

## Quantum-mechanical states of dipolar crystals with two magnetic ions per unit cell

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(Received 26 July 1985; revised manuscript received 21 April 1986)

This paper deals with the quantum-mechanical states of dipolar crystals with two equivalent magnetic ions per unit cell, with or without the presence of an external homogeneous magnetic field. The method used is an extension of the Niemeijer-Meijer method which is based on the classical Luttinger-Tisza approach. The approximation used is that the expectation values of the spin operators, and the spin correlations, are periodic with respect to lattice translations along one crystallographic direction and double lattice translations along the other crystallographic directions. Thus, the problem is reduced to finding the minima of an effective Hamiltonian in the space of wave functions describing a cluster of eight magnetic ions. The eight-spin-wave functions are constructed by using the theory of irreducible representations of the translation and inversion group. The method developed here is applied for the calculation of the ground state of dysprosium trichloride hexahydrate, the results of which appear in the following companion paper.

### I. INTRODUCTION

Crystals with exclusively dipole-dipole interactions are of special theoretical interest, because no phenomenological terms or parameters appear in their Hamiltonian, contrary to the crystals where the exchange interaction is present. Thus one can directly compare theoretical and experimental conclusions about many-spin systems. The main difficulty of the study of dipolar crystals, in addition to the very large number of magnetic moments, is the long range of dipole-dipole interactions and the low symmetry of their Hamiltonian with respect to the Heisenberg one. For this reason special approximation methods have to be used for the calculation of the ground state of dipolar crystals.

The first quantum-mechanical approach to the problem was made by Niemeijer and Meijer,<sup>1,2</sup> and was based on the classical Luttinger-Tisza<sup>3,4</sup> approximation. Thanos and Theophilou<sup>5,6</sup> made some improvements on the method of solution of the Niemeijer-Meijer equations and applied the method to the dipolar crystal cerium magnesium nitrate (CMN). The results fitted the experimental data well.

The quantum-mechanical calculations so far are restricted to crystals in which the magnetic ions are situated on a simple Bravais lattice. Nevertheless, except for CMN, most of the dipolar crystals on which measurements have been performed have two equivalent magnetic ions per unit cell. Equivalent magnetic ions are those having the same total angular momentum and the same  $g$ -tensor components in the crystal field.

Niemeijer and Blöte,<sup>7</sup> and Felsteiner and Misra,<sup>8</sup> made a simple generalization of the classical Luttinger-Tisza method, in order to calculate the ground state of dipolar crystals with two equivalent magnetic ions per unit cell. Friedman and Felsteiner<sup>9</sup> showed that this method is equivalent to the Fourier-transform expansion in order to find the ground state of these crystals. Litvin<sup>10</sup> developed a group-theoretical method which takes into account the

space-group symmetry of the crystal, whereas the earlier methods relied only on the translational symmetry of the crystal. In addition, he showed that the Luttinger-Tisza conjecture is equivalent to a sufficient, but not necessary condition, for the energy minimum. Misra<sup>11</sup> showed that the method of Refs. 7 and 8 cannot be directly extended for the case of more than two magnetic ions per unit cell in the case of dipole-dipole interactions, whereas for the case of the exchange interactions the method is applicable provided the  $2^m$  ions per unit cell occupy special positions. A similar generalization of the quantum-mechanical Niemeijer-Meijer method is numerically impossible, because it requires the calculation of thousands of independent matrix elements and the diagonalization of matrices with dimension higher than 8000, after the simplifications resulting from the translational symmetry have been taken into account.

In the present paper we extend the Niemeijer-Meijer method for calculating the ground state of dipolar crystals with two equivalent magnetic ions per unit cell, with or without the presence of an external homogeneous magnetic field. In contrast to the original Niemeijer-Meijer method, we made the hypothesis that the expectation values of the spin operators, and the spin correlations, are periodic with respect to lattice translations along one crystallographic direction and double lattice translations along the other two crystallographic directions. Thus, we use a smaller basic cell than Niemeijer and Meijer did, consisting of four adjacent unit cells. We assume then that a cluster of eight magnetic ions is repeated throughout the crystal.

A quantum-mechanical method for dealing with non-isotropic spin interactions, which is applicable to crystals with many magnetic ions per unit cell, was developed earlier by Felsteiner and Friedman.<sup>12</sup> The case of isotropic crystals has been considered by Villain.<sup>13</sup> The Felsteiner-Friedman method is based on the molecular-field approximation. This approach offers the possibility of deriving transition temperatures and other thermodynamic proper-

ties. In addition, the equations derived are much easier to solve than ours. However, in the molecular-field approximation no spin correlations are taken into account, whereas part of this effect is taken into account in our approach. An extension of the present approach for the calculation of thermodynamic properties will follow.

To our knowledge this is the first time that a quantum-mechanical method is developed which takes into account spin correlations for the case of two magnetic ions per unit cell. This is an advantage over the classical method, although some aspects of the classical theory concerning the direction of simple periodicity are incorporated in our treatment. As earlier work has shown, when the external magnetic field is zero, no serious deviations between the classical<sup>14</sup> and the quantum-mechanical<sup>15</sup> method appear. However, this is not the case when an external magnetic field is present.<sup>15</sup>

In Sec. II we present our basic assumptions and derive the effective cluster Hamiltonian. In Sec. III we classify the eigenstates according to the irreducible representations of the symmetry group of the effective Hamiltonian and build a basis in the eight-spin space which transforms accordingly. In Sec. IV we comment on our method. Numerical applications will be presented in a sequent paper.<sup>16</sup>

## II. DERIVATION OF THE EFFECTIVE HAMILTONIAN

The Hamiltonian of a system of spins interacting with dipole-dipole and exchange interactions, in a homogeneous external magnetic field, is

$$\mathcal{H} = \frac{1}{2} \sum_{\substack{i,j \\ i \neq j}} \frac{1}{|\mathbf{R}_{ij}|^3} \left[ \boldsymbol{\mu}_i \cdot \boldsymbol{\mu}_j - 3 \frac{(\boldsymbol{\mu}_i \cdot \mathbf{R}_{ij})(\boldsymbol{\mu}_j \cdot \mathbf{R}_{ij})}{|\mathbf{R}_{ij}|^2} \right] - \frac{1}{2} \sum_{\substack{i,j \\ i \neq j}} V(\mathbf{R}_{ij}) \mathbf{S}_i \cdot \mathbf{S}_j - \sum_i \boldsymbol{\mu}_i \cdot \mathbf{h}, \quad (1)$$

where  $\mathbf{R}_{ij} = \mathbf{R}_i - \mathbf{R}_j$ .

By  $\mathbf{R}_i$  we denote the magnetic ion sites, by  $\mathbf{S}_i$  or  $\mathbf{S}(\mathbf{R}_i)$  we denote the spin (total angular momentum) operator for the magnetic ion at  $\mathbf{R}_i$ , and by  $\boldsymbol{\mu}_i$  we denote its magnetic moment operator:

$$\boldsymbol{\mu}_i^\alpha = m_B \sum_{\beta=x,y,z} g_{\alpha\beta} S^\beta(\mathbf{R}_i), \quad \alpha=x,y,z \quad (2)$$

where  $m_B$  is the Bohr magneton and  $g$  the gyromagnetic tensor.

The first term of the Hamiltonian  $\mathcal{H}$  is the dipolar interaction, the second term is the exchange interaction, and the third is the action of the homogeneous external magnetic field  $\mathbf{h}$ .

When two equivalent magnetic ions are present per unit cell in a crystal, the sites of the ions are determined by two identical Bravais lattices, the one resulting from the other after a translation  $\mathbf{d}$ . It must be noted that  $2\mathbf{d}$  is not a lattice translation. Such crystals have higher symmetry than lattice translations, as inversion with center at  $\mathbf{d}/2$  leads to sites of equivalent magnetic ions (see Fig. 1). This symmetry does not commute with the lattice translations. This additional symmetry was also used by Niemeijer and Blöte<sup>7</sup> and by Felsteiner and Misra<sup>8</sup> to develop their classical treatment.

In the original Niemeijer-Meijer (NM) method<sup>1</sup> the expectation values of the spin operators and spin correlations are taken as having periodicity twice that of the crystal translations. Because of this hypothesis the wave functions of a cluster of eight magnetic ions is needed. The space of these wave functions is of dimension  $2^8 = 256$  for the case of  $s = \frac{1}{2}$ . A direct application of this method for the case of two magnetic ions per unit cell requires the wave functions of a cluster of 16 ions. This leads to a linear space of dimension  $2^{16} = 65536$ .

In order to have a smaller space we make the hypothesis that along one of the directions of the lattice translations the expectation values of the spins and the spin correlations have the periodicity of the lattice, while we keep the assumption of double periodicity for the other directions. Thus our assumptions take the following mathematical form:

$$\langle \Psi | S^\alpha(\mathbf{R} + \mathbf{t}) | \Psi \rangle = \langle \Psi | S^\alpha(\mathbf{R}) | \Psi \rangle, \quad \mathbf{t} \in \Gamma' \quad (3)$$

$$\langle \Psi | S^\alpha(\mathbf{R} + \mathbf{t}) S^\beta(\mathbf{R} + \mathbf{t}') | \Psi \rangle = \langle \Psi | S^\alpha(\mathbf{R}) | \Psi \rangle \langle \Psi | S^\beta(\mathbf{R}) | \Psi \rangle, \quad \mathbf{t} \neq \mathbf{t}', \mathbf{t}, \mathbf{t}' \in \Gamma' \quad (4)$$

$$\langle \Psi | S^\alpha(\mathbf{R} + \mathbf{t}) S^\beta(\mathbf{R}' + \mathbf{t}') | \Psi \rangle = \langle \Psi | S^\alpha(\mathbf{R}) S^\beta(\mathbf{R}') | \Psi \rangle, \quad \mathbf{R} \neq \mathbf{R}', \mathbf{t}, \mathbf{t}' \in \Gamma' \quad (5)$$

where  $\alpha, \beta = x, y, z$ , and  $\mathbf{R}, \mathbf{R}'$  are magnetic ion sites:

$$\mathbf{R} = n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2 + n_3 \mathbf{a}_3 + m \mathbf{d}, \quad (6)$$

where  $n_1, n_2, n_3$  are integers and  $m$  takes the values 0 or 1.

By  $\Gamma$  we denote the group of lattice translations and by  $\Gamma'$  the subgroup of  $\Gamma$  which consists of the translations

$$\mathbf{t} = 2n_1 \mathbf{a}_1 + 2n_2 \mathbf{a}_2 + n_3 \mathbf{a}_3 \quad (7)$$

with  $n_1, n_2$ , and  $n_3$  integers.

Because of our assumptions only the wave functions for a cluster of eight spins are needed (see Fig. 1). Thus the problem is numerically tractable, although at the expense of a more limiting assumption than that of the NM method.

In choosing the direction of single periodicity, the classical solution for the ground state provides a lot of insight. A proper choice gives the possibility of an immediate comparison of the quantum-mechanical to the classical method which, from the experience we have from the

crystals treated so far, gives good results when the external magnetic field is equal to zero.

In some cases the assumption given by Eq. (4) may be eased (see Ref. 16).

In the following we will refer to the Niemeijer-Meijer method for the case of dipolar crystals with one magnetic ion per unit cell (see Refs. 2 and 5) as M1, and to our modification of method M1 for the case of dipolar crystals with two equivalent magnetic ions per unit cell as M2.

After the hypotheses (3), (4), and (5), the initial crystal Hamiltonian  $\mathcal{H}$  reduces to an effective Hamiltonian of the following form:<sup>5</sup>

$$H = \frac{1}{2} \sum_{\alpha, \beta=x,y,z} \sum_{\mathbf{R} \in C} \sum_{\substack{\mathbf{R}' \in C \\ \mathbf{R}' \neq \mathbf{R}}} A^{\alpha\beta}(\mathbf{R}-\mathbf{R}') S^{\alpha}(\mathbf{R}) S^{\beta}(\mathbf{R}') \\ + \frac{1}{2} \sum_{\alpha, \beta=x,y,z} A^{\alpha\beta}(0) \sum_{\mathbf{R} \in C} \langle \Psi | S^{\alpha}(\mathbf{R}) | \Psi \rangle S^{\beta}(\mathbf{R}) \\ - \sum_{\alpha=x,y,z} f^{\alpha} \sum_{\mathbf{R} \in C} S^{\alpha}(\mathbf{R}), \quad (8)$$

where by  $\mathbf{R} \in C$  we denote the eight magnetic ion sites in the basic cell (see Fig. 1);  $A^{\alpha\beta}(\mathbf{R})$  are lattice sums of the form:

$$A^{\alpha\beta}(\mathbf{R}) = m_B^2 \sum_{\mu, \nu=x,y,z} g_{\mu\alpha} g_{\nu\beta} \sum_{\substack{\mathbf{t} \in \Gamma' \\ \mathbf{t} \neq -\mathbf{R}}} \frac{\delta_{\mu\nu} |\mathbf{R} + \mathbf{t}|^2 - 3(R^{\mu} + t^{\mu})(R^{\nu} + t^{\nu})}{|\mathbf{R} + \mathbf{t}|^5} - \delta_{\alpha\beta} \sum_{\mathbf{t} \in \Gamma'} V(\mathbf{R} + \mathbf{t}), \quad \alpha, \beta=x,y,z \quad (9a)$$

and

$$f^{\alpha} = m_{\nu} \sum_{\nu=x,y,z} g_{\nu\alpha} h^{\nu}, \quad \alpha=x,y,z. \quad (9b)$$

Thus one gets a Hamiltonian for the cluster of eight magnetic ions which has the same form as the one obtained by the NM method in case M1. However the basic cell in the present case, M2, is different, and so is the symmetry. As in case M1,<sup>5</sup> we consider the following linearization of  $H$ :

$$H = H' + H_{\delta}, \quad (10)$$

$$H' = \frac{1}{2} \sum_{\alpha, \beta=x,y,z} \sum_{\mathbf{R} \in C} \sum_{\mathbf{R}' \in C} A^{\alpha\beta}(\mathbf{R}-\mathbf{R}') S^{\alpha}(\mathbf{R}) S^{\beta}(\mathbf{R}') \\ - \sum_{\alpha=x,y,z} f^{\alpha} \sum_{\mathbf{R} \in C} S^{\alpha}(\mathbf{R}), \quad (11)$$

$$H_{\delta} = \frac{1}{2} \sum_{\alpha, \beta=x,y,z} A^{\alpha\beta}(0) \sum_{\mathbf{R} \in C} [\langle \Psi | S^{\alpha}(\mathbf{R}) | \Psi \rangle S^{\beta}(\mathbf{R}) \\ - S^{\alpha}(\mathbf{R}) S^{\beta}(\mathbf{R})]. \quad (12)$$

In this way one can find the eigenvalues and eigenstates of the linear operator  $H'$  and treat  $H_{\delta}$ , the nonlinear part of  $H$ , by using perturbation theory. This method is applicable when the perturbation term  $H_{\delta}$  is small compared to the ground-state energy.

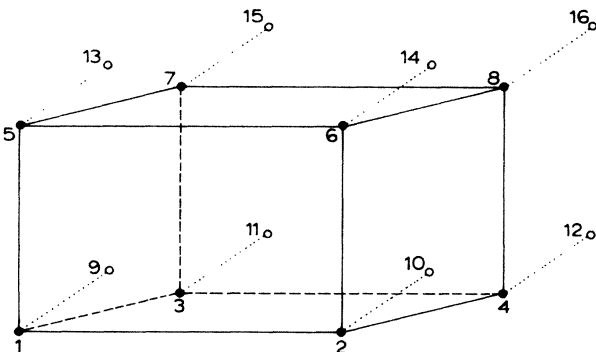


FIG. 1. The sites of 16 magnetic ions that correspond to eight adjacent unit cells, or to two basic cells.

### III. SYMMETRY PROPERTIES OF THE EIGENSTATES

In order to find the eigenstates of  $H'$  one needs to diagonalize a  $256 \times 256$  matrix. However, if the symmetry of  $H'$  is taken into account the matrices to be diagonalized are of smaller dimension, and in addition the derivation of the physical conclusions is more straightforward.

One can easily realize that  $H'$  has the same symmetry as the exact Hamiltonian discussed at the beginning of Sec. II, i.e., by lattice translations and inversions. However, the transformations corresponding to lattice translations and inversions here have a different meaning because of hypotheses (3), (4), and (5). The exact definition of the group of transformations,  $\hat{G}$ , under which  $H'$  is invariant is

$$\hat{P} S^{\alpha}(\mathbf{R}) \hat{P}^{-1} = S^{\alpha}(P\mathbf{R}), \quad \alpha=x,y,z, \quad \mathbf{R} \in C \quad (13)$$

where  $P$  is a transformation acting on the position variables  $\mathbf{R}$ , and  $\hat{P}$  is the transformation acting on the spin operators and the spin states. Because of hypotheses (3), (4), and (5),

$$\hat{P}^2 = \hat{E}, \quad \hat{P} \in \hat{G} \quad (14)$$

Thus when lattice translations are considered one has to take the translations belonging to the subgroup  $\Gamma'$  equal to the identity. The definition of  $\Gamma'$  is given by Eq. (7). The explicit form of the group  $G$ , through which the symmetry group  $\hat{G}$ , of  $H'$  is defined, is

$$\begin{aligned} E\mathbf{R} &= \mathbf{R}, \\ T_{\mathbf{a}_1}\mathbf{R} &= \mathbf{R} + \mathbf{a}_1, \\ T_{\mathbf{a}_2}\mathbf{R} &= \mathbf{R} + \mathbf{a}_2, \\ T_{\mathbf{a}_1+\mathbf{a}_2}\mathbf{R} &= \mathbf{R} + \mathbf{a}_1 + \mathbf{a}_2, \\ I\mathbf{R} &= -\mathbf{R} + \mathbf{d}, \\ IT_{\mathbf{a}_1}\mathbf{R} &= -\mathbf{R} + \mathbf{a}_1 + \mathbf{d}, \\ IT_{\mathbf{a}_2}\mathbf{R} &= -\mathbf{R} + \mathbf{a}_2 + \mathbf{d}, \\ IT_{\mathbf{a}_1+\mathbf{a}_2}\mathbf{R} &= -\mathbf{R} + \mathbf{a}_1 + \mathbf{a}_2 + \mathbf{d}. \end{aligned} \quad (15)$$

where  $E$  is the identity,  $T_{\mathbf{a}_1}$  is the translation by  $\mathbf{a}_1$ ,  $T_{\mathbf{a}_2}$  is the translation by  $\mathbf{a}_2$ ,  $T_{\mathbf{a}_1+\mathbf{a}_2}$  is the translation by  $\mathbf{a}_1+\mathbf{a}_2$ ,  $I$  is the inversion with center  $\mathbf{d}/2$ ,  $IT_{\mathbf{a}_1}$  is the inversion with center  $\frac{1}{2}(\mathbf{a}_1+\mathbf{d})$ ,  $IT_{\mathbf{a}_2}$  is the inversion with center  $\frac{1}{2}(\mathbf{a}_2+\mathbf{d})$ , and  $IT_{\mathbf{a}_1+\mathbf{a}_2}$  is the inversion with center  $\frac{1}{2}(\mathbf{a}_1+\mathbf{a}_2+\mathbf{d})$ . From the above definition one can easily conclude that the generators of  $\hat{G}$  are  $\hat{T}_{\mathbf{a}_1}$ ,  $\hat{T}_{\mathbf{a}_2}$ , and  $\hat{I}$ , and  $\hat{T}_{\mathbf{a}}^2 = \hat{E}$ ,  $\hat{I}^2 = \hat{E}$ ,  $\hat{I}\hat{T}_{\mathbf{a}}\hat{I}^{-1} = \hat{T}_{\mathbf{a}}$ ,  $\mathbf{a} = \mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_1 + \mathbf{a}_2$ . (16)

$\hat{G}$  is an Abelian group, which is isomorphic to the  $C_2 \otimes C_2 \otimes C_2$  cyclic group. Thus the irreducible representations of this group are the same as those of the symmetry group of the basic cell Hamiltonian resulting from M1. The  $+$  and  $-$  indices for the irreducible representations of the inversion subgroup will be used. For the translation subgroups the indexing of the irreducible representations by  $\mathbf{k}$  used previously<sup>5</sup> will be preserved:

$$\begin{aligned} \mathbf{k}_0 = 0, \quad \mathbf{k}_1 = \pi \frac{\mathbf{a}_2 \times \mathbf{a}_3}{\mathbf{a}_1 \cdot \mathbf{a}_2 \times \mathbf{a}_3}, \\ \mathbf{k}_2 = \pi \frac{\mathbf{a}_3 \times \mathbf{a}_1}{\mathbf{a}_1 \cdot \mathbf{a}_2 \times \mathbf{a}_3}, \quad \mathbf{k}'_3 = \mathbf{k}_1 + \mathbf{k}_2. \end{aligned} \quad (17)$$

$$|\phi_{\mathbf{k}^\pm}(\mathbf{R}')\rangle = \frac{1}{4} \sum_{\mathbf{R}} e^{i\mathbf{k} \cdot \mathbf{R}} [S^+(\mathbf{R})S^+(\mathbf{R}+\mathbf{R}') \pm S^+(\mathbf{R}+\mathbf{d})S^+(\mathbf{R}+\mathbf{R}'+\mathbf{d})] |0\rangle, \quad \mathbf{R} \in C \quad (20)$$

where by  $\sum_{\mathbf{R}}$  we denote summing over  $\mathbf{R}=0, \mathbf{a}_1, \mathbf{a}_2$ , and  $\mathbf{a}_1+\mathbf{a}_2$ .

The five-, six-, seven-, and eight-particle  $\mathbf{k}^\pm$  states are produced by operating with the spin-flip operator  $S$ ,

$$S = \prod_{\mathbf{R} \in C} [S^+(\mathbf{R}) + S^-(\mathbf{R})], \quad (21)$$

on their complementary three-, two-, and one-particle, and vacuum states, respectively.

Then, by the construction procedure, one can easily prove that there is an isomorphism, i.e., a one-to-one correspondence preserving group multiplication, between the elements of the present basis and the one constructed in method M1. The correspondence is given in Table I.

In order to simplify the calculation of the matrix elements of  $H'$ , we rewrite  $H'$  in terms of the operators  $b_{\mathbf{k}^\pm}^\alpha$ ,  $\alpha = x, y, z$ , where

$$b_{\mathbf{k}^\pm}^\alpha = \sum_{\mathbf{R}} e^{i\mathbf{k} \cdot \mathbf{R}} [S^\alpha(\mathbf{R}) \pm S^\alpha(\mathbf{R}+\mathbf{d})], \quad \alpha = x, y, z \quad (22a)$$

$$b_{\mathbf{k}^\pm}^\pm = b_{\mathbf{k}^\pm}^x \pm i b_{\mathbf{k}^\pm}^y, \quad (22b)$$

which one can prove transform according to the  $\mathbf{k}^\pm$  irreducible representations. Thus

$$\begin{aligned} H' = \sum_{\alpha, \beta = x, y, z} \sum_{\mathbf{k}} (L_{\mathbf{k}^+}^{\alpha\beta} b_{\mathbf{k}^+}^\alpha b_{\mathbf{k}^+}^\beta + L_{\mathbf{k}^-}^{\alpha\beta} b_{\mathbf{k}^-}^\alpha b_{\mathbf{k}^-}^\beta) \\ - \sum_{\alpha = x, y, z} f^\alpha b_{\mathbf{k}_0^+}^\alpha, \end{aligned} \quad (23a)$$

Since the elements of  $\hat{G}$  commute with  $H'$ , the eigenstates of  $H'$  belong to the irreducible representations  $\mathbf{k}^+$  and  $\mathbf{k}^-$  of  $\hat{G}$ . Thus the eigenstates of  $H'$  have the following transformation properties:

$$\hat{T}_{\mathbf{a}} |\Psi_{\mathbf{k}^\pm}\rangle = e^{i\mathbf{k} \cdot \mathbf{a}} |\Psi_{\mathbf{k}^\pm}\rangle, \quad \mathbf{a} = \mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_1 + \mathbf{a}_2 \quad (18a)$$

$$\hat{I} |\Psi_{\mathbf{k}^\pm}\rangle = \pm |\Psi_{\mathbf{k}^\pm}\rangle. \quad (18b)$$

The complete set of states belonging to the various irreducible representations is built by starting from a "vacuum" state  $|0\rangle$  defined as the state which is eigenstate of  $S^2(\mathbf{R})$  at all cluster sites  $\mathbf{R} \in C$  with eigenvalues  $-\frac{1}{2}$ . The "one-particle"  $\mathbf{k}^\pm$  states, i.e., states with total  $S^2 = -3$ , are built by operating on the vacuum state with the operators  $b_{\mathbf{k}^\pm}^\pm$  [see Eqs. (22b)]

$$|\phi_{\mathbf{k}^\pm}\rangle = \frac{1}{\sqrt{8}} b_{\mathbf{k}^\pm}^\pm |0\rangle. \quad (19)$$

The "two-, three-, and four-particle"  $\mathbf{k}^\pm$  states, i.e., those corresponding to total  $S^2 = -2, -1, 0$ , are defined through one, two, and three position parameters, e.g.,

$$L_{\mathbf{k}^\pm}^{\alpha\beta} = \frac{1}{16} \sum_{\mathbf{R}} e^{i\mathbf{k} \cdot \mathbf{R}} [A^{\alpha\beta}(\mathbf{R}) \pm A^{\alpha\beta}(\mathbf{R}+\mathbf{d})], \quad \alpha, \beta = x, y, z. \quad (23b)$$

The one-to-one correspondence between states of M1 and M2, and operators of M1 and M2, leads to a one-to-one correspondence between matrix elements of the  $b_{\mathbf{k}^\pm}^\alpha b_{\mathbf{k}^\pm}^\beta$  operators. Thus the same computer subroutines can be used. The perturbation term  $H_\delta$  has a simple form in the case of  $s = \frac{1}{2}$ :

TABLE I. The relation between the translation group used in dealing with one magnetic ion per unit cell (M1, see Ref. 5) and the translation-inversion group of the present method (M2) which deals with two magnetic ions per unit cell. The relation between the corresponding irreducible representations is also given.

$\mathbf{R} \in C$		Irreducible representations	
M1	M2	M1	M2
0	0	0	$\mathbf{k}_0^+$
$\mathbf{R}_1$	$\mathbf{a}_1$	$\mathbf{k}_1$	$\mathbf{k}_1^+$
$\mathbf{R}_2$	$\mathbf{a}_2$	$\mathbf{k}_2$	$\mathbf{k}_2^+$
$\mathbf{R}_3$	$\mathbf{a}_1 + \mathbf{a}_2$	$\mathbf{k}_3$	$\mathbf{k}_3^+$
$\mathbf{R}'_3$	$\mathbf{d}$	$\mathbf{k}_3$	$\mathbf{k}_0^-$
$\mathbf{R}'_2$	$\mathbf{a}_1 + \mathbf{d}$	$\mathbf{k}'_2$	$\mathbf{k}_1^-$
$\mathbf{R}'_1$	$\mathbf{a}_2 + \mathbf{d}$	$\mathbf{k}'_1$	$\mathbf{k}_2^-$
$\mathbf{R}'_z$	$\mathbf{a}_1 + \mathbf{a}_2 + \mathbf{d}$	$\mathbf{k}'_z$	$\mathbf{k}_3^-$

$$H_\delta = \frac{1}{2} \sum_{\alpha\beta=x,y,z} A^{\alpha\beta}(0) \sum_{\mathbf{R} \in C} \langle \Psi | S^\alpha(\mathbf{R}) | \Psi \rangle S^\beta(\mathbf{R}) - \sum_{\alpha=x,y,z} A^{\alpha\alpha}(0). \quad (24)$$

Thus all antiferromagnetic eigenstates of  $H'$  are exact eigenstates of the cluster Hamiltonian  $H$ , with eigenvalues corrected by the constant term:  $-\sum_{\alpha=x,y,z} A^{\alpha\alpha}(0)$ . The correction term of the energy, which by means of the eigenstates of  $H'$  gives the eigenvalues of  $H$  by first-order perturbation theory, is

$$E_\delta(|\Psi_{\mathbf{k}\pm}\rangle) = \frac{1}{16} \sum_{\alpha,\beta=x,y,z} A^{\alpha\beta}(0) \langle \Psi_{\mathbf{k}\pm} | b_{\mathbf{k}_0^+}^\alpha | \Psi_{\mathbf{k}\pm} \rangle \times \langle \Psi_{\mathbf{k}\pm} | b_{\mathbf{k}_0^+}^\beta | \Psi_{\mathbf{k}\pm} \rangle - \sum_{\alpha=x,y,z} A^{\alpha\alpha}(0). \quad (25)$$

It can be shown that (when  $s = \frac{1}{2}$ ) the sum  $\sum_{\alpha,\beta=x,y,z} |A^{\alpha\beta}(0)|$ , which only depends on the choice of the direction of single periodicity, is always an upper bound for the absolute value of the energy correction.

#### IV. DISCUSSION

The method we propose here makes the treatment of the ground state of dipolar crystals with two equivalent magnetic ions per unit cell analytically and numerically tractable. The main disadvantage is that some irreducible

representations are omitted.

This deficiency, however, does not have the disadvantages resulting from such an omission in the classical case. In the quantum-mechanical treatment spin correlations, such as  $\langle S_i^z S_j^z \rangle$ , may be different from  $+\frac{1}{4}$  even in the case that  $k=0$ , whereas in the classical treatment  $k=0$  implies ferromagnetism. In addition, in the method we developed the eigenstates of the  $k=0$  representation are always included, and since  $dE(k)/dk=0$  at  $k=0$ , it follows that  $E(k=0)$  is an energy extremum. Although we have not seen a proof that the minimum always occurs at this point, experience from the energy-band theory of crystals and the spin systems we dealt with, indicates that  $E(0)=E_{\min}$ . Thus, as far as the ground state is concerned our method is justifiable although our statement about the energy minimum relies on experience.

It should be noted that the present method, in addition to omitting several representations, restricts the search for the ground state to a space of lower dimensionality. For the identity ( $\mathbf{k}_0^+$ ) representation the dimension of the corresponding subspace for the general treatment is 4336, whereas for the present method it is 46, and for the other 15 irreducible representations the above dimensions are 4080 and 30, respectively.

As a final test of the validity of our method, we compare the theoretical results with the experimental ones. This is done in the following paper where we deal with the  $\text{DyCl}_3 \cdot 6\text{H}_2\text{O}$ , for which experimental data was available.<sup>16</sup>

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