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Effective Hamiltonians and the magnetic excitations of singlet ground-state systems

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Abstract. It is shown that at low temperatures the effective Hamiltonian, or spin-Hamiltonian, methods of magnetic resonance can be extended to the many-body problem of the magnetic excitation spectrum of singlet ground-state systems. This method of description is applied to the excitations of $\text{Cs}_2\text{Cr}_2\text{Br}_9$ and theoretical methods for calculating the effective-Hamiltonian parameters are discussed. It is shown that at low temperatures the magnetic interactions in perfectly crystalline singlet ground-state systems do not contribute to the excitation linewidths.

1. Introduction

The spin-wave-like excitation spectrum of magnetic systems with singlet ground states has been the object of study in many inelastic neutron scattering experiments. Rare-earth systems provide many examples, of which Pr is perhaps the most well documented (see the review by Stirling and McEwen (1987)) but examples can also be found in compounds of transition metals (see, e.g., Leuenberger *et al* 1984). The interpretation of the dispersion relationships of these materials is usually given by making random-phase approximations in the corresponding double-time-temperature Green functions. It is a striking fact that excellent fitting of the dispersion curves is obtained in this way. The excellence of this fitting cannot, however, be taken as indicative of the physical validity of the approximation employed. Leuenberger and Güdel (1985) for example illustrate a case where random-phase approximations in first or in second order can both give equally excellent fits to the low-temperature data, but with markedly different exchange and crystal-field parameters.

This paper presents some quite general observations relevant to the question of the fitting and theoretical interpretation of these dispersion curves. It will be shown that, for these materials at low temperatures, it is possible to construct quite general effective Hamiltonians which can give a perfect fit to experimental data, quite independently of any specific dynamical approximation. These effective Hamiltonians are in fact a generalisation to the many-body problem of the effective Hamiltonians so well known in the magnetic resonance of single ions. These generalised effective Hamiltonians serve the same purpose as do the spin Hamiltonians in magnetic resonance. They provide a theoretically well founded way of fitting experimental results, in terms of a limited number of parameters, while leaving quite open the theoretical interpretation of these results. An effective Hamiltonian in this sense means that the basis states within which

the Hamiltonian is defined are small enough in number to allow the Hamiltonian matrix to be diagonalised without any approximation. This will not be the case for the full physical Hamiltonian even though this itself is likely to be effective in the somewhat different sense of being a phenomenological rather than an *ab initio* construction. A theoretical connection between these different levels of description is given and it will be seen to offer a way of interpreting the experimental results which is an alternative to the more usual Green function methods. One immediate benefit of this method is that it makes clear that the excitation linewidths must vanish at $T = 0$ in the case of an array of interacting magnetic centres having perfect translational symmetry. The prediction of non-zero residual linewidths by some Green function calculations is therefore a spurious result associated with the higher-order decoupling approximations involved in calculations of this kind.

2. Magnetic excitations at $T = 0$

The problem concerns the dynamical behaviour of a set of interacting magnetic centres arranged on a perfectly periodic lattice. Each such localised centre is characterised by a set of crystal-field states, $|\alpha\rangle$ ($\alpha = 0, 1, \dots, p$) where $|\alpha = 0\rangle$ is a singlet ground state. In the general case there may be several centres in each primitive unit cell and these may be of different types. A general Hamiltonian describing two-body interactions within such a set of interacting centres is of the form

$$\hat{H} = \sum_{n,i,\alpha} \Delta_{i\alpha} |ni\alpha\rangle\langle ni\alpha| + \frac{1}{2} \sum_{\substack{n\alpha\beta \\ mj\gamma\delta}} J_{ni\alpha\beta,mi\gamma\delta} (|ni\alpha\rangle\langle ni\beta|)(|mj\gamma\rangle\langle mj\delta|) \quad (2.1)$$

where $n = 1, \dots, N$ labels the unit cell and i, j the particular centre in each cell. The operators in (2.1) are all written in the so-called 'standard basis' form so that

$$\hat{O}_{\alpha,\beta}(ni) = |ni\alpha\rangle\langle ni\beta|$$

is an operator which acts only on the states of the i th centre in the n th cell (Haley and Erdős 1972). These standard basis states are eigenstates of the spin Hamiltonian for each isolated centre. The corresponding eigenvalues $\Delta_{i\alpha}$ incorporate all the crystal-field and Zeeman splittings of each centre.

The states representing the whole assembly of N such centres are formed from the direct products of these standard basis states and will be distinguished from them by parentheses. Thus the non-interacting ground state will be

$$|0\rangle = \prod_{n,i} (|ni0\rangle). \quad (2.2)$$

Similarly, excited eigenstates of the non-interacting assembly can be generated by the action of the various single operators on this ground state. Of these excited states the simplest correspond to the creation of a single excitation, i.e.

$$|ni\alpha\rangle = \hat{O}_{\alpha,0}(ni)|0\rangle. \quad (2.3)$$

For N unit cells each containing m centres with $p + 1$ states there will be a total of

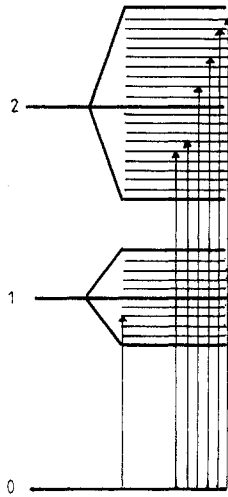


Figure 1. The energies of the ground state and the excited states corresponding to one and two excitations in a system where there is one magnetic centre per unit cell each having only one excited state. The creation of single excitations corresponds to sharp transitions because only one state in this group satisfies the selection rule $\Delta k = -Q$. There are many such states covering a wide energy range corresponding to the creation of two excitations.

Nmp such single excitation states. Linear combinations of these states can be formed to give irreducible representations of the translational symmetry group of the crystal, i.e.

$$|k i \alpha\rangle = \frac{1}{\sqrt{N}} \sum_n e^{ik \cdot r_n} \hat{O}_{\alpha,0}(ni) |0\rangle \quad (2.4)$$

These irreducible representations will all be one dimensional, each labelled by the N different values of the wavevector k in (2.4), and every representation occurs mp times.

The symmetry character of each state will of course not be changed by the interactions between centres. Such interactions have the translational symmetry of the lattice and so can only bring about mixing between states which have the same k -value. Inelastic neutron scattering involves transitions corresponding to sharply defined changes of k and this selection rule is likewise unaffected by these interactions. At low temperatures these transitions predominantly correspond to the creation of elementary excitations within the interacting magnetic assembly rather than to their destruction. The limit $T \rightarrow 0$ can therefore be represented as transitions from the interacting ground state as shown in figure 1. Provided that the interactions preserve the continuity between unperturbed and perturbed states which is implicit in figure 1 then this interacting ground state may be very different from the non-interacting ground state but it still has the symmetry character corresponding to $k = 0$. Likewise the interacting or the perturbed single excitation states will be different from the unperturbed states (2.4) but they will still be characterised by N different values of k and each k -value will occur mp times. Thus it is clear that, for this group of states, inelastic neutron scattering, with a neutron wavevector change Q , will only occur at sharply defined energies corresponding to the eigenvalues of the single excitation states with $k = -Q$. The number of such excitations equals the number of such states, namely mp , the product of the number of centres per unit cell and the number of excited states per centre. The situation is far more complicated in groups of states corresponding to multiple excitations. For example, in the group with two excitations there will be $N(N - 1)(mp)^2$ states; so each irreducible symmetry representation k occurs $(N - 1)(mp)^2$ times. Under favourable conditions this multitude

of transitions may be grouped into narrow energy ranges, giving rise to scattering resonances which are still recognisable as such, although broadened somewhat in energy.

The simplicity of the group of single excitation states also shows that the energy of these states and hence the dispersion relationships can be described in a simple general way. It is always possible to fit the energies of a set of states to the eigenvalues of a Hermitian operator acting within these states. This effective Hamiltonian becomes a particularly useful construct when it acts only within a subspace of states of limited dimension, so that the Hamiltonian matrix can be diagonalised, at least numerically, without approximation. This method is in use throughout magnetism but most notably in the spin Hamiltonians of magnetic resonance theory. An extension of the spin-Hamiltonian concept to the present case is possible because the group of single excitation states, although of large dimension (Nmp), factorises into N subspaces each characterised by the N different values of k lying in the first Brillouin zone. Thus an effective Hamiltonian \hat{H}^e can easily be constructed which acts within the space of the single excitation states defined by (2.3) and (2.4) to give as its eigenvalues the experimentally observed excitation energies

$$\begin{aligned} \hat{H}^e &= \sum_{ni\alpha} \Delta_{i\alpha}^e |ni\alpha\rangle\langle ni\alpha| + \sum_{\substack{ni\alpha \\ mj\beta}} J_{ni\alpha, mj\beta}^e (|ni\alpha\rangle\langle ni0|) (|mj0\rangle\langle mj\beta|) \\ &= \sum_{ni\alpha} \Delta_{i\alpha}^e \hat{O}_{\alpha, \alpha}(ni) + \sum_{\substack{ni\alpha \\ mj\beta}} J_{ni\alpha, mj\beta}^e \hat{O}_{\alpha, 0}(ni) \hat{O}_{0, \beta}(mj). \end{aligned} \quad (2.5)$$

It can easily be verified that the effective Hamiltonian \hat{H}^e , unlike the original Hamiltonian in (2.1), has no matrix elements connecting the single excitation states of (2.4) with any states outside this group. Furthermore the matrix representation of \hat{H}^e within the states defined by (2.4) factorises into block diagonal form, where each block is at most of dimension $mp \times mp$. Thus the diagonalisation of \hat{H}^e reduces to the diagonalisation of a matrix of small dimension, or equivalently to solving an (mp) th-order polynomial. When the parameters Δ^e and J^e are properly adjusted, the roots of this (mp) th-order polynomial should fit the energy dispersion spectrum perfectly at $T = 0$ provided that (2.1) is itself an adequate representation of the situation.

3. Application to $\text{Cs}_3\text{Cr}_2\text{Br}_9$

This material is one member of a large class containing relatively isolated pairs of Cr^{3+} ions. The antiferromagnetic coupling between members of an ion pair produces a singlet ground state together with an excited triplet and higher states. Within each unit cell of the hexagonal lattice there are two equivalent pairs forming two sublattices. Weaker exchange interactions exist between pairs, both within and between the sublattices, as shown schematically in figure 2.

Following the procedure of Leuenberger *et al* (1984), only the ground and triplet states of the pairs will be considered. This then corresponds to a case where $m = 2$, $p = 3$. In fact for isotropic exchange interactions the degeneracy of the triplet states is preserved and the problem reduces to one corresponding to $m = 2$, $p = 1$. Using a

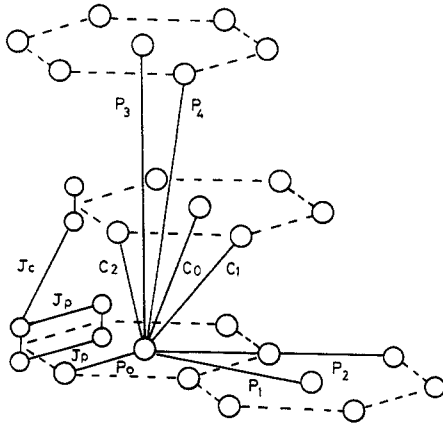


Figure 2. Schematic structure of $\text{Cs}_3\text{Cr}_2\text{Br}_9$ showing the exchange interaction paths to first- and second-nearest-neighbour pairs. The Cr_2Cl_9 pairs are shown only as open circles except in a few sites where they are shown as two open circles joined with a line in order to indicate the interactions between the individual Cr^{3+} ions assumed in section 4.2.

notation similar to that of Leuenberger *et al* (1984) an effective Hamiltonian consistent with this symmetry is easily constructed as

$$\begin{aligned} \hat{H}^e = & - \sum_{ni} J^e \hat{P}_1(ni) - \frac{1}{4} \sum_{nmi} J_{pnm}^e [(\hat{P}_1 \hat{L} \hat{P}_0)_{(ni)} \cdot (\hat{P}_0 \hat{L} \hat{P}_1)_{(mi)} + (\hat{P}_0 \hat{L} \hat{P}_1)_{(ni)} \cdot (\hat{P}_1 \hat{L} \hat{P}_0)_{(mi)}] \\ & + \frac{1}{4} \sum_{nm} J_{cnm}^e [(\hat{P}_1 \hat{L} \hat{P}_0)_{(n1)} \cdot (\hat{P}_0 \hat{L} \hat{P}_1)_{(m2)} + (\hat{P}_0 \hat{L} \hat{P}_1)_{(n1)} \cdot (\hat{P}_1 \hat{L} \hat{P}_0)_{(m2)}] \end{aligned} \quad (3.1)$$

where n, m label lattice cells and $i = 1, 2$ distinguishes between the two sublattices. J_p^e and J_c^e are effective exchange parameters within the same sublattice and between different sublattices, respectively. The operators \hat{P}_0 and \hat{P}_1 are projection operators acting on the ground and triplet states of each pair respectively, i.e.

$$\hat{P}_0(n, i) = |ni0\rangle\langle ni0| \quad \hat{P}_1(n, i) = \sum_{\alpha=1,2,3} |ni\alpha\rangle\langle ni\alpha|.$$

The operator $\hat{L} = \hat{S}_1 - \hat{S}_2$, where \hat{S}_1 and \hat{S}_2 are the spin operators of the individual Cr^{3+} ions within each pair.

The triply degenerate single excitation states are constructed like (2.4) as

$$|kiu\rangle = \frac{1}{\sqrt{N}} \sum_n \frac{e^{ik \cdot r_n}}{\sqrt{c}} \hat{L}_u(ni)|0\rangle \quad (3.2)$$

where $i = 1, 2$ as before and $u = x, y, z$ and $c = \langle 0 | L_u^2 | 0 \rangle = 5$.

It can readily be verified that linear combinations of $|k, 1, u\rangle$ and $|k, 2, u\rangle$ are eigenstates of \hat{H}^e with energies $E(k)$ given by

$$E(k) = -J^e - \frac{5}{2} J_p^e(k) \pm \frac{5}{4} J_c^e(k) \quad (3.3)$$

where

$$J_p^e(k) = \sum_n J_{pnm}^e e^{jk \cdot (r_n - r_m)}$$

and

$$J_c^e(k) = \sum_n J_{cnm}^e e^{jk \cdot (r_n - r_m)}.$$

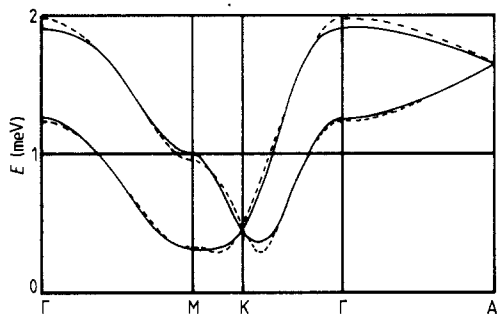


Figure 3. The dispersion curves obtained by using an effective Hamiltonian with the interactions to second-nearest neighbours given in (3.4) (full curves). The broken curves are the experimental results of Leuenberger *et al* (1984).

The experimental dispersion curves along various directions are given by Leuenberger *et al* (1984) who also give an equation, derived from a theory based on a random-phase approximation, which fits these curves to within their experimental accuracy. A least-squares fitting procedure was used to determine the effective-Hamiltonian parameters which allows (3.3) to fit these experimental data. Using interactions in (3.1) only to second nearest neighbours gives quite a good fit. This is illustrated in figure 3 where it is compared with the experimental fitting of Leuenberger *et al*. It corresponds to non-zero values for the following parameters defined in figure 2:

$$\begin{aligned}
 J_e &= -950 \mu\text{eV} & J_{p_0}^e &= -52 \mu\text{eV} & J_{p_1}^e &= +6 \mu\text{eV} \\
 J_{p_2}^e &= +2 \mu\text{eV} & J_{p_3}^e &= +6 \mu\text{eV} & J_{p_4}^e &= +0.4 \mu\text{eV} \\
 J_{c_0}^e &= -72 \mu\text{eV} & J_{c_1}^e &= +2 \mu\text{eV} & J_{c_2}^e &= +23 \mu\text{eV}.
 \end{aligned}
 \tag{3.4}$$

Extending this fitting procedure out to third-nearest neighbours introduces only very small third-neighbour coupling parameters (less than $1 \mu\text{eV}$) while leaving the second-neighbour parameters given above essentially unchanged. Using interactions out to third neighbours gives a fitting which cannot be distinguished in figure 3 from that of Leuenberger *et al*.

In $\text{Cs}_3\text{Cr}_2\text{Br}_3$ the strength of the interactions between pairs is close to the critical value at which a transition to long-range spin ordering occurs. In view of this it seems perhaps surprising that such good empirical fitting of the experimental data is achieved by using only short range interactions. It can, however, be seen that this fitting procedure, represented by (3.3), is very similar to a Fourier analysis of the dispersion curves, with the effective exchange parameters playing the role of Fourier coefficients. For this reason it is to be expected that a fitting by short-range interactions, involving the specification of only a few parameters, will be equally successful in other cases. Only where the dispersion curves have sharp features should it be necessary to include longer-range interactions in (3.1).

4. The relationship between \hat{H} and \hat{H}^e

As the previous results illustrate, the effective Hamiltonian \hat{H}^e can be a useful way of separating the problem of the summarising of experimental results from the more difficult task of their theoretical interpretation. Experimental measurements only directly determine the parameters of the effective Hamiltonian. Some theoretical interpretation is required to relate these effective parameters to the parameters of the 'real'

Hamiltonian \hat{H} in (1.1). It is a feature of the effective-Hamiltonian method that there is in principle a very clear and direct relationship between \hat{H} and \hat{H}^e .

For the Hamiltonian \hat{H} of (1.1) the unperturbed states of the isolated magnetic centres form a complete set. A unitary transformation operator will always exist which reduces \hat{H} to a fully diagonal form with respect to these states. There must therefore be a unitary operator which does less than this and reduces \hat{H} to a block diagonal form, such that the transformed Hamiltonian has no matrix elements between groups of states having different numbers of magnetic excitations. This transformed Hamiltonian acting within the group of single excitation states is then the effective Hamiltonian \hat{H}^e .

In most many-body problems, including that considered here, \hat{H} can be written as

$$\hat{H} = \hat{H}_0 + \hat{H}_1 \tag{4.1}$$

where \hat{H}_0 defines some non-interacting assembly of microscopic systems and \hat{H}_1 represents interactions between these systems. In the present case, \hat{H}_0 is to be identified with the crystal-field energies of the isolated magnetic centres. In formal terms the effective Hamiltonian \hat{H}^e can be defined by introducing the operator \hat{H}^T such that

$$\hat{H}^T = U^{-1} \hat{H} U \tag{4.2}$$

and the unitary transformation operator \hat{U} is to be chosen so that

$$[\hat{H}^T, \hat{H}_0] = 0. \tag{4.3}$$

Then the effective Hamiltonian is given by

$$\hat{H}^e = [\hat{H}^T - (0|\hat{H}^T|0)]\hat{Q}_1 \tag{4.4}$$

where \hat{Q}_1 is the projection operator for the group of states containing a single excitation, i.e.

$$\hat{Q}_1 = \sum_{n\alpha} |n\alpha\rangle\langle n\alpha|$$

where $|n\alpha\rangle$ is defined by (2.3). The presence of the projection operator \hat{Q}_1 in (4.4) explicitly demonstrates that \hat{H}^e has a defined operation only within the subspace of states defined by \hat{Q}_1 . The ground-state expectation value of \hat{H}^T is included in (4.4) so that the eigenvalues of \hat{H}^e are the excitation energies relative to the perturbed ground state.

4.1. Perturbation approximation of \hat{U}

Whenever the matrix elements of \hat{H} between different groups of states are small compared with the energy differences between groups, then \hat{U} may be approximated by a perturbation method. In doing this it is convenient to resolve the perturbation \hat{H}_1 into different components depending on their commutation properties with \hat{H}_0 . Thus

$$\hat{H} = \hat{H}_0 + \hat{H}_1 + \hat{H}_{10} + \sum_{E_\alpha} \hat{H}_{1,E_\alpha} \tag{4.5}$$

where

$$\hat{H}_{1,E_\alpha}^+ = \hat{H}_{1,-E_\alpha}$$

and

$$[\hat{H}_{10}, \hat{H}_0] = 0 \quad [\hat{H}_{1,E_\alpha}, \hat{H}_0] = -E_\alpha \hat{H}_{1,E_\alpha}. \quad (4.6)$$

All unitary operators can be written in the exponential form

$$\hat{U} = \exp \hat{A} \quad (4.7)$$

where \hat{A} is some anti-Hermitian operator ($\hat{A}^+ = -\hat{A}$) (see, e.g., Roman (1975) for mathematical details). It is very convenient therefore to develop a perturbation approximation of \hat{H}^T by expressing the exponent of (4.7) as a power series in some multiplicative parameter of the perturbation \hat{H}_1 :

$$\hat{A} = \hat{A}_1 + \hat{A}_2 + \hat{A}_3 + \dots$$

With this form for \hat{U} , equation (4.2) becomes

$$\hat{H}^T = \hat{U}^{-1} \hat{H} \hat{U} = \hat{H} + [\hat{H}, \hat{A}] + \frac{1}{2} [[\hat{H}, \hat{A}], \hat{A}] + \dots \quad (4.8)$$

Choosing \hat{A}_1 to ensure that (4.3) is satisfied to first order gives

$$\hat{A}_1 = - \sum_{E_\alpha} \frac{\hat{H}_{1,E_\alpha}}{E_\alpha}.$$

The higher-order terms \hat{A}_2, \hat{A}_3 , etc. can be determined in a similar manner. Carrying this procedure out to second order in \hat{A} gives \hat{H}^T to third order as

$$\begin{aligned} \hat{H}^T = \hat{H}_0 + \hat{H}_{10} - \frac{1}{2} \sum_{E_\alpha} \frac{[\hat{H}_{1,-E_\alpha}, \hat{H}_{1,E_\alpha}]}{E_\alpha} - \frac{1}{2} \sum_{E_\alpha} \frac{[[\hat{H}_{1,0}, \hat{H}_{1,E_\alpha}], \hat{H}_{1,-E_\alpha}]}{E_\alpha^2} \\ - \frac{1}{3} \sum_{E_\alpha, E_\beta \neq -E_\alpha} \frac{[[\hat{H}_{1,E_\beta}, \hat{H}_{1,E_\alpha}], \hat{H}_{1,-(E_\alpha+E_\beta)}]}{E_\alpha(E_\alpha + E_\beta)}. \end{aligned} \quad (4.9)$$

4.2. Non-perturbational approximation

For many applications the perturbation series (4.9) will converge quickly enough to give an adequate account of the relationship between \hat{H} and \hat{H}^e in just the first few terms. This is unlikely to be the case, however, for materials such as $\text{Cs}_3\text{Cr}_2\text{Br}_9$ which are close to the condition of critical coupling. Here a non-perturbational approximation to \hat{U} in (4.7) may be required or at least a sum of a very large number of terms in (4.8) and (4.9). One well known method of doing this makes use of the fact that the number z of neighbours interacting with any given centre is usually large enough to allow neglect of terms in (4.8) and (4.9) which are of order $1/z$. This is equivalent to the neglect of multiple interactions involving the same site, since a repeated site interaction eliminates one free summation over site indices in (4.8) and (4.9). In formal terms this amounts to approximating the commutators in (4.8) and (4.9) by

$$\sum_{nlm} [\hat{A}_n, \hat{B}_l \hat{C}_m] = \sum_{nm} (0 | [\hat{A}_n, \hat{B}_n] | 0) \hat{C}_m + \sum_{nl} (0 | [\hat{A}_n, \hat{C}_n] | 0) \hat{B}_l \quad (4.10)$$

where $\hat{A}_n, \hat{B}_l, \hat{C}_m$ are operators acting on the states of sites, n, l, m . This random-phase type of approximation could be used to perform infinite sums of the leading terms of (4.8) and (4.9). Such a non-perturbational treatment would, however, be unable to provide any reliable estimation of the difference between real and effective crystal-field parameters. It would not be able to distinguish between Δ of (2.1) and Δ^e of (2.5)

because the random-phase approximation disregards the correlations between single-site operators on which this distinction depends.

A less severe approximation, which avoids some of this difficulty, would be to use the random-phase approximation only to incorporate the secular part of the perturbation, i.e. \hat{H}_{10} in (4.5), into the unperturbed Hamiltonian \hat{H}_0 . This would lead to a modified perturbation expansion in terms only of the non-secular part of the perturbation, i.e. $\sum_{\alpha} \hat{H}_{1E_{\alpha}}$ of (4.5). Such a modified perturbation expansion might be expected to have improved convergence properties.

This does appear to be the case for $\text{Cs}_3\text{Cr}_2\text{Br}_9$. For this material the model Hamiltonian used by Leuenberger *et al* (1984) can be written as

$$\hat{H} = \hat{H}_0 + \hat{H}_{10} + \hat{H}'_1$$

where

$$\hat{H}_0 = -\sqrt{NJ} \sum_a (\hat{P}_{1a})(0)$$

$$\begin{aligned} \hat{H}_{10} = & - \sum_{k,a} \frac{J_p(k)}{4} [(\hat{P}_0 \hat{L}_a \hat{P}_1)(-k) \cdot (\hat{P}_1 \hat{L}_a \hat{P}_0)(k) + (\hat{P}_1 \hat{L}_a \hat{P}_0)(-k) \cdot (\hat{P}_1 \hat{L}_a \hat{P}_0)(k)] \\ & + \sum_k \frac{J_c(k)}{4} [(\hat{P}_0 \hat{L}_1 \hat{P}_1)(-k) \cdot (\hat{P}_1 \hat{L}_2 \hat{P}_0)(k) \\ & + (\hat{P}_1 \hat{L}_1 \hat{P}_0)(-k) \cdot (\hat{P}_0 \hat{L}_2 \hat{P}_1)(k)] \end{aligned}$$

$$\begin{aligned} \hat{H}'_1 = \hat{H}_1 - \hat{H}_{10} = & - \sum_{k,a} \frac{J_p(k)}{4} [(\hat{P}_0 \hat{L}_a \hat{P}_1)(-k) \cdot (\hat{P}_0 \hat{L}_a \hat{P}_1)(k) \\ & + (\hat{P}_1 \hat{L}_a \hat{P}_0)(-k) \cdot (\hat{P}_1 \hat{L}_a \hat{P}_0)(k)] \\ & + \sum_k \frac{J_c(k)}{4} [(\hat{P}_0 \hat{L}_1 \hat{P}_1)(-k) \cdot (\hat{P}_0 \hat{L}_2 \hat{P}_1)(k) \\ & + (\hat{P}_1 \hat{L}_1 \hat{P}_0)(-k) \cdot (\hat{P}_1 \hat{L}_2 \hat{P}_0)(k)] \end{aligned} \quad (4.11)$$

where $a = 1, 2$ and J_p and J_c are the exchange constants for interactions between nearest-neighbour spins in the same sublattice and in different sublattices, respectively, as shown in figure 2. The Fourier-transformed operators in (4.11) are defined by

$$(\hat{P}_0 \hat{L}_a \hat{P}_1)(k) = \frac{1}{\sqrt{N}} \sum_n (\hat{P}_0 \hat{L}_a \hat{P}_1)(na) e^{-jk \cdot r_{na}}$$

If a perturbation expansion such as (4.7) and (4.8) is formed in terms only of powers of the non-secular perturbation \hat{H}'_1 , then, to first order in such an expansion of \hat{A} , one obtains

$$\begin{aligned} A_1 = \sum_{E_{\alpha}} A_{1E_{\alpha}} = & - \sum_{k,a} K_p(k) [(\hat{P}_1 \hat{L}_a \hat{P}_0)(-k) \cdot (\hat{P}_1 \hat{L}_a \hat{P}_0)(k) \\ & - (\hat{P}_0 \hat{L}_a \hat{P}_1)(-k) \cdot (\hat{P}_0 \hat{L}_a \hat{P}_1)(k)] \\ & + \sum_k K_c(k) [(\hat{P}_1 \hat{L}_1 \hat{P}_0)(-k) \cdot (\hat{P}_1 \hat{L}_2 \hat{P}_0)(k) \\ & - (\hat{P}_0 \hat{L}_1 \hat{P}_1)(-k) \cdot (\hat{P}_0 \hat{L}_2 \hat{P}_1)(k)] \end{aligned} \quad (4.12)$$

where

$$\begin{aligned} K_p(\mathbf{k}) &= \{J_p(\mathbf{k}) [8J + 20J_p(\mathbf{k})] - 5|J_c(\mathbf{k})|^2\} [1/D(\mathbf{k})] \\ K_c(\mathbf{k}) &= [8JJ_c(\mathbf{k})] [1/D(\mathbf{k})] \\ D(\mathbf{k}) &= [8J + 20J_p(\mathbf{k})]^2 - 100|J_c(\mathbf{k})|^2. \end{aligned}$$

It can be verified that to the accuracy of the approximation (4.10)

$$[(\hat{H}_0 + \hat{H}_{10}), \hat{A}_1] = -\hat{H}'_1 = -\sum_{E_\alpha} \hat{H}_{1,E_\alpha} \quad (4.13)$$

and so to second order in \hat{H}^T

$$\hat{H}^T = \hat{H}_0 + \hat{H}_{10} + \sum_{E_\alpha} \frac{1}{2} [\hat{H}_{1,E_\alpha}, \hat{A}_{1,-E_\alpha}]. \quad (4.14)$$

The projection of (4.14) onto the single excitation states and the subtraction of constant terms corresponding to ground-state energy shifts gives the effective Hamiltonian in the form shown in (3.1) and hence the excitation energy dispersion relationship (3.3).

The effective Hamiltonian derived from (4.14) in this way was used to fit the experimental results of Leuenberger *et al.* A least-squares fitting procedure was used to select the values of J , J_p and J_c in (4.11) which best fit the experimental dispersion curves. The fitting was done in two slightly different ways. The experimental data are fitted equally well either way but with slightly different parameters. Firstly the commutator in (4.14) can be evaluated approximately using the same approximation (4.10) as is used in (4.13). The fitting achieved in this way corresponds to the parameters

$$J = -1.01 \text{ meV} \quad J_p = -54 \text{ } \mu\text{eV} \quad J_c = -65 \text{ } \mu\text{eV}. \quad (4.15)$$

In comparing the results (4.15) with those of Leuenberger *et al* it is necessary to take into account an error in the equation used by Leuenberger *et al* for the dispersion relationship. As a result of an algebraic error from their equation (2) to equation (4) the J_c -value that they used should be twice the value quoted. When this error is corrected, the results (4.15) agree very well with the corresponding parameters given by Leuenberger *et al* (1984).

A more accurate evaluation of the commutator in (4.14) would go beyond the random-phase approximation (4.13) and take proper account of the correlations involved in multiple-spin interactions on the same lattice site. Only by including these correlations can an account be given of the renormalisation of the single-site crystal-field parameters. When these correlations are taken into account, the least-squares fitting of the experimental data is as shown in figure 4. It corresponds to the parameters

$$J = -0.757 \text{ meV} \quad J_p = -56 \text{ } \mu\text{eV} \quad J_c = -66 \text{ } \mu\text{eV}. \quad (4.16)$$

The parameters in (4.16) could be compared with the results of the higher-order random-phase calculations of Leuenberger and Güdel (1985). In both cases the renormalised crystal-field splitting parameter J is reduced in magnitude compared with the random phase approximation value. Here, however, no correspondingly large increase in the inter-pair-exchange parameters are found, contrary to the results reported by Leuenberger and Güdel.

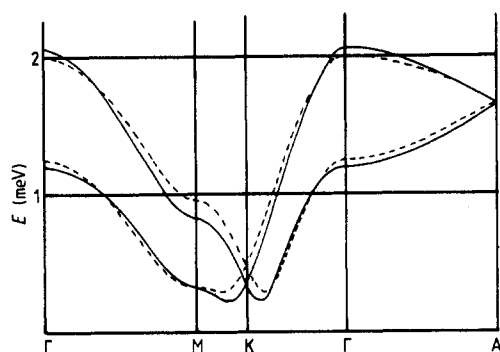


Figure 4. The dispersion curves obtained from the perturbational calculations in section 4.2 using the parameters given in (4.16) (full curves). The broken curves are the experimental results of Leuenberger *et al* (1984).

5. Conclusion

It has been shown that the concept of a spin Hamiltonian originally developed for the description of isolated magnetic centres can be extended to the case of interacting centres. This offers a new method both for the empirical description of such interacting systems and for their theoretical interpretation. One prediction of this new method is that, for a periodic array having a singlet ground state, the linewidth due to magnetic interactions should vanish at $T = 0$.

This raises the question of the origin of the residual linewidths that are observed in these materials at $T = 0$. There are several possibilities. Crystal defects or chemical impurities will have the effect of destroying, to some extent, the perfect translational symmetry of the lattice. Such defects will therefore relax the selection rule of wavevector conservation which is the cause of the sharpness of these transitions. Another possibility is the coupling between the magnetic centres and other low-energy excitations, such as lattice vibrations or free electrons.

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