Effects of symmetry lowering of spin systems and comparison with experiment.

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Abstract. The Heisenberg Hamiltonian is a highly symmetric Hamiltonian where group theory is very effective for the qualitative as well as the quantitative study of its eigenstates. For this matter, a system of nested algebras related to the Irreps of the symmetry group of the Hamiltonian was developed. Recently, experimental facts on magnetic materials showed that interactions lowering the symmetry, like the Dzialoshinski term, are necessary for their interpretation. A perturbation theory is developed for such Hamiltonians and applied to experimental data with very good agreement between theory and experiment.

1. Introduction

The Heisenberg Hamiltonian

\[ H = \sum_{ij} J_{ij} S_i \cdot S_j \]  

(1)

in spite of its simplicity, has been a successful model Hamiltonian for studying the magnetic properties of solids, molecules and clusters. This is a highly symmetric Hamiltonian as it is invariant under a permutation group reflecting the geometric symmetries of the physical system under consideration and a rotation group in the spin space. The geometric symmetries of the physical system under consideration can be represented by a permutation group of the spin indices. In practice it is more convenient to think in terms of the group of rotations and translation instead of the permutation group. Thus, one can replace the index i by the position \( \mathbf{R}_i \) and define the translations \( T_{\mathbf{R}_i} \) as follows

\[ T_{\mathbf{R}_i} S_{\mathbf{R}_j} T_{\mathbf{R}_i}^{-1} = S_{\mathbf{R}_i + \mathbf{R}_j} \]  

(2)

while the rotation operator is defined accordingly,

\[ R_\omega S_{\mathbf{R}_j} R_\omega^{-1} = S_{(R_\omega \mathbf{R}_j)}. \]  

(3)

The rotations \( \hat{R}_\theta \) in the spin space are defined as

\[ \hat{R}_\theta S_{\mathbf{R}_j} \hat{R}_\theta^{-1} = S'_{\mathbf{R}_j} \]  

(4)

or explicitly

\[
\begin{bmatrix}
S'_{ij}^x \\
S'_{ij}^y \\
S'_{ij}^z
\end{bmatrix} = \hat{R}_\theta \begin{bmatrix}
S_{ij}^x \\
S_{ij}^y \\
S_{ij}^z
\end{bmatrix}
\]  

(5)
where $\hat{R}_\theta$ is the rotation matrix in the three dimensional Euclidean space.

Beyond these symmetries, dynamical symmetries also exist [1, 2]. In most studies particular emphasis is given on the Bethe ansatz. The physical picture of this type of solution is that it considers the holes (spin down lattice sites) as particles possessing a linear momentum. However, the existence of such type of solutions is not implied by any symmetry group of the Hamiltonian. The success of the Bethe ansatz is that it starts from a good physical picture, related to the fact that the number of holes is preserved under the action of the Hamiltonian $H$, as the total angular momentum $S^z = \sum S_j^z$ commutes with $H$. Beyond this, no advantage is made of the symmetry group of the Hamiltonian. The Bethe ansatz solutions have been investigated extensively in a series of papers by [1, 2, 3, 4]. In this paper we shall follow a different approach.

In a series of papers [5, 6, 7, 8, 9] we made full exploitation of the symmetry. Further, we classified the algebras of the spins in a sequence of algebras $A_i$ with the inclusion relation, i.e. $A_i \subset A_{i+1}$. The advantage of this classification of algebras is that one can write part of the Heisenberg Hamiltonian $H$ in terms of the Casimir operators of these algebras. The next step is to construct eigenstates of the Casimir operators which also belong to the Irreps of the permutation group of the indices. In this way, a part of the Hamiltonian $H_0$, is a linear combination of these operators and is automatically diagonal. The next step is to find the nonvanishing matrix elements of $H_a = H - H_0$ and diagonalize it. For this purpose it is much more convenient to write the operators of the various algebras as Irreducible tensor operators of $G$.

Thus the operators

$$b_k = \sum e^{ik \cdot R_i} S_{R_i}$$

transform according to the $k$ Irrep of the group of the lattice translations. By taking into account the commutation relations

$$[S_{R_i}^x, S_{R_j}^y] = i \delta_{ij} S_{R_j}^z$$

we find

$$[b_k^x, b_{k'}^y] = ib_{k+k'}^z$$

for the case of the space groups. Then it follows that the operators $b_0$ form the $A_0$ algebra since

$$[b_0^x, b_0^y] = ib_0^z$$

Similarly when $K$ is a reciprocal lattice vector, it follows that

$$b_{K+k} = b_k$$

and therefore

$$[b_{K/2}^x, b_{K/2}^y] = ib_0^z$$

since the label $K$ is equivalent to 0 as far as the Irrep of the translation group is concerned. The new operators have the following commutation relations with those of the $A_0$ algebra

$$[b_0^x, b_{K/2}^y] = ib_{K/2}^z.$$ 

Notice that $b_{-K/2} = b_{K/2}$ since $b_{-K + K/2} = b_{K/2}$.

In this way we get the $A_1$ algebra containing $A_0$ when our system is the one-dimensional lattice with periodic boundary conditions to be referred to as the linear ring in the following. For the multidimensional lattice where the reciprocal lattice vectors are $K_1, K_2, K_3$, the vectors of the Brillouin zone are the $\frac{1}{2} K_i$ and their linear combinations together with 0 label the $A_1$ algebra.
The Casimir operators are \( C_0 = b_0 \cdot b_0 \) for \( A_0 \) and \( C_1 = b_0 \cdot b_0 + b_{K/2} \cdot b_{K/2} \) and in this way the eigenvalues of \( b_0 \cdot b_0 \) and \( b_{K/2} \cdot b_{K/2} \) can be directly determined from the values of the Casimir operators.

In general, the operators \( B_n = C_n - C_{n-1} \) form a commuting set. For this reason the eigenvalues and eigenstates of the operator
\[
H_0 = \sum \Lambda_n B_n
\]
with \( \Lambda_n \) real numbers can be found and they can be used as a complete orthonormal set by means of which one can find the exact eigenstates by diagonalizing the matrix \( D \) resulting from the matrix elements of \( H - H_0 \). In this way one can assign a physical meaning to the eigenstates considering the predominant eigenstate coefficient in the expansion of the exact solution. More details in the implementation of the hierarchy of algebras method can be found in Refs [5, 6].

2. Results and comparison with experiments.

One of the crystals extensively studied experimentally is the \((\text{N2H5})\text{CuCl3}\) compound. We shall use here the data given by Hagiwara and coworkers\[10\]. For this crystal we adopted the model of 16-spin-1/2 ring with nearest neighbor (nn) and next nearest neighbor (nnn) interactions\[11\]. This model can simulate with excellent accuracy the magnetic behavior of this system. We have approached this problem with two different methods. First, we calculated the susceptibility of the 16-spin ring from the exact eigenstates with the appropriate coupling constants \( j_1 \) and \( j_2 \). Second, the same physical quantity was calculated for a 32-spin-1/2 ring, in which the interaction of the nearest neighbors was treated as a perturbation, because \( j_1 < j_2 \) according to Hagiwara \[10\]. In the latter case, we used the Landau thermodynamic perturbation theory for the free energy and the Gibbs average for the thermodynamic quantities, i.e. the thermal average of a physical quantity \( A \) is given by
\[
< A >_T = \frac{\text{Tr}[Ae^{-\beta H}]}{\text{Tr}[e^{-\beta H}]}
\]
where \( \beta = 1/kT \). Our theoretical results about the magnetic susceptibility as a function of temperature are presented in figure 1. The relation \( j_1 = 0.2j_2 \) gives the best fitting of the theory to the experimental results. Both models give practically the same results for the magnetic susceptibility and are in good agreement with those derived experimentally\[10\]. In the low temperature limit the 32-spin model gives a better fit to the experimental results, as expected.

We come now to the NENP crystal, \( \text{Ni(}C2H6N2)\text{NO2(ClO4)} \), which is an one dimensional antiferromagnet with \( S=1 \), with only nn interactions. This crystal was studied experimentally by Nojiri and coworkers \[12\]. By adopting an 8-spin-1 rings model and applying the methodology of hierarchy of algebras we determined the exact eigenstates and eigenvalues of this system which are \( 3^8 = 6561 \). We used these energy eigenstates to determine the thermal magnetization vs. magnetic field by applying the Gibbs thermal average. In figure 2 we present our theoretical results for NENP and compare them with the experimental ones from \[12\], using \( j_1 = 45.5^\circ K \) and \( g=2.23 \). The theoretically derived critical magnetic field is 122 Tesla in complete agreement to its experimental value. The coincidence between experimental and theoretical results is remarkable although a model of only 8 spins was used.

Another application of our method was to square lattice compounds and in particular to \( \text{K}_2\text{V}_2\text{O}_5 \). The above system presents a weak ferromagnetic behavior at low temperatures, when the external magnetic field is perpendicular to the \( z \)-axis, i.e. parallel to the \( xy \) plane of the square lattice \[13\]. This ferromagnetism was attributed to an additional interaction \( H_{DM} \), introduced by Dzialoshinski and Moriya (DM) \[14\] which has the form
\[
H_{DM} = j_{DM} \sum_{nn} (\text{S}_{R_i} \times \text{S}_{R_j})^z.
\]
Figure 1. Magnetic susceptibility vs. temperature of (N$_2$H$_5$)CuCl$_3$ (circles) divided by its maximum value [10]. The solid line is the magnetic susceptibility of a 32-spin-1/2 ring and the dashed line that of a 16-spin-1/2, obtained theoretically by including nnn interaction and $j_1 = 0.2j_2$.

Figure 2. Magnetization of NENP at $T=10^9$K vs. magnetic field. The magnetic field is divided by its critical value and the magnetization by its maximum value. The circles are the experimental values [12] and the solid line the theoretical results of an 8-spin-1 ring, without nnn-interaction.

In fact this is the smallest symmetry breaking interaction. Thus, the Hamiltonian considered is the following

$$H = \sum_{ij} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j + j_{DM} \sum_{nn} (\mathbf{S}_{R_i} \times \mathbf{S}_{R_j})^z - gh \sum \mathbf{S}_{R_i}$$  \hspace{1cm} (16)$$

where the first term is the nearest neighbor Heisenberg Hamiltonian, the second term the DM interaction between nearest neighbors and the third term is due to the external magnetic field. It is evident that the above Hamiltonian has lower symmetry than the typical Heisenberg one, due
to the DM term, which is invariant only under rotations about the z-axis, while the Heisenberg one is invariant under any rotations. One can show that this lowering of symmetry causes the weak ferromagnetic effect at low temperatures when the external magnetic field is normal to the z-axis.

We dealt with the DM term of the Hamiltonian supposing that every spin at a site of the lattice interacts with the thermal average of the others. We treated this interaction in second order perturbation theory and the susceptibility of the crystal was calculated self-consistently.

**Figure 3.** Experimental magnetic susceptibility vs. temperature of K$_2$V$_2$O$_5$ divided by its maximum value (circles), when the external magnetic field (H=100 Oe) is in the z axis of the crystal [13]. The solid line is the theoretical magnetic susceptibility, including the DM interaction.

**Figure 4.** Theoretical (solid curve) and experimental (circles) magnetic susceptibility of K$_2$V$_2$O$_5$, when the external magnetic field (H=100 Oe) is in the xy plane of the crystal [13].

In figure 3 we present the theoretically calculated magnetic susceptibility together with the experimental one, for a magnetic field of 100 Oe in the z-direction of the crystal. No
ferromagnetism appears as expected. One can see from this figure that, our theoretical results for the square lattice are in remarkable agreement with the experimental results presently available. For the z-direction of the external magnetic field the DM interaction does not change the qualitative characteristics of the crystal. This is easily concluded from group theoretical arguments. The coupling constant \( j \) with the best fit of the theoretical to the experimental results of Ref [13] is equal to 11.2\( ^\circ \)K, while the value adopted by these authors is of 12.6\( ^\circ \)K.

In figure 4 we present the same physical quantities, when the external field of 100 Oe is in the xy-plane [13]. For the value of \( j_{\text{DM}} = 0.12j \), our theory gives a change of phase from the ferromagnetic state to the antiferromagnetic one at 4\( ^\circ \)K, in complete agreement with the experiment.

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