14}} = 1.3665$$

**B Multipole moments in the ground state of $T_{111}$**

$$A = \langle \phi_0 \vert T_{111} \vert \phi_0 \rangle = \langle \phi_0 \vert T_{1111} \vert \phi_0 \rangle = \langle \phi_0 \vert T_{1111} \vert \phi_0 \rangle = \langle \phi_0 \vert T_{111} \vert \phi_0 \rangle = -\frac{15}{105}\sqrt{22660 - 206\sqrt{206}\sqrt{14}} = -15.683$$

$$B/3 = \langle \phi_0 \vert O_{xy} \vert \phi_0 \rangle = \langle \phi_0 \vert O_{yz} \vert \phi_0 \rangle = \langle \phi_0 \vert O_{xz} \vert \phi_0 \rangle = 2.673$$

$$m = \langle \phi_0 \vert J_z \vert \phi_0 \rangle = \langle \phi_0 \vert J_y \vert \phi_0 \rangle = \langle \phi_0 \vert J_x \vert \phi_0 \rangle = 0$$