

## Spin-Exchange in Polynuclear Systems

R. W. Jotham and S. F. A. Kettle

Received July, 26, 1969

The energy levels of spin coupled systems containing up to six polyhedrally arranged magnetic centres are detailed, together with some appropriate to distorted polyhedral arrangements.

### Introduction

There has recently been considerable interest in polynuclear transition metal complexes and in magnetic properties of mononuclear complexes over an extended range of temperature. These have combined to direct attention on the phenomenon of antiferromagnetism because of the spin-spin coupling inherent in most polynuclear systems and the weak residual coupling often found even for magnetically dilute materials at low temperature. The interpretation of this antiferromagnetic behaviour requires a suitable theoretical treatment based on a spin-coupled model. Spin-spin coupling is involved not only in the interpretation of magnetic susceptibility data but also in that of electron-spin and magnetic resonance measurements.

In these latter a considerable number of situations have long been recognised and discussed in the literature. Where a parallel exists, these are at once transferable *mutatis mutandis* to the interpretation of magnetic susceptibility results. However, not all spin-coupling arrangements which are needed for the static measurements are available in the literature on resonance methods, and in this paper we give the results of calculation which are particularly appropriate to the former. In particular, we consider spin-coupled arrangements of magnetic centres arranged at the corners of regular or distorted polyhedra. We shall consider an effective Hamiltonian of the form

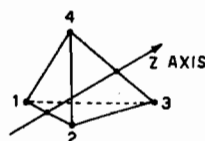
$$H = \sum_{i,j} -J_{ij} S_i \cdot S_j \quad (1)$$

A positive  $J$  indicates ferromagnetic spin-exchange.

System of spin  $\frac{1}{2}$  are discussed first and then some of the simpler systems of spin greater than one-half.

**Spin  $\frac{1}{2}$  systems.** For  $n$ -centres of spin  $\frac{1}{2}$  the basis set contains  $2^n$  spin-functions, which, with the above Hamiltonian, leads to a  $2^n \times 2^n$  secular determinant. This is already partially diagonalised, because the non-zero elements are restricted to the leading diagonal and those off-diagonal elements between basis functions of the same total spin. We note that the dimension of the blocks for the  $n$ -centre problem

may be found from an appropriate binomial expansion. However, these blocks are sufficiently large to be difficult to solve in cases involving four or more centres, unless the problem is further simplified by consideration of the symmetry of the cluster. This simplification may be achieved readily, as we illustrate by considering a tetranuclear cluster with a  $C_{2v}$  symmetry. The basis set contains sixteen spin functions.



$$\begin{aligned} J_{12} &= J_S \text{ (short)} \\ J_{34} &= J_L \\ J_{13} &= J_{14} = J_{23} = J_{24} = J_M \end{aligned}$$

Figure 1. A Distorted Tetrahedron of  $C_{2v}$  Symmetry

Adopting a nomenclature for the basis set illustrated by the following examples

$$\alpha^0 = \beta\beta\beta\beta, \quad \alpha_{13}^2 = \alpha\beta\alpha\beta, \quad \beta_2 = \alpha\beta\alpha\alpha (\equiv \alpha_{134}^2)$$

the following blocks are obtained:

$$\begin{aligned} &\langle \alpha^0 | && \langle \beta^0 | \\ | \alpha^0 \rangle &= -\frac{1}{4}(J_0 + J_1 + 4J_M) && | \beta^0 \rangle = -\frac{1}{4}(J_0 + J_1 + 4J_M) \quad (2) \\ &\langle \alpha^1 | && \langle \alpha^1 | && \langle \alpha^1 | && \langle \alpha^1 | \\ | \alpha^1 \rangle &= \frac{J_0 - J_1}{4} && -\frac{1}{2}J_1 && -\frac{1}{2}J_1 && -\frac{1}{2}J_1 \\ | \alpha^1 \rangle &= -\frac{1}{2}J_1 && \frac{J_0 - J_1}{4} && -\frac{1}{2}J_1 && -\frac{1}{2}J_1 \\ | \alpha^1 \rangle &= -\frac{1}{2}J_1 && -\frac{1}{2}J_1 && \frac{J_0 - J_1}{4} && -\frac{1}{2}J_1 \\ | \alpha^1 \rangle &= -\frac{1}{2}J_1 && -\frac{1}{2}J_1 && -\frac{1}{2}J_1 && \frac{J_0 - J_1}{4} \end{aligned} \quad (3)$$

and an analogous matrix for the  $\beta_1^1$ .

$$\begin{aligned} &\langle \alpha\alpha^1 | && \langle \alpha\alpha^1 | && \langle \alpha\alpha^1 | && \langle \alpha\alpha^1 | && \langle \alpha\alpha^1 | && \langle \alpha\alpha^1 | \\ | \alpha\alpha^1 \rangle &= \frac{4J_0 - J_1 - J_2}{4} && -\frac{1}{2}J_2 && -\frac{1}{2}J_2 && -\frac{1}{2}J_2 && -\frac{1}{2}J_2 && 0 \\ | \alpha\alpha^1 \rangle &= -\frac{1}{2}J_2 && \frac{J_1 + J_2}{4} && -\frac{1}{2}J_1 && -\frac{1}{2}J_1 && 0 && -\frac{1}{2}J_2 \\ | \alpha\alpha^1 \rangle &= -\frac{1}{2}J_2 && -\frac{1}{2}J_2 && \frac{J_1 + J_2}{4} && 0 && -\frac{1}{2}J_1 && -\frac{1}{2}J_2 \\ | \alpha\alpha^1 \rangle &= -\frac{1}{2}J_2 && -\frac{1}{2}J_2 && 0 && \frac{J_1 + J_2}{4} && -\frac{1}{2}J_1 && -\frac{1}{2}J_2 \\ | \alpha\alpha^1 \rangle &= -\frac{1}{2}J_2 && 0 && -\frac{1}{2}J_1 && -\frac{1}{2}J_1 && \frac{J_1 + J_2}{4} && -\frac{1}{2}J_2 \\ | \alpha\alpha^1 \rangle &= 0 && -\frac{1}{2}J_2 && -\frac{1}{2}J_2 && -\frac{1}{2}J_2 && -\frac{1}{2}J_2 && \frac{4J_0 - J_1 - J_2}{4} \end{aligned} \quad (4)$$

The  $4 \times 4$  and  $6 \times 6$  matrices may be diagonalised by eigenfunctions generated by symmetry using the  $C_{2v}$  character table. The  $z$  axis bisects the edges 12 and 34 and we arrange the other axes so that 12 is parallel to the  $xz$  plane and 34 is parallel to the  $yz$  plane.

For the  $\alpha_i^1$  functions the following orthogonal combinations are obtained.

$$\begin{aligned}\alpha^1(A_1)_1 &= \frac{1}{\sqrt{2}}(\alpha_1^1 + \alpha_2^1) \\ \alpha^1(A_1)_2 &= \frac{1}{\sqrt{2}}(\alpha_3^1 + \alpha_4^1) \\ \alpha^1(B_1) &= \frac{1}{\sqrt{2}}(\alpha_3^1 - \alpha_4^1) \\ \alpha^1(B_2) &= \frac{1}{\sqrt{2}}(\alpha_1^1 - \alpha_2^1)\end{aligned}\quad (5)$$

Using these functions the  $4 \times 4$   $\alpha_i^1$  matrix diagonalises partly to

$$\begin{array}{cccc|cccc} & \langle \alpha^1(A_1)_1 | & \langle \alpha^1(A_1)_2 | & \langle \alpha^1(B_1) | & \langle \alpha^1(B_2) | & & & & \\ \langle \alpha^1(A_1)_1 | & & & & & & & & \\ \langle \alpha^1(A_1)_2 | & & & & & & & & \\ \langle \alpha^1(B_1) | & & & & & & & & \\ \langle \alpha^1(B_2) | & & & & & & & & \end{array} \quad (6)$$

The two eigenvalues arising from the  $\alpha^1(A_1)$  eigenfunctions are obtained as solutions of

$$\begin{vmatrix} \frac{-J_1 - J_s}{4} - E & -J_m \\ -J_m & \frac{-J_1 - J_s}{4} - E \end{vmatrix} = 0 \quad (7)$$

whence

$$E = \frac{-J_1 - J_s - 4J_m}{4}, \quad \frac{-J_1 - J_s + 4J_m}{4}$$

The roots of the secular equation may be used to obtain the eigenfunctions corresponding to these eigenvalues

$$\alpha^1(A_1)_a = \frac{1}{2}(\alpha_1^1 + \alpha_2^1 + \alpha_3^1 + \alpha_4^1) \quad E_a = \frac{-1}{4}(J_1 + J_s + 4J_m)$$

$$\alpha^1(A_1)_b = \frac{1}{2}(\alpha_1^1 + \alpha_2^1 - \alpha_3^1 - \alpha_4^1) \quad E_b = \frac{-1}{4}(J_1 + J_s - 4J_m)$$

It is evident that  $\alpha^1(A_1)_a$  is the second component of a spin-multiplet  ${}^5A_1$  at energy  $E = \frac{-1}{4}(J_1 + J_s + 4J_m)$ .

The components of these multiplets are connected by the spin-shift operators  $S_{(+)}$  and  $S_{(-)}$ . For example, it is readily shown that

$$S_{(+)}(\alpha^0) = 1 \cdot \alpha_1^1 + 1 \cdot \alpha_2^1 + 1 \cdot \alpha_3^1 + 1 \cdot \alpha_4^1 = 2\alpha^1(A_1)_a$$

Thus when more than one symmetry function belongs to the same representation, the normal functions are generated by means of the spin shift operators\*.

The six  $\alpha_{ij}^2$  functions give rise to the following symmetry functions

$$\begin{aligned}\alpha^2(A_1)_1 &= \alpha_{12}^2 \\ \alpha^2(A_1)_2 &= \alpha_{34}^2 \\ \alpha^2(A_1)_3 &= \frac{1}{2}(\alpha_{13}^2 + \alpha_{14}^2 + \alpha_{23}^2 + \alpha_{24}^2) \\ \alpha^2(A_2) &= \frac{1}{2}(\alpha_{13}^2 - \alpha_{14}^2 - \alpha_{23}^2 + \alpha_{24}^2) \\ \alpha^2(B_1) &= \frac{1}{2}(\alpha_{13}^2 - \alpha_{14}^2 + \alpha_{23}^2 - \alpha_{24}^2) \\ \alpha^2(B_2) &= \frac{1}{2}(\alpha_{13}^2 + \alpha_{14}^2 - \alpha_{23}^2 - \alpha_{24}^2)\end{aligned}\quad (8)$$

$$S_{(+)}(\alpha^1(A_1)_a) \longrightarrow \alpha^2(A_1)_a = \frac{1}{\sqrt{6}}(\alpha_{12}^2 + \alpha_{13}^2 + \alpha_{14}^2 + \alpha_{23}^2 + \alpha_{24}^2 + \alpha_{34}^2) = \frac{1}{\sqrt{6}}(\alpha^2(A_1)_1 + \alpha^2(A_1)_2 + 2\alpha^2(A_1)_3)$$

$$S_{(+)}(\alpha^1(A_1)_b) \longrightarrow \alpha^2(A_1)_b = \frac{1}{\sqrt{2}}(\alpha_{12}^2 - \alpha_{34}^2) = \frac{1}{\sqrt{2}}(\alpha^2(A_1)_1 - \alpha^2(A_1)_2)$$

and the third, orthogonal,  $\alpha^2(A_1)$  function is  $\frac{1}{\sqrt{3}}(\alpha^2(A_1)_1 + \alpha^2(A_1)_2 - \alpha^2(A_1)_3)$

$$\alpha^2(A_1)_c = \frac{1}{\sqrt{12}}(2\alpha_{12}^2 + 2\alpha_{34}^2 - \alpha_{13}^2 - \alpha_{14}^2 - \alpha_{23}^2 - \alpha_{24}^2)$$

These 6  $\alpha_{ij}^2$  functions diagonalise the  $6 \times 6$  matrix. The final energies obtained are

$${}^5A_1 \quad \frac{-1}{4}(J_1 + J_s + 4J_m)$$

$${}^3B_1 \quad \frac{1}{4}(3J_1 - J_s)$$

$${}^3A_1 \quad \frac{1}{4}(4J_m - J_s - J_1)$$

$${}^3B_2 \quad \frac{1}{4}(3J_s - J_1)$$

$${}^1A_1 \quad \frac{1}{4}(8J_m - J_s - J_1)$$

$${}^1A_2 \quad \frac{1}{4}(3J_s + 3J_1)$$

These are shown in Figure 2.

$$(*) \quad -J_{S_1, S_2} = -J(S_{1(+)}S_{2(+)} + S_{1(+)}S_{2(-)} + S_{1(-)}S_{2(+)} + S_{1(-)}S_{2(-)})$$

where

$$S_{(+)} = S_x + iS_y \\ S_{(-)} = S_x - iS_y$$

$$S_{\pm} | M_s \rangle = \frac{\hbar}{2\pi} \sqrt{(S \pm M_s + 1)(S \mp M_s)} | M_s \pm 1 \rangle$$

We give below representations and eigenvalues for systems of 2 to 6 centres of spin 1/2 in various geometries, obtained in an entirely analogous manner.\*

n = 2	Point group $D_{\infty h}$	n = 3	$D_3$
$^3\Sigma_g^+$	$\frac{-J}{4}$	$J_{12}=J_{13}=J_{23}=J$	$^4A_1$
$^1\Sigma_u^+$	$\frac{3J}{4}$		$^2E$
			$\frac{-3J}{4}$
			$\frac{3J}{4}$
n = 3	$C_3$	n = 3	$D_{\infty h}$
$J_{12}=J_{13}=J_2$	$J_{23}=J_1$	$J_{12}=J_{23}=J_2$	$J_{13}=J_1$
$^4A'$	$\frac{-J_1}{4} - \frac{1}{2}J_2$	$^4\Sigma_g^+$	$\frac{-J_1}{4} - \frac{1}{2}J_2$
$^2A''$	$\frac{3J_1}{4}$	$^2\Sigma_u^+$	$\frac{3J_1}{4}$
$^3A'$	$J_2 - \frac{J_1}{4}$	$^2\Sigma_g^+$	$J_2 - \frac{J_1}{4}$

In the n = 3 ( $D_{\infty h}$ ) case if  $J_1=0$ ,  $J_2=J$  there is a quartet at  $-\frac{1}{2}J$ , and doublets at 0 and  $J$ .

n = 4	$T_d$	n = 4	$C_{2v}$
$J_{12}=J_{13}=J_{14}=J_{23}=J_{24}=J_{34}=J$		$J_{12}=J_{13}=J_{14}=J_1$	$J_{23}=J_{24}=J_{34}=J_2$
$^5A_1$	$\frac{-3J}{2}$	$^5A_1$	$-\frac{3}{4}J_1 - \frac{3}{4}J_2$
$^3T_2$	$\frac{1}{2}J$	$^3A_1$	$\frac{5}{4}J_1 - \frac{3}{4}J_2$
$^1E$	$\frac{3J}{4}$	$^3E$	$\frac{3}{4}J_2 - \frac{1}{4}J_1$
		$^1E$	$\frac{3}{4}J_1 + \frac{3}{4}J_2$

n = 4	$C_{2v}$	n = 4	$D_{2d}$
$J_{12}=J_1$	$J_{34}=J_1$	$J_{12}=J_{34}=J_2$	$J_{13}=J_{14}=J_{23}=J_{24}=J_1$
$^5A_1$	$-J_1 - \frac{1}{4}J_1 - \frac{1}{4}J_1$	$^5A_1$	$-J_1 - \frac{1}{2}J_2$
$^3B_1$	$\frac{3}{4}J_1 - \frac{1}{4}J_1$	$^3E$	$\frac{1}{2}J_2$
$^3A_1$	$J_1 - \frac{1}{4}J_1 - \frac{1}{4}J_1$	$^3B_2$	$J_1 - \frac{1}{2}J_2$
$^3B_2$	$\frac{3}{4}J_1 - \frac{3}{4}J_1$	$^3B_1$	$\frac{3}{2}J_2$
$^1A_1$	$2J_1 - \frac{1}{4}J_1 - \frac{1}{4}J_1$	$^1A_1$	$2J_1 - \frac{1}{2}J_2$
$^1A_2$	$\frac{3}{4}J_1 + \frac{3}{4}J_1$		

(\*) The symmetry labels describe only the spatial distribution of the spin vectors. Complete wavefunctions would in general be anti-symmetrised direct-product functions obtained by combination of these with orbital functions. A particular consequence of this nomenclature integral.

n = 4	$D_4$ (square)	n = 4	$D_2$ (rectangle)
$J_{12}=J_{23}=J_{34}=J_{41}=J_c$		$J_{12}=J_{34}=J_{13}$	$J_{23}=J_{41}=J_s$
$J_{13}=J_{24}=J_t$		$J_{13}=J_{24}=J_t$	
$^5A_1$	$-J_c - \frac{1}{2}J_t$	$^5A$	$-\frac{1}{2}(J_s + J_t + J_c)$
$^3E$	$\frac{1}{2}J_t$	$^3B_3$	$\frac{1}{2}J_1 + \frac{1}{2}J_2 - \frac{1}{2}J_3$
$^3B_2$	$J_c - \frac{1}{2}J_t$	$^3B_2$	$\frac{1}{2}J_1 + \frac{1}{2}J_2 - \frac{1}{2}J_3$
$^1B_1$	$\frac{3}{2}J_t$	$^3B_1$	$\frac{1}{2}J_1 + \frac{1}{2}J_2 - \frac{1}{2}J_3$
$^1A_1$	$2J_c - \frac{1}{2}J_t$	$^1A_{(a)}$	$\frac{1}{2}(J_s + J_t + J_c) - F$
		$^1A_{(b)}$	$\frac{1}{2}(J_s + J_t + J_c) + F$

where

$$F = (J_s^2 + J_t^2 + J_c^2 - J_s J_t - J_s J_c - J_t J_c)^{1/2}$$

n = 4	$D_2$ (rhombus)
$J_{13}=J_s$	$J_{24}=J_t$
$J_{12}=J_{23}=J_{34}=J_{41}=J_c$	

$^5A$	$-J_c - \frac{1}{4}J_t - \frac{1}{4}J_s$
$^3B_2$	$\frac{3}{4}J_t - \frac{1}{4}J_s$
$^3B_3$	$\frac{3}{4}J_s - \frac{1}{4}J_t$
$^3A$	$J_c - \frac{1}{4}J_t - \frac{1}{4}J_s$
$^1B_1$	$\frac{3}{4}J_t + \frac{3}{4}J_s$
$^1A$	$2J_c - \frac{1}{4}J_t - \frac{1}{4}J_s$

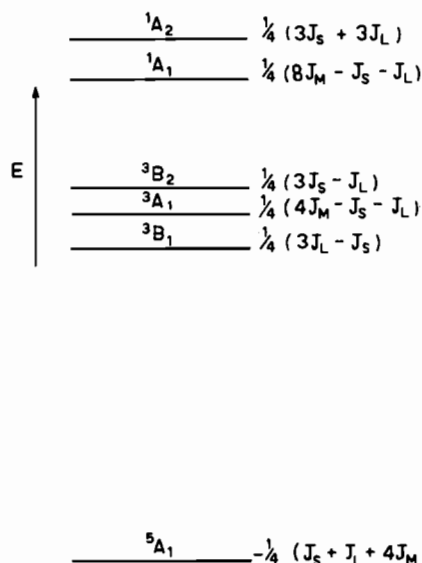


Figure 2. Energy Levels Arising from ferromagnetic spin-coupling between four centres of spin 1/2 arranged in a tetrahedron.

n=4 (Symmetric Trapezium) C<sub>s</sub>

$$J_{12} = J_M = J_M, \quad J_{23} = J_S$$

$$J_{13} = J_M = J_T, \quad J_{14} = J_L$$

$${}^3A' \quad -\frac{1}{4}(J_S + J_L + 2J_M + 2J_T)$$

$${}^3A' \quad \frac{1}{4}(2J_M + 2J_T - J_S - J_L)$$

$${}^3A'' \quad \frac{1}{4}(J_S + J_L - 2k)$$

$${}^3A'' \quad \frac{1}{4}(J_S + J_L + 2k)$$

$${}^1A' \quad \frac{1}{4}(J_S + J_L + 2J_M + 2J_T) - \frac{1}{2}k'$$

$${}^1A' \quad \frac{1}{4}(J_S + J_L + 2J_M + 2J_T) + \frac{1}{2}k'$$

where

$$k = ((J_S - J_L)^2 + (J_M - J_T)^2)^{1/2}$$

$$k' = (J_L^2 + J_S^2 + 4J_M^2 + 4J_T^2 + 2J_L J_S - 2J_L J_M - 2J_M J_S - 2J_L J_T - 2J_S J_T - 4J_M J_T)^{1/2}$$

n = 4

$$J_{12} = J_M = J_M$$

$$J_{13} = J_M = J_T$$

D<sub>∞h</sub>

$$J_{23} = J_S$$

$$J_{14} = J_L$$

eigenvalues same as the case of the case of the symmetric trapezium, C<sub>s</sub>.

n = 5

C<sub>s</sub>

$$J_{12} = J_{13} = J_{14} = J_1$$

$$J_{23} = J_{24} = J_{34} = J_2$$

$$J_{15} = J_1$$

$${}^1A_1 \quad -1_1 - 1_2 - \frac{1}{2}J_1$$

$${}^1E \quad \frac{1}{2}J_1 - \frac{1}{2}J_2$$

$${}^1B_1 \quad 1_1 - \frac{1}{2}J_1 - \frac{1}{2}J_2$$

$${}^1A_2 \quad \frac{3}{2}J_1 - 1_1 - \frac{1}{2}J_2$$

$${}^1B_2 \quad \frac{3}{2}J_1$$

$${}^1E \quad 1_1 + \frac{1}{2}J_1$$

$${}^1A_1 \quad 2J_1 - \frac{1}{2}J_2$$

$${}^1B_1 \quad 1_1 + 1_2 - \frac{1}{2}J_1$$

n = 5

D<sub>3h</sub>

$$J_{12} = J_{13} = J_{14} = J_{15} = J_1$$

$$J_{23} = J_{24} = J_{25} = J_2$$

$$J_{34} = J_1$$

$${}^1A_1 \quad -\frac{3}{2}J_1 - \frac{3}{4}J_2 - \frac{1}{4}J_1$$

$${}^1A_2 \quad \frac{3}{4}J_1 - \frac{3}{4}J_2$$

$${}^1A_1 \quad 1_1 - \frac{3}{4}J_1 - \frac{1}{4}J_2$$

$${}^1E \quad \frac{3}{4}J_1 - \frac{1}{2}J_2 - \frac{1}{4}J_1$$

$${}^1E'' \quad \frac{3}{4}J_1 + \frac{3}{4}J_2$$

$${}^1A_1 \quad \frac{5}{2}J_1 - \frac{3}{4}J_2 - \frac{1}{4}J_1$$

$${}^1E \quad 1_1 + \frac{3}{4}J_1 - \frac{1}{4}J_2$$

n = 6

O<sub>h</sub>

$$J_{12} = J_{13} = J_{14} = J_{15} = J_{16} = J_1$$

$$J_{23} = J_{24} = J_{25} = J_{26} = J_2$$

$$J_{34} = J_1$$

$${}^1A_{1g} \quad -3J_1 - \frac{3}{4}J_2$$

$${}^1T_{1g} \quad \frac{1}{4}J_1 - J_2$$

$${}^1E_g \quad -\frac{3}{4}J_2$$

$${}^1T_{2g} \quad \frac{3}{4}J_1$$

$${}^1T_{1g} \quad 1_1 + \frac{1}{4}J_1$$

$${}^1E_g \quad 2J_1 - \frac{3}{4}J_2$$

$${}^1A_{1g} \quad \frac{9}{4}J_1$$

$${}^1T_{2g} \quad 2J_1 + \frac{1}{4}J_1$$

$${}^1A_{1g} \quad 3J_1 - \frac{3}{4}J_2$$

Spin greater than 1/2. This procedure can be extended to centres of spin greater than 1/2. Whereas in the case of spin 1/2 the only off-diagonal elements which arise are of the form  $\langle \alpha\beta || \beta\alpha \rangle$ , for S=1 off-diagonal elements may arise in three ways, so that

$$\langle -10 || 01 \rangle, \quad \langle -10 || 0-1 \rangle \quad \text{and} \quad \langle -11 || 00 \rangle$$

are all non-zero.

For binuclear systems of S = 1/2n, a(n+1)<sup>2</sup> × (n+1)<sup>2</sup> matrix is obtained which is already in block form for the basis set. There are two 1 × 1 matrices, two 2 × 2 matrices... two n × n matrices and a central

(n+1) × (n+1) matrix. The eigenfunctions which diagonalise these blocks are readily obtained from the spin-shift operators.

For more than two centres the complexity rapidly increase and it becomes necessary to use computational methods of matrix diagonalisation. Eigenvalues for two centres of S = 1/2n for n = 1 to 7 are well known.

In general the ground state will be 4S<sub>n</sub>+1 degenerate in spin and of energy -(S<sub>i</sub>)<sup>2</sup>J. The higher levels descend regularly in multiplicity by two, at intervals of 2S<sub>i</sub>J, (2S<sub>i</sub>-1)J, ..., J, with the highest energy singlet at S<sub>i</sub>(S<sub>i</sub>+1)J. Thus if S' = 0 ... 2S<sub>i</sub> is the component of spin-momentum being considered, this has multiplicity 2S'+1 and its energy is 1/2J(S'(S'+1)) above that of the ground state.

Symmetry determined eigenvalues for n-centres of spin 1

n = 3	S = 1	D <sub>3</sub>	n = 3	S = 1	C <sub>s</sub>
J <sub>12</sub> = J <sub>13</sub> = J <sub>23</sub> = J			J <sub>12</sub> = J <sub>23</sub> = J <sub>2</sub>		J <sub>13</sub> = J <sub>1</sub>
<sup>1</sup> A <sub>1</sub>	-3J		<sup>1</sup> A'		-2J <sub>1</sub> - J <sub>1</sub>
<sup>1</sup> E	0		<sup>1</sup> A'		J <sub>1</sub> - J <sub>1</sub>
<sup>1</sup> E	2J		<sup>1</sup> A''		J <sub>1</sub> - J <sub>2</sub>
<sup>1</sup> A <sub>1</sub>	2J		<sup>1</sup> A'		2J <sub>1</sub>
<sup>1</sup> A <sub>2</sub>	3J		<sup>1</sup> A'		3J <sub>1</sub> - J <sub>1</sub> *
			<sup>1</sup> A''		J <sub>1</sub> + J <sub>2</sub>
			<sup>1</sup> A''		2J <sub>2</sub> + J <sub>1</sub>

n = 3	S = 1	D <sub>∞h</sub>
J <sub>12</sub> = J <sub>23</sub> = J <sub>2</sub>		J <sub>13</sub> = J <sub>1</sub>

the energy levels are the same as for the isosceles triangle, C<sub>s</sub>.

(\*<sup>3</sup>A' is the ground state for J<sub>1</sub>=0, J<sub>2</sub> negative)

n = 4	S = 1	T <sub>d</sub>
J <sub>12</sub> = J <sub>13</sub> = J <sub>14</sub> = J <sub>23</sub> = J <sub>24</sub> = J <sub>34</sub> = J		
<sup>1</sup> A <sub>1</sub>		-6J
<sup>1</sup> T <sub>2</sub>		-2J
<sup>1</sup> A <sub>1</sub>		J
<sup>1</sup> E		J
<sup>1</sup> T <sub>2</sub>		J
<sup>1</sup> T <sub>1</sub>		3J
<sup>1</sup> T <sub>2</sub>		3J
<sup>1</sup> A <sub>1</sub>		4J
<sup>1</sup> E		4J

The energy levels show extensive accidental degeneracy in this case.

We finally consider the effect of the pattern of energy levels on the calculated magnetic properties. The molar susceptibility χ<sub>M</sub> of a compound is normally calculated from the Van Vleck relationship.<sup>1</sup>

$$\chi_M = \frac{N \sum_n \left( \frac{[E_{nm}(1)]^2}{kT} + 2E_{nm}(2) \right) \exp(-E_n(O)/kT)}{\sum_n W_n \exp(-E_n(O)/kT)} \quad (9)$$

where the energy of the n<sup>th</sup> level, of degeneracy W<sub>n</sub>,

(1) B. N. Figgis, J. Lewis in « Progress in Inorganic Chemistry » ed. F. A. Cotton, 6, 37.

in the presence of an external field  $H$  is given by

$$E_n(O) + E_{nm}(1)H + E_{nm}(2)H^2 \quad (10)$$

and  $N$ ,  $k$ ,  $T$  have their usual significance. It should be noted that the term in  $H^2$  arises from mixing of the energy levels by the magnetic field itself and contributes the temperature-independent part of the susceptibility. It cannot be calculated using the present approach and so an arbitrary correction,  $N\alpha$ , has to be made for it.

It follows that the temperature dependence of the molar susceptibility of a binuclear complex with spin  $1/2$  at each centre is given by the relationship

$$\chi_m = \frac{2g^2N\beta^2}{3kT} \left( \frac{1}{1 + \frac{1}{3} \exp(J/kT)} \right) + N\alpha \quad (11)$$

For the more complex cases, a susceptibility equation is derived in the same way.

The first-order Zeeman effect is to split each spin-multiplet into its  $2S+1$  component levels, ranging in energy from  $-g\beta HS$  to  $+g\beta HS$ .

Thus we obtain the well known formula

$$\chi_m = \frac{Ng^2\beta^2}{3kT} \left( \frac{\sum_m S_m(S_m+1)(2S_m+1)e^{-E_m(O)/kT}}{\sum_n (2S_n+1)e^{-E_n(O)/kT}} \right) + N\alpha \quad (12)$$

By substitution of fundamental constants,

$$N\beta^2/3k = 0.1251 \approx \frac{1}{8}$$

For example, for four centres of spin  $1/2$  arranged in a tetrahedron, there is a quintet at  $O$ , a nonaplet at  $+2J$  which consists of 3 degenerate spin-triplets, and a degenerate pair of singlets at  $+3J$ , leading to

$$\begin{aligned} \chi_m &= \frac{g^2}{8T} \left( \frac{2 \cdot 3 \cdot 5 + 3 \cdot 1 \cdot 2 \cdot 3x^2 + 0}{5 + 9x^2 + 2x^3} \right) + N\alpha \\ &= \frac{g^2}{8T} \left( \frac{30 + 18x^2}{5 + 9x^2 + 2x^3} \right) + N\alpha \end{aligned} \quad (13)$$

and

$$x = e^{J/kT}$$

Whilst for four centres of spin  $1/2$  in a  $C_{2v}$ -distorted tetrahedron

$$\chi_m = \frac{g^2}{8T} \left( \frac{30 + 6(xy + x^2 + xz)}{5 + 3(xy + x^2 + xz) + (x^3 + xyz)} \right) + N\alpha \quad (14)$$

where

$$x = e^{J_m/kT}, \quad y = e^{J_l/kT}, \quad z = e^{J_s/kT}$$

(2) B. N. Figgis, R. L. Martin, *J. Chem. Soc.*, 3837 (1956).

It should be noted that the Van-Vleck approximation may break down at very low temperatures, when co-operative magnetic phenomena are observed for most compounds although there may be simplifying features for systems of spin  $\geq 1/2$ . This is because many antiferromagnetic materials form a magnetically ordered lattice on cooling. The symmetry properties of this lattice are described by a magnetic space group,<sup>3</sup> which includes spin-reversal as a basic operation. Thus such a lattice consists of ions whose spin angular momentum with respect to a given axis is restricted to  $\pm S_j$ , the eigenvalues obtained in this case being related to those obtained for  $S=1/2$  by the simple factor  $4S_j^2$ . Exploitation of such symmetry offers real hope of simple calculations on antiferromagnetic materials at low temperatures. Further many antiferromagnetic materials show high symmetry so that the number of symmetry-related magnetic centres in the unit cell is usually quite small.

The known ferromagnetic and antiferromagnetic polynuclear complexes have recently been reviewed by Martin.<sup>4</sup> In general it is necessary to adopt a « best-fit » procedure to determine the values of the several coupling constants in equations such as (14) describing the susceptibility. When, however, a Curie point has been observed for a ferromagnetic substance, or a Néel point for an antiferromagnetic substance, the procedure may be made a little more rigorous by requiring that

$$\frac{\partial \chi}{\partial T} = 0 \quad \text{at } T_c(T_N) \quad (15)$$

We may obtain a general expression for this second equation by differentiation of equation (12).

$$\begin{aligned} \frac{\partial \chi_m}{\partial T} &= \frac{Ng^2\beta^2}{3kT} \left( \frac{\partial}{\partial T} \frac{\sum_m S_m(S_m+1)(2S_m+1)e^{-E_m(O)/kT}}{\sum_n (2S_n+1)e^{-E_n(O)/kT}} \right) \\ &\quad - \frac{1}{T} (\chi_m - N\alpha) \end{aligned} \quad (16)$$

For example, differentiating equation (11) we obtain<sup>2</sup>

$$((J/kT_c) - 1) \exp(J/kT_c) = 3 \quad (17)$$

whence

$$J \approx 1.6 kT_c$$

*Acknowledgement.* We are indebted to I.C.I. and the S.R.C. for financial support (to R.W.J.).

(3) W. Opechowski and R. Guccione in « Magnetism », *IIa*, Edited by G. T. Rado, H. Suhl (Academic Press, 1963) p. 105.  
(4) R. L. Martin in « New Pathways in Inorganic Chemistry » Edited by E. A. V. Ebsworth, A. G. Maddock, A. G. Sharpe (Cambridge, 1968) p. 175.