Magnon Bound States in Anisotropic Linear Chains*

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The recent observation of two-, three-, four-, and five-magnon bound states in the linear chains of $CoCl_2 \cdot 2H_2O$ has prompted a theoretical examination of such states in an anisotropic linear ferromagnetic chain with $S=\frac{1}{2}$. A new method called the Ising-basis-function (IBF) method is developed. This method treats the conventional, localized Ising wave functions as Wannier functions, from which a complete, orthonormal set of Bloch functions (IBF's) is formed. Using these IBF's as basis functions, we obtain the expression for the energy of the two-magnon bound state originally found by Orbach for general longitudinal exchange anisotropy. Furthermore, we can calculate the energy of the ($n>2$)-magnon bound states for the case of strong longitudinal anisotropy. The method is also applied to describe the effect of transverse exchange anisotropy. It is shown that this anisotropy causes an interaction between bound states, particularly important near zero field, and gives rise to a finite probability of exciting the bound states by photon absorption. The generalization of this method to treat bound states in two and three dimensions and for $S>\frac{1}{2}$ is also discussed. The method is simple and has a direct physical interpretation. As an example, a physical description of the two-magnon bound state in a general system is given. Since the IBF method automatically contains some of the magnon-magnon interactions in zero order, it should be useful in other problems where these interactions are important.

INTRODUCTION

A SIMPLE starting point for a discussion of magnon bound states is the Ising model. We consider a general spin system where each spin S is coupled to its p nearest neighbors by a ferromagnetic exchange interaction J. According to the Ising model, the appropriate Hamiltonian is given by

$$\mathcal{H}=-\sum_{i,\delta} JS_i^z S_{i+\delta}^z-\sum_i g_{\parallel}\mu_B H_0 S_i^z, \quad (1)$$

where S_i^z may take on the values[1] $S, S-1, \ldots, -S$. The external magnetic field H_0 is along the axis of magnetization z, and the corresponding spectroscopic splitting factor is $g_{\parallel}$. The elementary excitations of this system are conveniently described in terms of spin clusters: an n-fold spin cluster is defined as n *neighboring* spin deviations. The excitation energy E_n of such an n-fold cluster may be calculated[2] from (1):

$$E_n(n')=nE_1-n'2J \quad (2)$$

with

$$E_1=2pSJ+g_{\parallel}\mu_B H_0, \quad (3)$$

where E_1 is the energy necessary to excite a single spin deviation and n' is the number of bonds between neighboring spin deviations. This result may be interpreted as showing that there is a binding energy $2J$ for each such bond, which lowers the energy of the n-fold cluster from the energy of n unclustered excitations. For the special case of a nonoverlapping string of n spin deviations, $n'=n-1$. Examples of the energies of such clusters, $|n\rangle$, are plotted versus the applied field in Fig. 1. In this figure the energy and field scales have been normalized so that the onefold cluster energies E_1 are the same.

The dependence of spin clusters on p and S is contained in (2). The energy E_n of an n-fold cluster is lower than the energy nE_1 of n independent spin deviations by the binding energy $2n'J$. For any particular cluster configuration, this binding energy depends only on J. However, if p and/or S were larger, both E_n and nE_1 would be larger, while the binding energy would remain the same. Thus, the *relative* binding energy is smaller for larger pS, as is illustrated in Fig. 1.

In the presence of transverse components of the exchange interaction, the first excited state is a (non-

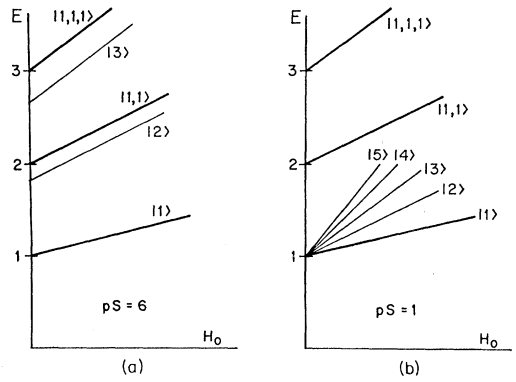

FIG. 1. The Ising energy spectrum for n-fold clusters $|n\rangle$, for (a) $pS=6$ and (b) $pS=1$. (Here $n'=n-1$.) For ease of comparison, the energy scales are in units of $2pSJ$ and the magnetic field scales have been normalized by similar factors so that the one fold cluster energies are the same in (a) and (b). $|1,1\rangle$ and $|1,1,1\rangle$ represent two and three onefold clusters, respectively.

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[1] Strictly speaking, the Ising model refers to this Hamiltonian with $S=\frac{1}{2}$, so that only two states are possible at a given site. We shall, in fact, concentrate on that case, but some general points can be illustrated by first considering a more general model in which S is unrestricted.

[2] J. B. Torrance, Jr., Ph. D. thesis, Harvard University, 1968 (unpublished); Harvard University, DEAP, Technical Report No. 1, 1969 (unpublished).

localized) magnon or spin wave. The spectrum of the higher-excited states is more complicated than the simple Ising result (Fig. 1). Nevertheless, excitations which resemble n-fold clusters may exist, i.e., there may exist n-spin excitations whose energy is less than the energy of n spin waves; these are called magnon bound states. In this case the binding energy, trivially obtained with the simple Ising model, is viewed as arising from the (attractive) interactions between magnons. From either viewpoint, however, the interactions giving rise to bound states are most important in the case of the linear chain with $S=\frac{1}{2}$, where pS has its minimum value 1. For this reason, and because of its relevance to our experimental results on $CoCl_2\cdot 2H_2O$,[2-4] we shall henceforth restrict our attention to this case.

LINEAR FERROMAGNETIC CHAIN WITH $S=\frac{1}{2}$

The general exchange Hamiltonian describing the $S=\frac{1}{2}$ linear chain is given by

$$\mathcal{H}=-2\sum_i (J^{zz}S_i^zS_{i+1}^z+J^{xx}S_i^xS_{i+1}^x+J^{yy}S_i^yS_{i+1}^y) -\sum_i g_{\parallel}\mu_B H_0 S_i^z. \quad (4)$$

Although the exchange interaction is often nearly isotropic, the anisotropy of the exchange is crucial for the existence and observation of magnon bound states. It is convenient to decompose the general exchange Hamiltonian (4) as follows:

$$\mathcal{H}=\mathcal{H}^I+\mathcal{H}^\perp+\mathcal{H}^a, \quad (5)$$

where

$$\mathcal{H}^I=-\sum_i (2J^{zz}S_i^zS_{i+1}^z+g_{\parallel}\mu_B H_0 S_i^z), \quad (6)$$

$$\mathcal{H}^\perp=-\sum_i J^\perp(S_i^+S_{i+1}^-+S_i^-S_{i+1}^+), \quad (7)$$

$$\mathcal{H}^a=-\sum_i J^a(S_i^+S_{i+1}^++S_i^-S_{i+1}^-), \quad (8)$$

with

$$S_j^\pm=S_j^x\pm iS_j^y, \quad J^\perp\equiv\tfrac{1}{2}(J^{xx}+J^{yy}), \quad J^a\equiv\tfrac{1}{2}(J^{xx}-J^{yy}). \quad (9)$$

$\mathcal{H}^I$ is the Ising part of the Hamiltonian, while $\mathcal{H}^\perp$ contains the effects due to the mean transverse component $J^\perp$ of the exchange. The amount of longitudinal exchange anisotropy is measured by $J^{zz}-J^\perp$, and J^a is a measure of the transverse anisotropy.

This problem has been solved for several special cases. For example, the solution for a pure Ising exchange interaction, i.e., $J^\perp=J^a=0$, is described in the Introduction. The eigenfunctions are n-fold clusters: an n-fold cluster in an $S=\frac{1}{2}$ linear chain is defined as n adjacent spins which are reversed with respect to the majority of the spins on the chain.[5] These clusters correspond to n-magnon bound states and their energy is [from (2) and (3) with $n'=n-1$] given by

$$E_n=2J^{zz}+ng_{\parallel}\mu_B H_0. \quad (10)$$

Physically, Zeeman energy is associated with each spin in the cluster, while exchange energy ($2J^{zz}$) is lost only at the ends of the cluster, giving a contribution independent of the size of the cluster.

In the case of pure Heisenberg, or isotropic, exchange, i.e., $J^{zz}=J^\perp$ and $J^a=0$, Bethe[6] found that n-magnon bound states exist in the $S=\frac{1}{2}$ linear chain and that their energy is given by

$$E_n(K)=(2J^{zz}/n)(1-\cos Ka)+ng_{\parallel}\mu_B H_0, \quad (11)$$

where K is the total momentum.

For arbitrary $j^\perp\equiv J^\perp/J^{zz}$, conventional spin-wave theory[7] gives the energy for one-magnon excitations:

$$E_1(K)=2J^{zz}(1-j^\perp\cos Ka)+g_{\parallel}\mu_B H_0. \quad (12)$$

Note that the energy at $K=0$, measured in ferromagnetic resonance experiments, is decreased from the Ising value linearly in $j^\perp$. The energy for the two-magnon bound state for arbitrary $j^\perp$ has been obtained by Orbach[8]:

$$E_2(K)=2J^{zz}[1-(j^\perp)^2\cos^2\tfrac{1}{2}Ka]+2g_{\parallel}\mu_B H_0. \quad (13)$$

Note that (12) and (13) agree with (10) for $j^\perp=0$ and with (11) for $j^\perp=1$.

Wortis[9] and Hanus[10] have used Green's functions to calculate the energy of the two-magnon bound state in one, two, and three dimensions for arbitrary spin S. Their results are qualitatively similar to the discussion of the Ising model in the Introduction.

Recently, magnon bound states with up to five magnons have been observed in far infrared measurements[2-4] on $CoCl_2\cdot 2H_2O$. These experiments also reveal important effects due to transverse exchange anisotropy, Eq. (8). It appears difficult to extend the exact solutions of Bethe, Orbach, Wortis, or Hanus to include this anisotropy or to describe bound states for $n>2$. For this reason, a new approach was developed. This approach is based on the Ising model and has the advantage that it is simple and that some of the magnon-magnon interactions are automatically included. We start with the Ising solution and consider the effects on this solution caused by $\mathcal{H}^\perp$, (7), and $\mathcal{H}^a$, (8).

[3] J. B. Torrance, Jr., and M. Tinkham, J. Appl. Phys. **39**, 822 (1968); Bull. Am. Phys. Soc. **13**, 390 (1968).
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[7] F. Keffer, in *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1966), Vol. 18 (1966).
[8] R. Orbach, Phys. Rev. **112**, 309 (1958).
[9] M. Wortis, Phys. Rev. **132**, 85 (1963); N. Fukuda and M. Wortis, J. Phys. Chem. Solids **24**, 1675 (1963).
[10] J. Hanus, Phys. Rev. Letters **11**, 336 (1963); J. G. Hanus, MIT Solid State and Molecular Theory Group, Quarterly Progress Report, Nos. 43, 44, 46 (unpublished).

ISING BASIS FUNCTIONS

In order to progress from the Ising results, we abandon the traditional localized Ising wave functions in favor of Bloch functions, which are known to be appropriate for any periodic Hamiltonian. (We imagine the linear chain looped to form a circle of N spins.) For example, the Bloch function corresponding to a onefold cluster $S_j^-|0\rangle$, localized at R_j, is the ordinary spin wave given by

$$|1;K\rangle\equiv 1/N^{1/2}\sum_j e^{iKR_j}S_j^-|0\rangle, \tag{14}$$

as first shown by Bloch.[11]

We now generalize this result to more elaborate excitations by considering an operator P_j. When this operator acts on the ground state, it generates a particular localized Ising excitation $P_j|0\rangle$, centered at $\bar{R}_j$. Treating this as a Wannier function,[12] we form the Bloch function corresponding to $P_j|0\rangle$ as follows:

$$|P;K\rangle\equiv 1/N^{1/2}\sum_j e^{iK\bar{R}_j}P_j|0\rangle. \tag{15}$$

Physically, (15) represents a normalized linear combination of localized functions centered at all possible sites $\bar{R}_j$ with the familiar $e^{iK\bar{R}_j}$ phase factor. These functions are called Ising basis functions, Ising Bloch functions, or simply IBF's. Since the Hamiltonian is periodic, the total momentum K is always a good quantum number and is used to label the Ising Basis Functions. The center of "mass" $\bar{R}_j$, conjugate to the total momentum, is determined as follows: If a localized excitation centered at $\bar{R}_j$ contains n spins deviated at R_{l_ν} $(\nu=1, 2, \ldots, n)$, $\bar{R}_j$ is given by

$$\bar{R}_j=\frac{1}{n}\sum_{\nu=1}^{n} R_{l_\nu}. \tag{16}$$

The Ising basis functions are best described by giving a few more examples:

(1) For the twofold cluster $S_j^-S_{j+1}^-|0\rangle$ the IBF is

$$|2;K\rangle=(1/\sqrt{N})\sum_j e^{iK(R_j+a/2)}S_j^-S_{j+1}^-|0\rangle; \tag{17}$$

(2) For two onefold clusters $S_j^-S_{j+\rho}^-|0\rangle$, the IBF is

$$|1,\rho,1;K\rangle=(1/\sqrt{N})\sum_j e^{iK(R_j+\rho a/2)}S_j^-S_{j+\rho}^-|0\rangle. \tag{18}$$

As seen in (18), this IBF is characterized by a parameter ρ, in addition to K. Physically, ρa is the separation between the two spin reversals which form the onefold clusters. For $S=\frac{1}{2}$, the two spin reversals may not be on the same site, and hence ρ may not take on the value zero. For $\rho=1$ (neighboring spin deviations), (18) reduces to (17), the expression for the twofold cluster; this case must be treated separately because it has a different Ising energy.

Just as the Ising excitation with deviations at R_1 and R_2 is equivalent to the one with deviations at R_2 and R_1, the IBF with ρ is equivalent to the one with $-\rho$, and also to the one $\rho+N$ (since we consider a circular chain of N spins). For these reasons, we consider the following values of ρ:

$$\begin{aligned} &2\leq\rho\leq\tfrac{1}{2}N, \quad \text{(even } N\text{)}\\ &2\leq\rho\leq\tfrac{1}{2}(N-1) \quad \text{(odd N)}. \end{aligned} \tag{19}$$

For $\mathcal{H}=\mathcal{H}^I$, (6), the two-onefold-cluster level is Q-fold degenerate, where Q is the number of possible values of ρ determined by (19). For odd N there are $Q=\frac{1}{2}(N-1)-1$ values of ρ. Including the twofold cluster, there are $Q+1$ IBF's to describe the possible states with two spin reversals for *each* of the N values of K. The total number of functions (for odd N) is then given by

$$N(Q+1)=\tfrac{1}{2}N(N-1)=\binom{N}{2}, \tag{20}$$

as required. There are also $\frac{1}{2}N(N-1)$ functions for the case of even N, but the counting is more subtle. Other IBF's containing two clusters are also characterized by a parameter ρ. For example:

(3) For the onefold-plus-twofold cluster

$$S_j^-S_{j+\rho}^-S_{j+\rho+1}^-|0\rangle,$$

the IBF is

$$|1,\rho,2;K\rangle=(1/\sqrt{N})\sum_j e^{iK[R_j+(2\rho+1)a/3]}\times S_j^-S_{j+\rho}^-S_{j+\rho+1}^-|0\rangle, \tag{21}$$

where $2\leq\rho\leq N-3$.

(4) For the three onefold cluster

$$S_j^-S_{j+\rho_1}^-S_{j+\rho_2}^-|0\rangle,$$

the IBF is

$$|1,\rho_1,1,\rho_2,1;K\rangle=(1/\sqrt{N})\sum_j e^{iK[R_j+(\rho_1+\rho_2)a/3]}\times S_j^-S_{j+\rho_1}^-S_{j+\rho_2}^-|0\rangle, \tag{22}$$

where there are complicated restrictions on ρ_1 and ρ_2. Ising basis functions corresponding to other local Ising excitations may be similarly defined.

Since the localized eigenfunctions $P_j|0\rangle$ of the Ising Hamiltonian form a complete orthonormal set, the Ising basis functions also do (as in the case of Wannier functions[12]). This fact enables us to find the solution to a general, time-independent magnetic problem,

$$\mathcal{H}|u\rangle=E_u|u\rangle, \tag{23}$$

by expressing the eigenfunctions $|u\rangle$ as linear combina-

[11] F. Bloch, Z. Physik **61**, 206 (1930); **74**, 295 (1932).
[12] G. H. Wannier, *Elements of Solid State Theory* (Cambridge University Press, London, 1960).

tions of the Ising basis functions $|\alpha\rangle$:

$$|u\rangle=\sum_{\alpha} C_{u,\alpha}|\alpha\rangle. \tag{24}$$

The solution to (23) is then given by

$$\det[\langle\beta|\mathcal{H}|\alpha\rangle-E_u\delta_{\alpha,\beta}]=0. \tag{25}$$

If one takes N_u terms in the expansion (24), the secular determinant will be $N_u\times N_u$.

EFFECTS OF $\mathcal{H}^\perp$

We temporarily neglect any effects due to $\mathcal{H}^a$ and consider the Hamiltonian $\mathcal{H}=\mathcal{H}^I+\mathcal{H}^\perp$. Since the $S_i^zS_{i+1}^z$ and $S_i^+S_{i+1}^-$ terms of $\mathcal{H}$ leave the total number m of spin reversals unchanged, the problem for each m value may be solved separately. The $m=0$ subspace contains only the ground state, where all of the spins in the chain are up. The ground-state energy is defined as zero. The subspace with one spin reversal ($m=1$) is spanned by the onefold cluster IBF or spin-wave states. In addition to the Ising energy E_1, Eq. (10), of the onefold cluster IBF, there is a diagonal matrix element of $\mathcal{H}^\perp$, so that the energy of the spin wave is given by

$$\begin{aligned}E_1(K)&=E_1+\langle 1;K|\mathcal{H}^\perp|1;K\rangle\\&=2(J^{zz}-J^\perp\cos Ka)+g_{11}\mu_BH_0,\end{aligned}$$

which is the familiar expression of spin-wave theory, Eq. (12).

Two-Magnon Bound State

For given K, the Ising basis functions for the case of two spin reversals in a linear chain are the twofold cluster IBF, $|2;K\rangle$, and Q two-onefold-cluster IBF's, $|1,\rho,1;K\rangle$. For $\mathcal{H}^I$, these IBF's are eigenfunctions with energies E_2 and $E_{1,1}=2E_1$, respectively. The effect of including $\mathcal{H}^\perp$ is to cause a coupling among these $Q+1$ different IBF's. For example, the $S_i^+S_{i+1}^-$ terms in $\mathcal{H}^\perp$ will couple the twofold IBF to the two onefold IBF which has $\rho=2$. Similarly, the state with ρ will be coupled to the states with $\rho+1$ and $\rho-1$. If we use the expressions (17) and (18) for the IBF's to calculate these matrix elements, we find[2]

$$\begin{aligned}&\epsilon_1\colon\langle 2;K|\mathcal{H}^\perp|1,\rho,1;K\rangle=-2J^\perp\cos\tfrac{1}{2}Ka\;\delta_{\rho,2}\equiv\epsilon_1\delta_{\rho,2},\\&\epsilon_2\colon\langle 1,\rho,1;K|\mathcal{H}^\perp|1,\rho',1;K\rangle\\&\quad=-2J^\perp\cos\tfrac{1}{2}Ka(\delta_{\rho,\rho'+1}+\delta_{\rho,\rho'-1})\\&\qquad\equiv\epsilon_2(\delta_{\rho,\rho'+1}+\delta_{\rho,\rho'-1}).\end{aligned} \tag{26}$$

For $J^\perp=0$ or $K=\pm\pi/a$, $\epsilon_1=\epsilon_2=0$. In this case the two-magnon bound state corresponds exactly to the twofold-cluster IBF and contains only two *neighboring* spin reversals. The Q unbound magnon states correspond to the two-onefold-cluster IBF's with energy $E_{1,1}=2E_1$. These two results are *exact*. On the other hand, if $J^\perp>0$ *and* K is away from the Brillouin zone boundary, the off-diagonal matrix elements are not zero and single IBF's are not eigenfunctions. Rather, the two-magnon bound state, for example, will contain not only the twofold cluster IBF but also an admixture (via ϵ_1) of the $\rho=2$ state, which in turn is coupled (by ϵ_2) to $\rho=3$, etc. Thus the two-magnon bound state generally contains a superposition of $\rho=1, 2, 3, 4, \ldots$, and the two spin reversals have some mean separation $\bar{\rho}a>a$. The energies of all the states are calculated in the Appendix using the IBF method, and they are plotted in Fig. 2 versus the coupling between the IBF's, $|\epsilon|=2J^\perp\cos\frac{1}{2}Ka$. A qualitative description of this calculation is given in the following paragraphs.

Temporarily neglecting the effects of ϵ_1, the Q ($\sim\frac{1}{2}N$) degenerate $|1,\rho,1;K\rangle$ states are coupled by ϵ_2. This coupling causes the levels to repel one another and form a continuous band of energies, whose width $4|\epsilon_2|$ is proportional to the coupling strength (Fig. 2). According to the IBF method, this band is formed by states with differing values of ρ, the separation between spin reversals. The simple spin-wave theory predicts an identical band, which is formed by the states of two noninteracting spin waves with different relative momenta.[2,7] From either point of view, the unbound magnons form an energy band or "continuum" of states, centered at the Ising energy $E_{1,1}=2E_1$.

The coupling of these states to the twofold cluster IBF caused by ϵ_1 is shared by all of the Q coupled states, so that ϵ_1 alters the energy of the *band* only to order $1/Q$ ($\sim 2/N$). The energy of the two-magnon bound state is lowered due to ϵ_1 as if this state were coupled to (and hence repelled from) a single level at the center of the band. This is illustrated in the expression for the bound-state energy, Eq. (13), which is just what would be expected from second-order perturbation theory, with an interaction ϵ_1, Eq. (26). For larger values of ϵ, the continuum is broader, while the bound-state energy falls. Although the width of the continuum increases linearly in ϵ and the bound-state energy falls only quadratically, the latter lies outside the continuum for all $\epsilon<1$, i.e., in the $S=\frac{1}{2}$ linear chain the two-magnon bound state exists for all cases except when

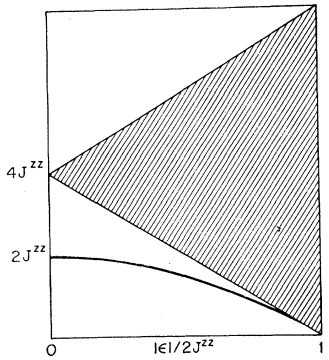

FIG. 2. The energy of the two-magnon bound state (lower curve) and the continuum (shaded area) are plotted as a function of the coupling ϵ between them, where $|\epsilon|=2J^\perp\cos(\frac{1}{2}Ka)$.

$j^{\perp}=1$ *and* $K=0$. The energy expression for the two-magnon bound state obtained using the IBF method (see Appendix) is the same as that found by Orbach,[8] Eq. (13); we have derived it in a different manner as an example of the IBF method and in order to show the physical interpretation of the results.

n-Magnon Bound States for $n>2$

Bethe[6] has found an expression, Eq. (11), for the energy of the n-magnon bound state for the special case of isotropic exchange ($j^{\perp}=1$). Also, in the Ising limit ($j^{\perp}=0$), one may calculate the n-magnon bound-state energy, (10). In general, however, the problem of n spin deviations, like the n-body problem, cannot be solved exactly without additional constants of the motion. We now indicate how the IBF method provides a convenient approximation scheme for the general case.

If we start from the Ising solution, the $S_i^+S_{i+1}^-$ terms in $\mathcal{H}^{\perp}$, Eq. (7), couple the n-fold cluster IBF directly to the onefold-plus-$(n-1)$-fold cluster and indirectly to the other clusters in the $m=n$ subspace. In the case of strong longitudinal anisotropy in the exchange $[(J^{\perp})^2\ll(J^{zz})^2]$, these couplings due to $\mathcal{H}^{\perp}$ are small and, for the purpose of calculating the energy of the n-magnon bound state, the *indirect* couplings may be neglected.[2] That is, for large longitudinal anisotropy, the n-magnon bound state consists mainly of the n-fold cluster IBF and the onefold-plus-$(n-1)$-fold cluster IBF's. This reduces the problem to one similar to that of the two-magnon bound state, in that the state is approximately spanned by a single IBF and a set of Q degenerate other IBF's. Using these IBF's, we may calculate the matrix elements of $\mathcal{H}^{\perp}$ connecting these states:

$$\begin{aligned}\epsilon_3:\ &\langle n;K|\mathcal{H}^{\perp}|1,\rho,(n-1);K\rangle\\ &\quad=-J^{\perp}(e^{-iKa/n}\delta_{\rho,-n}+e^{iKa/n}\delta_{\rho,2}),\\ \epsilon_4:\ &\langle 1,\rho,(n-1);K|\mathcal{H}^{\perp}|1,\rho',(n-1);K\rangle\\ &\quad=-J^{\perp}(e^{-iKa/n}\delta_{\rho,\rho'+1}+e^{iKa/n}\delta_{\rho,\rho'-1}).\end{aligned}\tag{27}$$

It is possible to use these matrix elements and carry out the detailed solution[2] in much the same way as for the two-magnon bound state (Appendix), but, as in that case, it is much easier simply to use perturbation theory. From (27), the n-fold cluster is coupled by ϵ_3 to two states, both with energy $2J^{zz}$ relative to the cluster; hence

$$\begin{aligned}E_n(K)&=E_n-2|\epsilon_3|^2/2J^{zz}\\ &=2J^{zz}[1-\tfrac{1}{2}(j^{\perp})^2]+ng_{\parallel}\mu_BH_0,\end{aligned}\tag{28}$$

valid for $n>2$ and $(j^{\perp})^2\ll 1$. In Fig. 3(a) the spin-wave energy, Eq. (12), and the bound-state energies, Eqs. (13) and (28), are plotted versus H_0 at $K=0$ and for $j^{\perp}=\frac{1}{4}$.

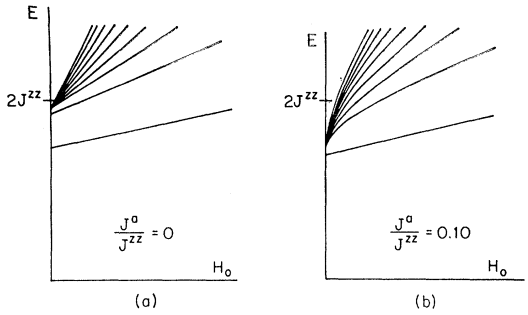

FIG. 3. The effects of $\mathcal{H}^{\perp}$ and $\mathcal{H}^{a}$ on the n-magnon bound-state energies at $K=0$ for $j^{\perp}\equiv J^{\perp}/J^{zz}=\frac{1}{4}$: (a) $j^{a}=0$; (b) $j^{a}=0.10$, where $j^{a}\equiv J^{a}/J^{zz}$. Compare with Fig. 1(b), in which $j^{\perp}=j^{a}=0$. The level $2J^{zz}$ on the ordinate here corresponds to unity on the ordinate of Fig. 1(b).

From (28), note that there is no dispersion in the bound-state energy for $n>2$, i.e., the slight downward shift from the Ising energy, (10), is independent of K. Mathematically, the difference in the form of the two-magnon bound-state energy, Eq. (13) (which has dispersion), and the energy for $n>2$, Eq. (28), arises from the different form of the matrix elements, (26) and (27), of $\mathcal{H}^{\perp}$. The source of this difference is the fact that the state of two onefold clusters separated by ρa is equivalent to the state where they are separated by $-\rho a$, but this is not true for the onefold-plus-$(n-1)$-fold cluster states for $n>2$.

For $\mathcal{H}=\mathcal{H}^{I}+\mathcal{H}^{\perp}$, the energy of the n-magnon bound state ($n>2$) for $j^{\perp}=1$ is given by (11), while for $(j^{\perp})^2\ll 1$ it is given by (28). Although it appears difficult to obtain an analytical expression for the energy for arbitrary $j^{\perp}$, we can predict the qualitative behavior of the solution between the two above limits. We are interested in the bound-state energy as a function of K for $H_0=0$, as we imagine $j^{\perp}$ to be increased from 0 to 1. For $j^{\perp}=0$, the energy is equal to the Ising energy $2J^{zz}$, which is independent of n *and* K. As $j^{\perp}$ is increased, the energy initially remains approximately independent of n and K, but is decreased quadratically in $j^{\perp}$, Eq. (28). This decrease may be pictured as arising from the coupling with the onefold-plus-$(n-1)$-fold cluster state. As $j^{\perp}$ is further increased, the coupling to higher cluster levels causes the energy to depend on both n and K. Since there are more interacting levels for larger n, these decreases are larger for larger n. The energy also falls more rapidly for small K than large K, giving rise to dispersion. In the limit of $j^{\perp}=1$, the exact result (11) shows that the $K=0$ energy is decreased to zero (for $H_0=0$) and the zone-boundary energy is $4J^{zz}/n$, which is less for larger n, consistent with our discussion. This picture would indicate that n-magnon bound states exist for all n and all $K>0$ for arbitrary $j^{\perp}$.

In $CoCl_2\cdot 2H_2O$, $j^{\perp}=0.15$ and the decrease predicted from (28) is ~ 0.3 cm^{-1}. This decrease is too small to permit experimental confirmation of (28) with certainty, but the data appear consistent with the predictions.[4]

EFFECTS OF $\mathcal{H}^a$

$\mathcal{H}^a$, Eq. (8), is caused by a transverse anisotropy in the exchange interaction, i.e., an inequivalence of the x and y directions. This anisotropy greatly complicates the problem of the linear chain, but is found to be extremely important in the experimental measurements[4] on $CoCl_2 \cdot 2H_2O$. $\mathcal{H}^a$ contains $S_i^- S_{i+1}^-$ and $S_i^+ S_{i+1}^+$ terms, which create or destroy two spin deviations. This is, therefore, a $\Delta m = \pm 2$ term which can cause a coupling between states with different m values. For example, the n-fold cluster IBF is coupled to the $(n+2)$-fold and the $(n-2)$-fold cluster IBF's. This coupling may be calculated[2] using the appropriate IBF's, giving

$$\langle n; K | \mathcal{H}^a | (n \pm 2); K \rangle = -2J^a \cos Ka. \qquad (29)$$

We now consider the effects of $\mathcal{H}^a$ on the solution to $\mathcal{H} = \mathcal{H}^I + \mathcal{H}^1$ [Fig. 3(a)]. The interaction (29) between levels caused by $\mathcal{H}^a$ is largest when the levels are closest together, i.e., at low fields. At $H_0 = 0$, the Ising model, Eq. (10), predicts that all the levels are degenerate. The addition of $\mathcal{H}^1$ causes the spin wave and two-magnon bound state to be shifted relative to the other $N-2$ levels [Fig. 3(a)]. These $N-2$ degenerate levels are coupled in the presence of J^a and mutually repel to form a band whose width is given by $8J^a \cos Ka$, following the arguments used above and in the Appendix in connection with $\mathcal{H}^1$. For $H_0 > 0$, the levels in Fig. 3(a) are slightly separated and the interaction caused by $\mathcal{H}^a$ is less. This interaction is illustrated in Fig. 3(b), where the $K = 0$ energies of a few of the n-fold clusters are plotted versus H_0 for $j^a \equiv J^a/J^{zz} = 0.10$. Clearly, J^a gives rise to curvature in the bound-state spectrum, especially at low fields. Note that at $H_0 = 0$ the three-fold cluster level is shifted down by $4J^a \cos Ka$ from its value in the absence of J^a, so that the effects on the energies may be quite large.

In addition to the curvature of the levels, the $\Delta m = \pm 2$ nature of $\mathcal{H}^a$ allows the admixture of IBF's with different m values. This admixture makes it possible effectively to relax the $\Delta m = \pm 1$ selection rule on the transition probability, so that a $\Delta m = \pm n$ transition may be made to excite the n-magnon bound state by photon absorption. These transition probabilities are discussed in greater detail and compared to experimental observation in the following paper.[4]

Certain effects of $\mathcal{H}^a$ may be understood by a crude model: Consider a spin precessing about the external magnetic field and an internal field due to its neighbors. Normally, the precession is circular and the z component S^z of the spin is constant and equal to its maximum value S. This is the ground state. However, if the x and y directions are inequivalent ($J^a \neq 0$), the spin will tend to deviate further out in one direction than the other, i.e., the precession will become elliptical. In this case S^z will oscillate below S, resulting in a time-average decrease in the saturation magnetization.

The presence of $\mathcal{H}^a$, therefore, alters the *ground* state. Mathematically, this problem is quite similar to the antiferromagnetic ground-state problem[7] (but there the complications are caused by J^1). As in that case, the problem is particularly difficult when examined in terms of the elementary excitations from the fully aligned ground state. From that point of view, there is a $\Delta m = 2$ coupling between the twofold cluster and the ground state which admixes even-fold clusters into the ground state, decreasing the magnetization. As in the antiferromagnetic problem, we assume that the energy required to create an n-magnon bound state from this new ground state is negligibly different from the energy required in the case of the fully aligned ground state.

CONCLUSION AND GENERAL DISCUSSION

Magnon bound states are obtained using conventional spin-wave theory only if nonlinear interaction terms between magnons are included. The Ising basis function (IBF) method, developed here, has the advantage that some of these interactions are automatically included, so that bound states exist from the start. We then consider the deviations from the Ising solution caused by the non-Ising terms in the Hamiltonian. The IBF approach is particularly powerful when the non-Ising terms are small, but it is still useful even when they are quite large. Furthermore, the method is simple and allows a direct physical interpretation of the results at each step.

As an example of this method, we have treated the $S = \frac{1}{2}$ linear ferromagnetic chain. The energy expression for the two-magnon bound state, originally found by Orbach,[8] is rederived. In addition, the energy of the n-magnon bound state for $n > 2$ is obtained for the case of large longitudinal anisotropy. The effects of transverse anisotropy in the exchange interaction are also examined. The coupling between bound states caused by this anisotropy gives rise to curvature in the field dependence of the bound-state energy, especially near $H_0 = 0$. This anisotropy is also responsible for the ability to excite the bound states spectroscopically. These theoretical results are in excellent agreement with the experimental observations[4] on $CoCl_2 \cdot 2H_2O$. It is straightforward to generalize the IBF method to two and three dimensions, arbitrary spin, more exchange interactions, impurity spins, more complex terms in the Hamiltonian, etc. The method may also be applied to antiferromagnets, but that problem is more complicated.

Finally, we shall recapitulate how the IBF method can simply reproduce the qualitative features of the two-magnon bound-state energy spectrum in a general spin system. (For simplicity, we consider only $H_0 = 0$.) For a cubic spin system with $j^1 = 1$ (Heisenberg exchange) and $S = \frac{1}{2}$, for example, the spectrum obtained by Wortis[9] for K along the (1,1,1) direction is shown in Fig. 4(a). In Fig. 4(b), the two-magnon

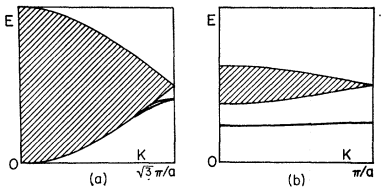

FIG. 4. The energy of the two-magnon bound state and the continuum are plotted versus K: (a) for K along (1,1,1) in a cubic crystal with $j^{\perp}=1$; (b) for a linear chain with $j^{\perp}=\frac{1}{4}$. $S=\frac{1}{2}$ and $H_0=0$ (schematic).

bound state and continuum are shown for the $S=\frac{1}{2}$ linear chain with $j^{\perp}=\frac{1}{4}$. (These parameters are appropriate for $CoCl_2\cdot 2H_2O$).[4] For ease of comparison, the energies are normalized to $4pSJ^{zz}$.

The energy of the *continuum* is obtained from simple spin-wave theory: the band lies between $(1+j^{\perp}\cos\pi K/K_0)$ and $(1-j^{\perp}\cos\pi K/K_0)$, where $K=\frac{1}{2}K_0$ at the zone corner. The band has zero width at the zone corner and maximum width $2j^{\perp}$ at $K=0$. In the case of large longitudinal anisotropy, the band is quite narrow [Fig. 4(b)] because $J^{\perp}\ll J^{zz}$.

In beginning the discussion of the *bound* states, it is important to recognize that the two-magnon bound-state energy at the zone corner is given *in general* by the *Ising* energy, i.e.,

$$E_2/4pSJ^{zz}=1-1/2pS\,, \tag{30}$$

obtained from Eq. (2), with $n'=1$ and $n=2$. For a K value less than the zone-corner value, the S^+S^- terms give rise to a coupling between the bound state and the continuum. Due to this interaction, the bound-state energy is lowered approximately quadratically in the coupling, but the width of the continuum increases linearly. Hence, at some critical value of K, the continuum will generally engulf the bound state. If we use (30) to give the bound-state energy at the zone corner, we may qualitatively sketch the bound-state energy and continuum versus K, as in Figs. 4(a) and (b). In three dimensions [Fig. 4(a)], the exact solution is complicated by the fact that there are three bound states. At the zone corner these states are degenerate and correspond to three pairs of spin reversals, which are neighboring along x, y, and z. For K values away from the zone corner, these states are no longer degenerate and we must rely on the exact calculations of Wortis.[9] From (30), the bound state lies closer to the continuum in cases where p and/or S are larger. In these cases, the threshold value of K is larger and the bound state exists in a smaller volume of K space. On the other hand, for $pS=1$ the two-magnon bound state exists for all $K>0$.

Physically, the two-magnon bound state at the zone corner contains two *neighboring* spin deviations (two-fold cluster IBF), as was recognized by Fukuda and Wortis.[9] For K values away from the zone corner, however, the S^+S^- terms cause the bound state to contain admixtures of *non*-neighboring deviations, so that the state may be described as two spin deviations separated by a mean distance $\bar{\rho}a$. For K values farther from the zone corner, the mean separation is larger and the deviations are less strongly bound. Near the threshold value of K, Fukuda and Wortis[9] have shown that the wavefunction is quite spread out.

For K less than the threshold value, the *bound* state does not exist. Within the continuum, however, there are still effects of the magnon-magnon interactions. These effects are evidenced in the resonant states, which have been described by Boyd and Callaway[13] and Silberglitt and Harris.[14] Similar states have been experimentally observed in certain antiferromagnets, where it is possible to excite two spin reversals (magnons) by far-infrared absorption or by Raman scattering.[15] Furthermore, these spin reversals are created in close proximity,[16] with total momentum $K=0$. The line shape and (broad) line width are characteristic of two independent magnons, but the energy of the observed band is slightly less than the energy of the band formed by two noninteracting magnons.[15,17] The magnon-magnon interaction thus modifies the energy of the observed magnons, but they still behave much like two nearly independent magnons. In $CoCl_2\cdot 2H_2O$, on the other hand, this interaction is so strong that it binds the two magnons together to form a single bound state, whose energy lies below the bottom of the band formed by two unbound magnons. These two types of excitations (scattering, or resonant, states and bound states) illustrate complimentary effects of magnon-magnon interactions.

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APPENDIX: DETAILED SOLUTION OF TWO-MAGNON BOUND STATE AND CONTINUUM

Let us first examine the properties of the solutions to the following problem: Q degenerate states with an energy $2E_1$ are each labelled by an index ρ, which may be pictured as the position along a chain, with $1\leq\rho\leq Q$ and $Q\sim N\sim 10^8$. Now let a perturbation $\mathcal{H}'$ couple

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each state ρ to its neighbors at $\rho+1$ and $\rho-1$, such that

$$\begin{aligned}\langle\rho|\mathcal{H}'|\rho-1\rangle&=\epsilon_2,\\ \langle\rho|\mathcal{H}'|\rho+1\rangle&=\epsilon_2^*.\end{aligned}\tag{A1}$$

If we assume a solution of the form $|u\rangle=\sum_\rho c_{u,\rho}|\rho\rangle$, we obtain

$$(2E_1-\lambda_u)c_{u,\rho}+\epsilon_2^*c_{u,\rho-1}+\epsilon_2c_{u,\rho+1}=0.\tag{A2}$$

In order to obtain an explicit solution to (A2), it is convenient to introduce cyclic or periodic boundary conditions, i.e., $c_{u,\rho}=c_{u,\rho+Q}$. These conditions imply that we should imagine the chain as forming a loop, so that $\rho+Q$ is the same position as ρ. We then assume a solution of the form

$$c_{u,\rho}=c_ue^{ik\rho}\tag{A3}$$

and obtain

$$\lambda_u=2E_1+2|\epsilon_2|\cos(k+\phi),\tag{A4}$$

where $\epsilon_2=|\epsilon_2|e^{i\phi}$. There are Q values of k, which correspond to the Q solutions. For large Q, k is virtually continuous and the λ_u form a continuous band of energies centered at $2E_1$ and having width $4|\epsilon_2|$.

We expect similar results, to order $1/Q$, for the problem *without* periodic boundary conditions, since only the end sites are directly affected. This problem can be formulated mathematically as finding the eigenvalues λ_Q such that the determinant $|M_Q(\lambda_Q)|=0$, where M_Q is a $Q\times Q$ matrix whose diagonal elements are $(2E_1-\lambda)$ and whose off-diagonal elements are those of $\mathcal{H}'$, quoted in (A1). (For the problem with periodic boundary conditions, similar off-diagonal matrix elements are also introduced between states $\rho=Q$ and $\rho=1$.) Although we shall not solve the problem explicitly, we note that we can set up a difference equation for $|M_Q(\lambda)|$ by expanding $|M_Q(\lambda)|$ in minors. This yields

$$|M_Q(\lambda)|=(2E_1-\lambda)|M_{Q-1}(\lambda)|-|\epsilon_2|^2|M_{Q-2}(\lambda)|.\tag{A5}$$

This difference equation may be solved by a conventional technique,[18] leading to the iterative result that

$$\begin{aligned}&|M_Q(\lambda)|/|M_{Q-1}(\lambda)|\\ &\quad=\tfrac{1}{2}(2E_1-\lambda)+[(2E_1-\lambda)^2-4|\epsilon_2|^2]^{1/2},\end{aligned}\tag{A6}$$

provided that $(2E_1-\lambda)^2>4|\epsilon_2|^2$.

We now use this result to work out the energy of the two-magnon bound state. From (25) and (26), the desired eigenvalues for the $m=2$ subspace of the Hamiltonian are the values of λ satisfying

$$\det\begin{pmatrix} E_2-\lambda & \epsilon_1 & & & & & \\ \epsilon_1^* & 2E_1-\lambda & \epsilon_2 & & & & \\ & \epsilon_2^* & 2E_1-\lambda & \epsilon_2 & & & \\ & & & \ddots & & & \\ & & & & \epsilon_2^* & 2E_1-\lambda & \epsilon_2 \\ & & & & & \epsilon_2^* & 2E_1-\lambda \end{pmatrix}=0,\tag{A7}$$

where only nonzero values are indicated. Expanding in minors, we obtain

$$(E_2-\lambda)|M_Q(\lambda)|-|\epsilon_1|^2|M_{Q-1}(\lambda)|=0,\tag{A8}$$

where $M_Q(\lambda)$ is the matrix described above. There are $Q+1$ solutions to (A8), Q of which are essentially the band of width $4|\epsilon_2|=8J^\perp\cos(\frac{1}{2}Ka)$ centered at $2E_1$ found above in (A4). The remaining one, which gives the two-magnon bound-state energy, can be found by equating the values of $|M_Q|/|M_{Q-1}|$ found from (A6) and (A8), which is valid provided this value of λ lies outside the band. This gives

$$|\epsilon_1|^2/E_2-\lambda=\tfrac{1}{2}(2E_1-\lambda)+\tfrac{1}{2}[(2E_1-\lambda)^2-4|\epsilon_2|^2]^{1/2}.$$

Solving for λ, with $\epsilon_1=\epsilon_2=\epsilon=-2J^\perp\cos(\frac{1}{2}Ka)$ and $E_1=E_2=2J^{zz}$, we find

$$\begin{aligned}\lambda&=E_2(K)=E_2+\epsilon^2/(E_2-2E_1)\\ &=2J^{zz}[1-(j^\perp)^2\cos^2(\tfrac{1}{2}Ka)],\end{aligned}\tag{A9}$$

which agrees exactly with the result (13) of Orbach[8] and is valid for $E_2(K)$ outside the continuum band of λ_Q. Since we noted above that the continuum extends only down to $4J^{zz}-4J^\perp\cos(\frac{1}{2}Ka)=4J^{zz}[1-j^\perp\cos(\frac{1}{2}Ka]$, this condition for validity is satisfied, and the state is truly bound, except when $j^\perp\cos(\frac{1}{2}Ka)=1$, i.e., for completely isotropic exchange *and* $K=0$.

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