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MAGNETIC EXCHANGE IN POLYNUCLEAR METAL COMPLEXES

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CONTENTS

A. INTRODUCTION

Magnetic exchange interactions in various materials have been of interest to physicists and mathematicians for some considerable time[1-8], though this interest has been concentrated on lattice (intermolecular) ferromagnetism and antiferromagnetism[1-14]. The chemical literature has only very recently embraced this field, but from the exponential increase of relevant publications there is no doubt that the concept of exchange has fired the imagination of physical and inorganic chemists[15–17]. However, the chemist is mainly interested in discrete (intramolecular) antiferromagnetic interactions, for the excellent reasons that this is by far the commonest type of interaction in chemical compounds, and that the concept is easier to understand than intermolecular interactions. Even this concept was pioneered by physicists, but it attracted little immediate attention[18]. The ultimate interest appears to have been stimulated essentially by the explanation of the anomalous magnetic properties of copper(II) acetate[19] in terms of exchange interactions resulting from a binuclear structure which was subsequently verified[20]. There appears to be no limit to the number and different types of multinuclear metal complexes suitable to magnetic exchange interactions that can be prepared.

Some of the concepts of discrete magnetic interactions still appear to be little understood. Moreover, the existing theory can no longer describe all the cases known at present, nor can it be applied to a truly general case. Another problem, that has so far been overcome by ignoring it, is what to do about orbital contribution, which is normally considered in detail in theoretical calculations of magnetic properties[16,21,22]. It happens that the magnetic properties of discrete antiferromagnets can usually be explained in terms of spin contributions only, ignoring orbital contributions (or equating orbital contribution to a constant factor), but this has never been justified.

It is the aim of this review to generalise the theory of exchange interactions in discrete clusters of paramagnetic atoms, to indicate the extent of applicability and the limitations of the theory, and to examine the approximations commonly made in exchange systems, justifying them when they are valid, and indicating when they are not No attempt will be made at a comprehensive review of the literature, which is too immense ever to be reviewed completely. Instead, examples will merely be drawn from the literature where they seem appropriate to the discussion.

B. THE IDEA OF EXCHANGE

For completeness, we must say what we mean by exchange, but as the subject has already been covered extensively[1–10,17], no detailed discussion will be entered into. Fermi–Dirac statistics requires that electron wave-functions be antisymmetrical with respect to exchange of electrons. Thus if a wavefunction for two electrons 1 and 2 is divided into a product of orbital and spin parts $\varphi(1, 2) \cdot \varphi_s(1,2)$, one, but not both of φ and φ_s must be antisymmetric. Electrostatic interaction, $\mathscr{H}$ between the electrons involves only φ and results in matrix elements

$$K = \langle \phi(1, 2) \,|\, \mathscr{H} \,|\, \phi(1, 2) \rangle = \langle \phi(2, 1) \,|\, \mathscr{H} \,|\, \phi(2, 1) \rangle$$

(direct, or coulomb integral)

and

$$J = \langle \phi(1,2)\,|\,\mathscr{H}\,|\,\phi(2,1)\rangle = \langle \phi(2,1)\,|\,\mathscr{H}\,|\,\phi(1,2)\rangle \qquad \text{(exchange integral)}$$

where $\varphi(1,2)$ and $\varphi(2,1)$ represent the same orbital wavefunction, but with the electrons interchanged. Diagonalisation of this matrix leads to the symmetrical wavefunction

$$\psi_1 = \frac{1}{\sqrt{2}}\left[\varphi(1,2)+\varphi(2,1)\right]$$

with eigenvalue $K+J$ and the antisymmetrical wavefunction

$$\psi_2 = \frac{1}{\sqrt{2}}\left[\varphi(1,2)-\varphi(2,1)\right]$$

with eigenvalue $K-J$. For the two electrons, the total spin S is 1 or 0; $S = 1$ corresponds to an antisymmetric φ_s, and $S = 0$ to a symmetric φ_s. Thus ψ_1 and ψ_2 are associated with $S = 1$ and $S = 0$ respectively. Clearly the exchange interaction is not an interaction in the true sense, but it enables us to determine which wavefunctions and eigenvalues are allowed, given the electron spin. Exchange interaction is purely a consequence of quantisation, and vanishes (like the electron spin itself) in the passage to the limit of classical mechanics. The eigenvalues $K \pm J$, can be expressed in terms of the electron spins, via the relation

$$\begin{aligned} 2\boldsymbol{s}_1\cdot\boldsymbol{s}_2 &= (S)^2-(s_1)^2-(s_2)^2, \qquad (s_1 = s_2 = \tfrac{1}{2})\\ &= S(S+1)-s_1(s_1+1)-s_2(s_2+1) = -\tfrac{3}{2} \text{ if } S = 0, \tfrac{1}{2} \text{ if } S = 1\end{aligned}$$

Thus the eigenvalues are given by $K-\frac{1}{2}J-2J\,\boldsymbol{s}_1\cdot\boldsymbol{s}_2$. The energy origin may be shifted to remove the constant terms $K-\frac{1}{2}J$, leaving an effective spin–spin coupling "Heisenberg" operator, $\mathscr{H} = -2J\,\boldsymbol{s}_1\cdot\boldsymbol{s}_2$, which may now be used in the same manner as $\boldsymbol{l}\cdot\boldsymbol{s}$ is used in the calculation of spin–orbit coupling, $\boldsymbol{I}_1\cdot\boldsymbol{I}_2$ in NMR, $\boldsymbol{I}\cdot\boldsymbol{s}$ in ESR, and so forth. The argument may be extended to exchange between two paramagnetic atoms with quantised total spins S_1, S_2, which may have values greater than $\frac{1}{2}$.

From the Heisenberg operator we may obtain energy levels in which electrons are paired and unpaired to various extents and the calculation may be visualised as a way of obtaining high spin and low spin states in a group of metal atoms rather than just one. The exchange integral J is then roughly analogous to the ligand field strength Δ normally defined in transition metal complexes.

C. EXTENSION OF HEISENBERG'S THEORY OF FERROMAGNETISM

The Hamiltonian appropriate to Heisenberg's theory of ferromagnetism is

$$\mathscr{H} = -2J\sum \boldsymbol{s}_i\cdot\boldsymbol{s}_j \tag{1}$$

The pair-wise spin–spin coupling is considered between nearest neighbours only, and the summation is taken over the entire lattice. In a lattice ferromagnet, each individual spin couples with the magnetic field produced (the magnetisation) by the net alignment of other spins in the lattice, as well as with any applied magnetic field. The same arguments apply to lattice antiferromagnets. The detailed theory for such exchange interactions in various types of lattice is quite complicated, but is usually not relevant to the magnetic behaviour of transition metal complexes, since in most complexes organic ligands separating the metal atoms prevent the formation of a lattice of closely linked paramagnetic atoms.

One type of lattice exchange interaction that does apply to some transition metal complexes, is the Ising model which describes interactions between an infinite linear chain of neighbouring paramagnetic atoms If $s = \frac{1}{2}$ for each member of the chain, the Ising model yields expressions for the magnetic susceptibilities parallel ($\chi_{\parallel}$) and perpendicular ($\chi_{\perp}$) to the magnetic field direction, which reduce to

$$\chi_{\parallel} = \frac{Ng^2\beta^2}{4kT} \, e^{J/kT} \tag{2}$$

$$\chi_{\perp} = \frac{Ng^2\beta^2}{8J} \, [\tanh K + K \operatorname{sech}^2 K], \quad K = \frac{J}{kT} \tag{3}$$

Most experimental measurements are made on powdered sample, in which only the average susceptibility χ_M is determined and the theoretical value of χ_M is given by Eqn. 4[23] obtained by summing 2 and 3 over all orientations

$$\chi_M = \tfrac{1}{3}\chi_{\parallel} + \tfrac{2}{3}\chi_{\perp}$$

or

$$\chi_M = \frac{Ng^2\beta^2}{12kT} \times \frac{e^{4K} + (2+K^{-1})\,e^{2K} - K^{-1}\,e^{-2K} + 5}{e^{2K} + e^{-2K} + 2} \tag{4}$$

The Ising model should apply fairly well to any system which can be visualised as a linear chain of interacting paramagnetic atoms, and comparison of observed magnetic properties with Eqn 4 can help to elucidate the structure of an unknown compound[23–26]. Eqn. 4 or its equivalent has been successfully applied to oxovanadium(IV) acetate and analogous polymeric vanadyl alkanoates[24], to copper(II) chloride and methoxide[25], and is probably also applicable to copper(II) oxalate[27,28].

When the pair-wise interactions in linear chains are assumed to be of the isotropic "Heisenberg" type, Eqn. 1, instead of the anisotropic Ising type, the treatment becomes more involved and exact solutions can be obtained only in the classical limit, $S \to \infty$[29]. In reality, the coupling is expected to be somewhere between complete anisotropy and isotropy, and the theoretical treatment has been extended to include such situations, using the "intermediate" Hamiltonian[29]

$$\mathscr{H} = -2J \sum [\gamma S_i \cdot S_j + (1-\gamma) S_{iz} S_{jz}] \tag{5}$$

which reduces to the Ising case when $\gamma = 0$ and the Heisenberg case when $\gamma = 1$. For powder samples of the type discussed above[23-28] the difference between the two types of couplings becomes important only at very low temperatures, so that no choice between the two models can or need as yet be made, and Eqn. 4 remains adequate for the higher temperature range normally of interest to inorganic chemists. In one particular case, a detailed single crystal magnetic susceptibility study has been made at low temperatures: $CsMnCl_3 \cdot 2H_2O$, containing relatively isolated chains of manganese atoms[30]. It was found that the susceptibility can be described quite well from 77 to 5 °K using Heisenberg coupling, with minor deviations at hydrogen temperatures attributed mainly to single-ion effects. Below 5 °K, interchain interactions are also evident, causing some long-range antiferromagnetic ordering, and at 0.35 °K, an as yet unexplained anomalous temperature dependence is seen. The Ising and Heisenberg models can also be applied to two- and three-dimensionally infinite systems though these are not usually of interest to chemists[11,12,23,29,31]. In powdered infinite antiferromagnetic systems both models predict the commonly observed residual zero temperature magnetism, so that it is not always possible to distinguish experimentally between the two models. For finite systems, only the Heisenberg model predicts the zero temperature fall off to zero magnetism observed in many such systems.

By far the commonest type of exchange interactions observed in inorganic complexes involves small clusters of n paramagnetic atoms separated from one another by diamagnetic organic ligands, and Eqn. 1 becomes

$$\mathscr{H} = -2 \sum_{j > i = 1}^{n} J_{ij} S_i \cdot S_j \tag{6}$$

where J_{ij} is the exchange integral between the i^{th} and j^{th} atoms, with spins S_i and S_j. Under certain conditions, which will be elaborated in Section E, we may write down the eigenvalues of (6) using the vector model

$$2S_i \cdot S_j = S_{ij}(S_{ij}+1) - S_i(S_i+1) - S_j(S_j+1) \tag{7}$$

where $S_{ij} = S_i + S_j$. This procedure was adopted by Kambe[18] who first treated antiferromagnetic interactions in discrete trinuclear complexes.

D. LOGICAL EXTENSION OF KAMBE'S APPROACH

(i) Kambe's calculation

Substitution of the vector model (7) into Eqn. 6 for the case where $n = 3$ and two of the J_{ij} are equal ($J_{12} = J_{23} = J = (J_{13}/\alpha)$) leads to the eigenvalue equation

$$E(S_T) = -J[S_T(S_T+1)-(1-\alpha)S^*(S^*+1)-(1+2\alpha)S(S+1)] \tag{8}$$

where $S_1 = S_2 = S_3 = S$, $S^* = S_1+S_3$ $S_T = S_1+S_2+S_3$. The allowed values of S^* and S_T are given by

$$\begin{aligned} S^* &= S_1+S_3, S_1+S_3-1, \ .\ |S_1-S_3| = 2S, 2S-1, \ldots 0 \\ S_T &= S^*+S, S^*+S-1, \ldots |S^*-S| \end{aligned} \tag{9}$$

A value of $E(S_T)$ occurs for each allowed value of S_T (*i.e.* for each pair of values of S_T and S^* in this case). The magnetic susceptibility of the system can now be calculated.

(ii) *General calculation of magnetic susceptibility*

The effect of an applied magnetic field $\boldsymbol{H}$ is represented by adding a term $g\beta \boldsymbol{H}\cdot \boldsymbol{S}_T$ to Hamiltonian (6), where g and β are the Landé splitting factor and the Bohr magneton respectively. Without loss of generality we can define the z-axis along the direction of $\boldsymbol{H}$. Then $(\boldsymbol{H})_z = H$, $H_x = H_y = 0$, and our extra term becomes $g\beta HS_z$. This splits each of the eigenvalues in (8) into $2S_T+1$ levels and leads to the eigenvalue equation

$$E_i = E(S_T)+g\beta HM_{S_T} \tag{10}$$

This is shown schematically in Fig. 1 for the case $S = \frac{1}{2}$.

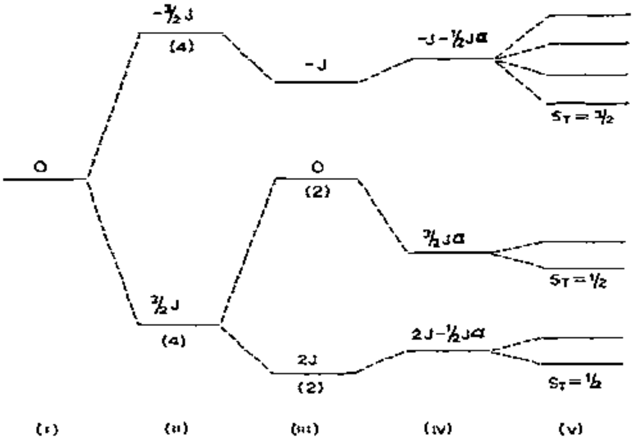


Fig. 1 Energy levels given by Eqn 10 for a cluster of three interacting paramagnetic atoms, with one unpaired electron For level (i) $J = 0$, $H = 0$, for the other levels the interaction is antiferromagnetic $J < 0$ For (ii) $\alpha = 1$, $H = 0$ For (iii) $\alpha = 0$, $H = 0$ For (iv) $0 < \alpha < 1$, $H \rightarrow 0$ For (v) $0 < \alpha < 1$, $H > 0$

The magnetic susceptibility per mole of complex, χ_M is now obtained by assuming a Boltzmann distribution of molecules over the various levels E_i

$$\chi_M = -\frac{N}{H}\sum_{i=1}^{p}\frac{\partial E_i}{\partial H}\,\mathrm{e}^{-E_i/kT}\Big/\sum_{i=1}^{p}\mathrm{e}^{-E_i/kT} \tag{11}$$

where p is the total number of eigenvalues E_i (Eqn. 10). Since $g\beta H \ll kT$ in the temperature range of interest [$g\beta H \sim 1$ cm^{-1} for magnetic fields ($\sim$10 kG) normally accessible in laboratories, and $kT \sim 0.7\,T\,\mathrm{cm}^{-1}$], we may to good approximation simplify Eqn. 11 to

$$\chi_M = \frac{Ng^2\beta^2}{3kT}\,\frac{\sum\limits_{S_T} S_T(S_T+1)\,(2S_T+1)\,\mathrm{e}^{-E(S_T)/kT}}{\sum\limits_{S_T}(2S_T+1)\,\mathrm{e}^{-E(S_T)/kT}} \tag{12}$$

where the summation is over all the allowed values of S_T. The generality of Eqn. 12 may be tested by inserting in it the simple "spin-only" case where no exchange interactions occur, so that $S_T = S^* = S$, $J = 0$ and hence $E(S_T) = 0$, reducing the equation to the Curie law, $\chi_M = Ng^2\beta^2S(S+1)/3kT$. (Here we have used $\Sigma M_S{}^2 = \frac{1}{3}S(S+1)\,(2S+1)$, $\Sigma M_S = 0$ and $\Sigma 1 = 2S+1$, where the summation is over all M_S).

Kambe[18] obtained good agreement between theoretical and experimental χ_M values by assuming equal strengths of interaction between each pair of paramagnetic atoms (all $J_{ij} = J$) in the trinuclear complexes $[(\mathrm{H_2O\cdot M})_3\mathrm{O\cdot(R\cdot COO)_6}]^+$ where $\mathrm{M = Fe^{III}}$ or $\mathrm{Cr^{III}}$ and R·COOH is an alkanoic acid[32,33]. Thus substitution of $\alpha = 1$ and the appropriate values of S^*, S_T($S^* = 3$; $S_T = \frac{9}{2}, \frac{7}{2}, \frac{5}{2}, \frac{3}{2}$. 2; $\frac{7}{2}, \frac{5}{2}, \frac{3}{2}, \frac{1}{2}$. 1; $\frac{5}{2}, \frac{3}{2}, \frac{1}{2}$. 0; $\frac{3}{2}$) in Eqn. 8 yields the $E(S_T)$ values for the trinuclear chromium complexes, and substitution of the $E(S_T)$ and S_T values into Eqn. 12 reproduces Kambe's equation for these complexes[18]. The equation for trinuclear iron(III)[18,34] is obtained similarly from Eqn. 8 and Eqn 12. Kambe's hypothesis was confirmed by subsequent X-ray work[35] which showed the metal atoms to be grouped in equivalent positions about a central oxygen atom and bridged by pairs of alkanoate groups. Later magnetic studies[35–43] confirmed the interpretation as well as the original results with only minor modifications. J is about 10 cm^{-1} and 30 cm^{-1} for the chromium and iron complexes respectively.

(iii) Generalised Kambe approach

Recently various extensions of Kambe's theory have been used in specific cases[17,44–53], and a treatment of the general case has been given[51–53]. The latter treatment will be followed here.

Hamiltonian (6) is readily expanded into the form

$$\mathscr{H} = -\left(2\sum_{j>i=1}^{n-1} J_{ij}S_i\ \ S_j + 2\sum_{i=2}^{n-1} J_{in}S_i\cdot S_n + 2\ {}_{1n}S_1\cdot S_n\right) \tag{13}$$

Using the relation

$$2S_1\cdot S_n = S_T(S_T+1) - \sum_{i=1}^{n} S_i(S_i+1) - 2\sum_{j>i=1}^{n-1} S_i\cdot S_j - 2\sum_{i=2}^{n-1} S_i\cdot S_n$$

and Eqn. 8 in Hamiltonian (13), we obtain the eigenvalue equation

$$\begin{aligned}E(S_T) = & -\sum_{j>i=1}^{n-1} (J_{ij}-J_{1n})\,[S_{ij}(S_{ij}+1)-S_i(S_i+1)-S_j(S_j+1)] \\ & -\sum_{i=2}^{n-1} (J_{in}-J_{1n})\,[S_{in}(S_{in}+1)-S_i(S_i+1)-S_n(S_n+1)] \\ & -J_{1n}S_T(S_T+1)+J_{1n}\sum_{i=1}^{n} S_i(S_i+1) \qquad (14)\end{aligned}$$

In real situations, suitable simplifications of the problem can often be made from symmetry considerations in order to reduce Eqn. 14 to an unambiguous and simple expression, from which the energy values available to the system and hence the magnetic susceptibility are readily obtained

Thus, when $n = 2$

$$E(S_T) = -J_{12}[S_T(S_T+1)-S_1(S_1+1)-S_2(S_2+1)] \qquad (15)$$

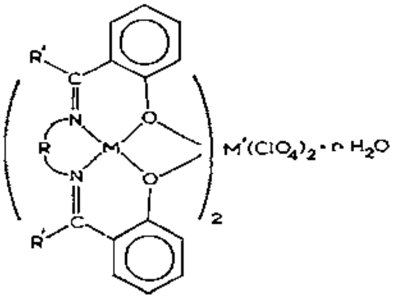
where S_T has allowed values $S_1+S_2, S_1+S_2-1, \ldots |S_1-S_2|$. When this and Eqn. 11 are applied to the case $S_1 = S_2 = \frac{1}{2}$, we obtain the Bleaney–Bowers equation[19] which describes the magnetic properties of a large variety of dimeric complexes in which the metal atoms each contain one unpaired *d*-electron, *e.g* complexes of copper(II)[15–17,19,23,25–28,44,51,53–69], oxovanadium(IV)[16,17,70], titanium (III)[71] and probably iron(III)[16,17,72–80] and molybdenum(V)[16,17,81,82]. For other binuclear complexes, the magnetic properties are obtained similarly, using the appropriate values of S_1, S_2 and S_T in Eqns. 15 and 11, but the calculation is trivial and the details not worth listing here, though data have been given at length elsewhere[83]. A variety of transition metal complexes known or believed to be dimeric can be described more or less well by the above calculation, *e g.* $\mathrm{Cu^{II}–Ni^{II}}$ $(d^9–d^8)$, $S_1 = \frac{1}{2}$, $S_2 = 1$[84], $\mathrm{Ni^{II}–Ni^{II}}$ $(d^8–d^8)$, $S_1 = S_2 = 1$[85–93], $\mathrm{W^{III}–W^{V}}$, $S_1 = \frac{1}{2}$, $S_2 = \frac{3}{2}$ (or $\mathrm{W^{IV}–W^{IV}}$, $S_1 = S_2 = 1$)[94], $\mathrm{Cu^{II}–Co^{II}}$ $(d^9–d^7)$, $S_1 = \frac{1}{2}$, $S_2 = \frac{3}{2}$[84], $\mathrm{Cu^{II}–Fe^{II}}$ $(d^9–d^6)$, $S_1 = \frac{1}{2}$, $S_2 = 2$[84,95], $\mathrm{Cu^{II}–Mn^{II}}$ $(d^9–d^5)$, $S_1 = \frac{1}{2}$, $S_2 = \frac{5}{2}$[84,88–90], $\mathrm{Co^{II}–Co^{II}}$ $(d^7–d^7)$, $S_1 = S_2 = \frac{3}{2}$[85,88–90], $\mathrm{Cr^{III}–Cr^{III}}$ $(d^3–d^3)$, $S_1 = S_2 = \frac{3}{2}$[96–99], $\mathrm{Mo^{III}–Mo^{III}}$ $(d^3–d^3)$, $S_1 = S_2 = \frac{3}{2}$[100], $\mathrm{Fe^{III}–Co^{II}}$ $(d^5–d^7)$, $S_1 = \frac{5}{2}$, $S_2 = \frac{3}{2}$[84], $\mathrm{Mn^{III}–Mn^{III}}$ $(d^4–d^4)$, $S_1 = S_2 = 2$[101], $\mathrm{Cr^{II}–Cr^{II}}$ $(d^4–d^4)$, $S_1 = S_2 = 2$[102], $\mathrm{Fe^{II}–Fe^{II}}$ $(d^6–d^6)$, $S_1 = S_2 = 2$[103], $\mathrm{Fe^{III}–Fe^{III}}$ $(d^5–d^5)$, $S_1 = S_2 = \frac{5}{2}$[104,107], and $\mathrm{Mn^{II}–Mn^{II}}$ $(d^5–d^5)$, $S_1 = S_2 = \frac{5}{2}$[108]. We will return later to some cases where the theory does not apply too well.

When $n = 3$, Eqn. 14 gives

$$\begin{aligned}E(S_T) = & -J_{13}S_T(S_T+1)+S_{12}(S_{12}+1)\,[J_{13}-J_{12}]+ \\ & +S_{23}(S_{23}+1)\,[J_{13}-J_{23}]+J_{12}S_1(S_1+1)+ \\ & +S_2(S_2+1)\,[J_{12}+J_{23}-J_{13}]+J_{23}S_3(S_3+1) \qquad (16)\end{aligned}$$

When two or all three of the J_{ij} in Eqn. 16 are equal, the allowed values of S_T and of one of the S_{ij} (whichever does not cancel) are given by the vector coupling rules, (9). However, in the completely general case (none of the J_{ij} necessarily equal) not all the allowed values can be given unambiguously, and the problem cannot be solved by the extended Kambe approach. We will examine the reason for this, and how to overcome it in Section E.

Fortunately, symmetry considerations in many trinuclear complexes permit adequate simplifications of Eqn. 16. This is illustrated by Kambe's complexes (above) and by a series of complexes of type 1, containing interacting metal atoms at the corners of an isosceles triangle 2[42,51–53,109,110]. Since the positions of the interacting atoms are undefined in the above equation, the atoms in a given symmetry may be numbered arbitrarily in any convenient way. The series where M = Cu and M′ is some other transition metal, has been most closely examined. From the symmetry we have $J_{12} = J_{13} = J$; $J_{23} = J_{\mathrm{CuCu}}$; and $S_1 = S_M$, $S_2 = S_3 = \frac{1}{2}$. Eqn. 16 then reduces to



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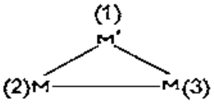


2

$$E(S_T) = -JS_T(S_T+1)+S_{23}(S_{23}+1)[J_{13}-J_{23}]+JS_M(S_M+1)+\tfrac{3}{2}J_{\mathrm{CuCu}} \quad (17)$$

where the allowed values of $(S_{23};\, S_T)$ are $(1;\, S_M+1,\, S_M,\, S_M-1)$, $(0;\, S_M)$ from (9). Application of Eqns. 17 and 12 now yields for the magnetic susceptibility of these complexes:

$$\chi_M = \frac{Ng^2\beta^2}{kT}\sum_{i=1}^{4} a_i\, e^{-E_i/kT} \Big/ \sum_{i=1}^{4} b_i\, e^{-E_i/kT}$$

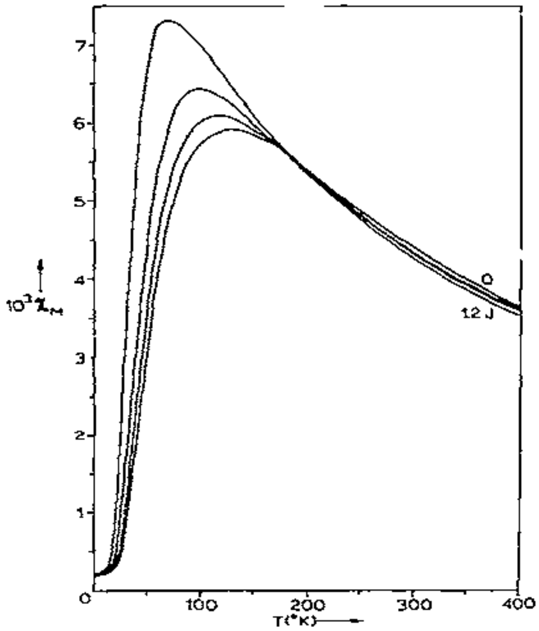
where

$$a_1 = \sum_{q=0}^{m-4} (S_M-1-q)^2 \qquad b_1 = m-3 \qquad E_1 = mJ-\tfrac{1}{2}J_{\mathrm{CuCu}}$$

$$a_2 = a_3 = \sum_{q=0}^{m-4} (S_M-q)^2 \qquad b_2 = b_3 = m-1 \qquad E_2 = 2J-\tfrac{1}{2}J_{\mathrm{CuCu}}$$

$$a_4 = \sum_{q=0}^{m} (S_M+1+q)^2 \qquad b_4 = m+1 \qquad E_3 = \tfrac{3}{2}J_{\mathrm{CuCu}}$$

$$m = 2S_M+2 \qquad E_4 = (2-m)J+\tfrac{1}{2}J_{\mathrm{CuCu}}$$



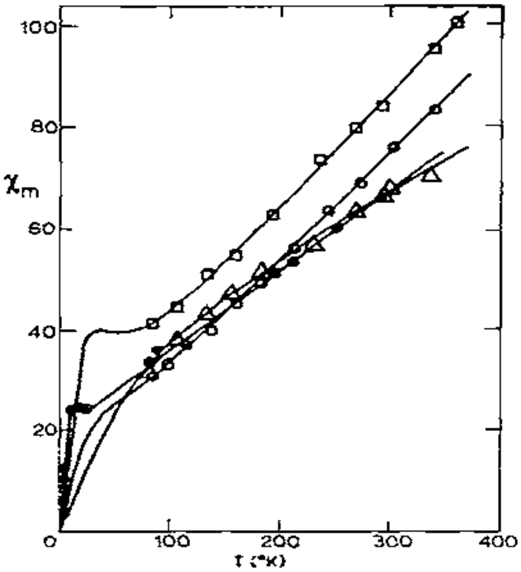


Fig. 2 Temperature dependence of the reduced molar susceptibility χ_M' ($= -\chi_M/g^2$) of the system CuNiCu, where $J_{\mathrm{CuNi}} = J_{\mathrm{NiCu}} = J$, and J_{CuCu} has the four values $J_{\mathrm{CuCu}} = 0$, $0.4J$, $0.8J$ and $1.2J$. In the four curves shown here the value of J is taken as $-50\ \mathrm{cm}^{-1}$.

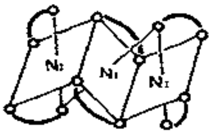
Fig. 3. Temperature dependence of the inverse magnetic susceptibility χ_M^{-1} for trinuclear complexes containing the groupings CuCoCu (d^9–d^7–d^9), CuFeCu (d^9–d^6–d^9), CuMnCu (d^9–d^5–d^9) and CrCrCr (d^3–d^3–d^3). The curves are calculated from Eqn 16 using the J values given; □ $(\mathrm{CuPHA})_2\mathrm{Co(ClO_4)_2} \cdot 3\mathrm{H_2O}$, $J_{\mathrm{CuCo}} = -24\ \mathrm{cm}^{-1}$, $J_{\mathrm{CuCu}} = 0$, ○ $(\mathrm{CuPS})_2\mathrm{Fe(ClO_4)_2} \cdot 2\mathrm{H_2O}$, $J_{\mathrm{FeCu}} = -15\ \mathrm{cm}^{-1}$, $J_{\mathrm{CuCu}} = 0$; △ $(\mathrm{CuPHA})_2\mathrm{Mn(ClO_4)_2} \cdot 3\mathrm{H_2O}$, $J_{\mathrm{MnCu}} = -30\ \mathrm{cm}^{-1}$, $J_{\mathrm{CuCu}} = 0$, ● $[(\mathrm{H_2O \cdot Cr})_3\mathrm{O} \cdot (\mathrm{CH_3COO})_6]\mathrm{Cl} \cdot 6\mathrm{H_2O}$ $J_{12} = J_{13} = J_{23} = -15\ \mathrm{cm}^{-1}$, PHA = N,N'-1,3-propylenebis(*o*-hydroxyacetophenimine), PS = N,N'-1,3-propylenebis(salicylaldimine)

When the central metal M′ in **2** is octahedral nickel(II), (d^8, $S = 1$) and J is negative, the ground state is $S_T = 0$. Thus, the susceptibility passes through a maximum at some temperature and is expected to tend to zero as temperature decreases (Fig. 2). In other cases, where the ground state is non-zero, curves of the same general shape are obtained (Fig. 3). Curves of this shape, differing only in minor details such as slope, are in fact obtained generally for antiferromagnetically interacting clusters of paramagnetic metal atoms with a non-zero ground state.

The same calculation applies to trimeric nickel(II) acetylacetonate[111,112] **3** in which three octahedral nickel(II) atoms arranged linearly interact ferromagnetically (*i.e.* J positive)[17,45,46]. Substituting into Eqn 16 we obtain

$$E(S_T) = -JS_T(S_T+1)+S_{23}(S_{23}+1)\,[J-J']+4J'+2J \tag{18}$$

Here $S_1 = S_2 = S_3 = 1$ so that the allowed values of (S_{23}; S_T) are (2; 3, 2, 1), (1, 2, 1, 0) and (0; 1) respectively. Comparison of the calculated (Eqns. 12 and



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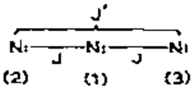

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18) and experimental χ_M values down to 4.3 °K leads to $J = 26$ cm^{-1} and $J' = -7$ cm^{-1} (Refs. 45, 46). This complex was the first well-documented discrete ferromagnet, though similar behaviour has been suggested in other trinuclear nickel(II) complexes[52,113]. Ferromagnets, in which only nearest neighbour interactions are important, have previously been observed — $(NH_4)_2CuCl_4 \cdot 2H_2O$ and its analogues — but the interaction is weak ($T_c = 0.7$ °K) and extends over a three-dimensionally infinite lattice rather than a discrete cluster[114,115]. Discrete ferromagnetism also seems likely in some binuclear copper(II) complexes[23].

When $n = 4$, Eqn. 14 becomes

$$\begin{aligned} E(S_T) = {} & -J_{14}S_T(S_T+1) - S_{12}(S_{12}+1)[J_{12}-J_{14}] - S_{13}(S_{13}+1)[J_{13}-J_{14}] \\ & -S_{24}(S_{24}+1)[J_{24}-J_{14}] - S_{34}(S_{34}+1)[J_{34}-J_{14}] \\ & +S_1(S_1+1)[J_{12}+J_{13}-J_{14}] + S_2(S_2+1)[J_{12}+J_{23}+J_{24}-2J_{14}] \\ & +S_3(S_3+1)[J_{12}+J_{13}+J_{34}-2J_{14}] \\ & +S_4(S_4+1)[-J_{14}+J_{24}+J_{34}] \end{aligned} \tag{19}$$

When either

$$J_{12} = J_{14} = J_{34} \quad \text{or} \quad J_{13} = J_{14} = J_{24} \tag{20}$$

the allowed values of S_T are given by either

$$S_{13}+S_{24},\ S_{13}+S_{24}-1, \ldots |S_{13}-S_{24}|$$

or

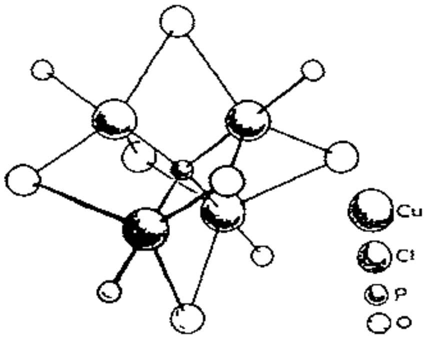
$$S_{12}+S_{34},\ S_{12}+S_{34}-1, \ldots |S_{12}-S_{34}|$$

where the S_{ij} are given by the coupling rules (9). When condition (20) is not satisfied, the allowed values of S_T cannot be given by vector coupling, a difficulty also noted above *when* $n = 3$ and all three J_{ij} are different.

In particular, when four identical paramagnetic atoms lie at the corners of a tetrahedron (all $S_i = S$, all $J_{ij} = J$), Eqn. 20 reduces to[17,52]

$$E(S_T) = -J[S_T(S_T+1) - 4S(S+1)] \tag{21}$$

A complex for which Eqn. 21 may be appropriate is $[Cu_4OBr_6(C_5H_5N)_4]$[116] (where C_5H_5N is pyridine). This complex was postulated to contain bridging bromine groups, a bridging oxygen, and four copper atoms whose environments appear to be quite similar. A structure containing two pairs of identical coppers bridged by a two-coordinated oxygen was therefore considered possible, but



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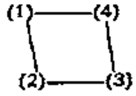
comparison with the stoichiometrically analogous complex $[Cu_4OCl_6\{OP(C_6H_5)_3\}_4]$[117,118], **5**, suggests that $[Cu_4OBr_6(C_5H_5N)_4]$ is also likely to contain a tetrahedral arrangement of copper atoms. The magnetic properties of both complexes have been investigated[17,84,119] and will be discussed below. A series of analogous $Cu_4OX_6L_4$ complexes[120,121] is presently under investigation[122].

Eqn. 21 is also applicable to the cubane Ni_4O_4 skeleton of $[Ni(OMe)sal(ROH)]_4$ which has been shown to contain four nickel(II) atoms at the corners of a tetrahedron which acts as a discrete ferromagnet (J positive)[123,124].

For four identical paramagnetic atoms arranged in a square (or a tetrahedrally distorted square, D_{2d}), $J_{12} = J_{23} = J_{34} = J_{14} = J$ and $J_{13} = J_{24} = J'$ we have[17]

$$E(S_T) = -JS_T(S_T+1)+(J-J')\,[S_{13}(S_{13}+1)+S_{24}(S_{24}+1)]+4J'S(S+1) \tag{22}$$

The analogous equation for a more unusual arrangement of four identical paramagnetic atoms has also been given: a rhombus **6** corresponding to the



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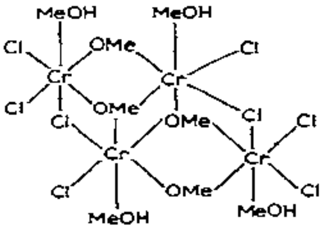


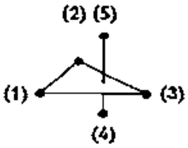
7

postulated structure, **7**, of the complex $Cr(OMe)Cl_2 \cdot CH_3OH$[125]. We obtain this equation by putting $J_{12} = J_{23} = J_{34} = J_{14} = J$ in Eqn. 19:

$$\begin{aligned} E(S_T) = & -JS_T(S_T+1)+(J-J_{13})S_{13}(S_{13}+1) \\ & +(J-J_{24})S_{24}(S_{24}+1)+2(J_{13}+J_{24})S(S+1) \end{aligned} \tag{23}$$

Although complex **7** and its iron(III) and vanadium(III) analogues exhibit magnetic properties compatible with Eqn. 23[50,125], these data alone cannot discriminate uniquely between **7** and a number of other possible arrangements of metal atoms (Section F). Because of the insolubility of the complexes, molecular weight determinations and the formation of crystals for X-ray study are ruled out, but structure **7** is not unreasonable from analogy with the known structures of [$TiOCH_3$] and [$TiOC_2H_5$]$_4$[126-128]. However, Eqn. 23 is definitely applicable to the [$Cr_4(OH)_6(en)_6$]$^{6+}$ cation, which is known to contain the arrangement **6** of metal atoms[47-49].

Except for very specialised cases such as those leading to Eqns. 21–23, exchange interactions in a discrete tetramer of paramagnetic atoms cannot be described by an extended Kambe approach. This difficulty increases as the number of interacting paramagnetic atoms increases. When $n = 5$, Eqn. 14 reduces to an equation analogous to Eqns. 16 and 19, and for the special case of a perfect trigonal bipyramidal arrangement, **8**, of identical interacting paramagnetic atoms (all angles $\frac{\pi}{3}$, $J_{45} = J'$, all other $J_{ij} = J$, all $S_i = S$), this equation reduces to $E(S_T) = -JS_T(S_T+1)+S_{45}(S_{45}+1)(J-J')+S(S+1)(3J+2J')$, which does define a unique set of energy levels. When $n > 5$, suitable equations for $E(S_T)$ are obtained by substituting in Eqn. 14, but again, for nearly all physically probable arrangements of paramagnetic atoms, the equations cannot be evaluated because the allowed values of the various spin states cannot be given unambiguously. Substitution of a few simple numbers into vector coupling rules of type (9) will quickly show that if $S_T = S_{ij}+S_{kl}+\ldots$, we may simultaneously evaluate S_T, S_{ij}, S_{kl}, …, and hence $E(S_T)$, provided that no other (non-independent) spin quantum numbers such as S_{ik}, S_{jk} *etc.* are required. For example, when $n = 3$, we can use S_T together with not more than one of S_{12}, S_{23}, S_{13} in Eqn. 16 and when $n = 4$, either of the pairs (S_{12}, S_{34}) or (S_{13}, S_{24}) but not both, may be used in Eqn. 18. In general, if $n \geqslant 3$, the eigenvalue Eqn. (14) can be applied only if we can equate to zero, or to each other, sufficient of the J_{ij} to remove all non-independent S_{ij} from the equation, and this requires an increasingly symmetrical arrangement of the paramagnetic atoms as n increases. The difficulty arises because of mixing of wavefunctions with the same S_T value; this will be discussed in Section E.



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It is now apparent that while the extension outlined above of Kambe's theory is very useful in a number of cases, it becomes increasingly limited in applicability when the number of paramagnetic atoms in a cluster increases beyond 2, and it cannot be applied to the general case. It is therefore desirable to evolve a completely general treatment, which would permit complete freedom of choice in the magnitudes of the exchange integrals of J_{ij} between pairs of spins S_i and S_j, where none of the J_{ij} or S_i, S_j need be equal.

E. GENERAL TREATMENT OF EXCHANGE INTERACTIONS IN DISCRETE CLUSTERS OF PARAMAGNETIC ATOMS

The procedure for the general calculation of exchange interactions is quite straightforward. Beginning again with Heisenberg's theory of ferromagnetism, and assuming non-degenerate ground states, we rewrite Hamiltonian (6):

$$\begin{aligned}\mathscr{H} &= -2\sum_{j>i=1}^{n} J_{ij}\mathbf{S}_i\cdot\mathbf{S}_j\\ &= -2\sum_{j>i=1}^{n} J_{ij}[\tfrac{1}{2}S_{i+}S_{j-}+\tfrac{1}{2}S_{i-}S_{j+}+S_{iz}S_{jz}] \qquad (24)\end{aligned}$$

operate on the wavefunctions $\psi_k = | S_1, M_{S_1}; S_2, M_{S_2}; \ldots S_n, M_{S_n} >$, determine the matrix elements $\langle\psi_k | \mathscr{H} | \psi_l\rangle$, $k = l$ and $k \neq l$, and diagonalise the resulting matrix. The eigenvalues $E(S_T)$ are then given by the diagonal elements of the matrix, and these are substituted into Eqn. 12 to obtain the magnetic susceptibility. Note that in each case

$$M_{S_T} = \sum_{i=1}^{n} M_{S_i}$$

Using this technique, it is possible to calculate the magnetic properties of any given interacting cluster. For simple systems, the diagonalisation of the matrix is carried out by simple algebra, but when large matrices are involved it is more expedient to use a computor and a standard eigenfunction–eigenvalue program. The use of this general procedure is best demonstrated by example and illustrative calculations are given below for simple systems. Anisotropy of the exchange integral can be allowed for by multiplying Hamiltonian (24) by an isotropy parameter γ_{ij} and adding terms in $(1-\gamma_{ij})J_{ij}S_{iz}S_{jz}$ [*cf.* Hamiltonian (5)], so that the mathematics for anisotropic interactions is amply illustrated by the treatment of isotropic (Heisenberg) exchange given in this section. The anisotropic treatment should be used with caution, since in the absence of direct evidence in favour of anisotropic interactions, it is likely to do no more than introduce an unwanted set of parameters γ_{ij}.

The case $S_1 = S_2 = \frac{1}{2}$ is trivial, and Hamiltonian (24) plus the term $g\beta HS_z$ leads to the matrix

$$\begin{array}{lllll} & |\phi_1\rangle & |\phi_2\rangle & |\phi_3\rangle & |\phi_4\rangle \\ \langle\phi_1| & -\dfrac{J}{2}+g\beta H & 0 & 0 & 0 \\ \langle\phi_2| & 0 & -\dfrac{J}{2} & 0 & 0 \\ \langle\phi_3| & 0 & 0 & -\dfrac{J}{2}-g\beta H & 0 \\ \langle\phi_4| & 0 & 0 & 0 & \dfrac{3J}{2} \end{array}$$

where, to simplify the algebra, the wavefunctions are in the form (S_T, M_{S_T}), and

$$\begin{aligned}
\phi_1 &= (1, 1) = |\tfrac{1}{2}\,\tfrac{1}{2}\rangle \\
\phi_2 &= (1, 0) = \tfrac{1}{\sqrt{2}}(|\tfrac{1}{2}\,-\tfrac{1}{2}\rangle + |-\tfrac{1}{2}\,\tfrac{1}{2}\rangle) \\
\phi_3 &= (1, -1) = |-\tfrac{1}{2}\,-\tfrac{1}{2}\rangle \\
\phi_4 &= (0, 0) = \tfrac{1}{\sqrt{2}}(|\tfrac{1}{2}\,-\tfrac{1}{2}\rangle - |-\tfrac{1}{2}\,\tfrac{1}{2}\rangle)
\end{aligned}$$

In each case wavefunctions with the same S_T are given by the relation $S_-(S_T, M_{S_T}) = k(S_T, M_{S_T}-1)$, where k is a normalisation constant, and wavefunctions with different S_T values are obtained from orthogonality conditions. The above matrix leads immediately to the well-known Bleaney–Bowers equation, which describes the magnetic properties of copper(II) acetate and many other binuclear complexes[15–17,19,23,25–28,44,51–69].

Next we consider a slightly more complicated case, still with $n = 2$; $M_{S_1} = \frac{3}{2}$, $M_{S_2} = 1$. Proceeding as outlined above with Hamiltonian (13), we obtain the eigenfunctions and eigenvalues $E(S_T)$ listed in Table 1. The eigenvalues are readily checked by comparison with Eqn. 15 and the appropriate magnetic susceptibility

TABLE 1

EIGENVALUES AND EIGENFUNCTIONS FOR BINUCLEAR COMPLEXES WITH $S_1=\frac{3}{2}$, $S_2=1$

Eigenvalues $E(S_T)$	*Eigenfunctions*
$-3J$	$(\frac{5}{2}, \frac{5}{2}) = |\frac{3}{2}\,1\rangle$
	$(\frac{5}{2}, \frac{3}{2}) = \sqrt{\frac{3}{5}}\,|\frac{1}{2}\,1\rangle + \sqrt{\frac{2}{5}}\,|\frac{3}{2}\,0\rangle$
	$(\frac{5}{2}, \frac{1}{2}) = \sqrt{\frac{3}{10}}\,|-\frac{1}{2}\,1\rangle + \sqrt{\frac{6}{10}}\,|\frac{1}{2}\,0\rangle + \frac{1}{\sqrt{10}}\,|\frac{3}{2}\,-1\rangle$
	$(\frac{5}{2}, -\frac{1}{2}) = \sqrt{\frac{3}{10}}\,|\frac{1}{2}\,-1\rangle + \sqrt{\frac{6}{10}}\,|-\frac{1}{2}\,0\rangle + \frac{1}{\sqrt{10}}\,|-\frac{3}{2}\,1\rangle$
	$(\frac{5}{2}, -\frac{3}{2}) = \sqrt{\frac{3}{5}}\,|-\frac{1}{2}\,-1\rangle + \sqrt{\frac{2}{5}}\,|-\frac{3}{2}\,0\rangle$
	$(\frac{5}{2}, -\frac{5}{2}) = |-\frac{3}{2}\,-1\rangle$
$2J$	$(\frac{3}{2}, \frac{3}{2}) = \sqrt{\frac{2}{5}}\,|\frac{1}{2}\,1\rangle - \sqrt{\frac{3}{5}}\,|\frac{3}{2}\,0\rangle$
	$(\frac{3}{2}, \frac{1}{2}) = 2\sqrt{\frac{2}{15}}\,|-\frac{1}{2}\,1\rangle - \frac{1}{\sqrt{15}}\,|\frac{1}{2}\,0\rangle - \sqrt{\frac{6}{15}}\,|\frac{3}{2}\,-1\rangle$
	$(\frac{3}{2}, -\frac{1}{2}) = 2\sqrt{\frac{2}{15}}\,|\frac{1}{2}\,-1\rangle - \frac{1}{\sqrt{15}}\,|-\frac{1}{2}\,0\rangle - \sqrt{\frac{6}{15}}\,|\frac{3}{2}\,-1\rangle$
	$(\frac{3}{2}, -\frac{3}{2}) = \sqrt{\frac{2}{5}}\,|-\frac{1}{2}\,-1\rangle - \sqrt{\frac{3}{5}}\,|-\frac{3}{2}\,0\rangle$
$5J$	$(\frac{1}{2}, \frac{1}{2}) = \frac{5}{2\sqrt{21}}\,|-\frac{1}{2}\,1\rangle - 2\sqrt{\frac{2}{21}}\,|\frac{1}{2}\,0\rangle + \frac{3}{2\sqrt{7}}\,|\frac{3}{2}\,-1\rangle$
	$(\frac{1}{2}, -\frac{1}{2}) = \frac{5}{2\sqrt{21}}\,|\frac{1}{2}\,-1\rangle - 2\sqrt{\frac{2}{21}}\,|-\frac{1}{2}\,0\rangle + \frac{3}{2\sqrt{7}}\,|-\frac{3}{2}\,1\rangle$

equation is obtained by substitution in Eqn. 12. An example of a complex to which this situation would apply could be obtained using "metal complexes as ligands"[44,51-61] although none has been reported as yet. The wavefunctions, eigenvalues and magnetic susceptibilities of all other interacting binuclear complexes are obtained similarly.

When $n = 3$ and $S_1 = S_2 = S_3 = \frac{1}{2}$ (*e.g.* trinuclear $\mathrm{Cu^{II}}$), the wavefunctions for the positive M_S values can be written

$$(\tfrac{3}{2}, \tfrac{3}{2}) = |\tfrac{1}{2}\,\tfrac{1}{2}\,\tfrac{1}{2}\rangle$$
$$(\tfrac{3}{2}, \tfrac{1}{2}) = \tfrac{1}{\sqrt{3}}(|\tfrac{1}{2}\,\tfrac{1}{2}\,-\tfrac{1}{2}\rangle + |\tfrac{1}{2}\,-\tfrac{1}{2}\,\tfrac{1}{2}\rangle + |-\tfrac{1}{2}\,\tfrac{1}{2}\,\tfrac{1}{2}\rangle)$$
$$(\tfrac{1}{2}, \tfrac{1}{2}, a) = \tfrac{1}{\sqrt{2}}(|\tfrac{1}{2}\,\tfrac{1}{2}\,-\tfrac{1}{2}\rangle - |\tfrac{1}{2}\,-\tfrac{1}{2}\,\tfrac{1}{2}\rangle)$$
$$(\tfrac{1}{2}, \tfrac{1}{2}, b) = \tfrac{1}{\sqrt{6}}(|\tfrac{1}{2}\,\tfrac{1}{2}\,-\tfrac{1}{2}\rangle + |\tfrac{1}{2}\,-\tfrac{1}{2}\,\tfrac{1}{2}\rangle - 2\,|-\tfrac{1}{2}\,\tfrac{1}{2}\,\tfrac{1}{2}\rangle)$$

The wavefunctions for the negative M_S values are obtained by changing the signs of all the M_S values in these equations. Operation with Hamiltonian (23) on these wavefunctions leads to off-diagonal matrix elements between $(\frac{1}{2}, \frac{1}{2}, a)$ and $(\frac{1}{2}, \frac{1}{2}, b)$ as well as between the corresponding negative M_S values $(\frac{1}{2}, -\frac{1}{2}, a)$ and $(\frac{1}{2}, -\frac{1}{2}, b)$. Diagonalisation of the matrix gives the eigenvalues $E(S_T)$ listed in Table 2. These can no longer be checked against Eqn. 16 since that equation no longer applies, but if we equate any two of the J_{ij} to each other, the eigenvalues in Table 2 will correspond to those obtained from Eqn. 16 for the same situation[51-55]. Substitution into Eqn. 12 now leads to the theoretical magnetic susceptibility χ_M for any trinuclear complex with $S_1 = S_2 = S_3 = \frac{1}{2}$, and the corresponding Bohr magneton number (per metal atom), μ_{eff}, which has been given previously[23,51,53]

TABLE 2

EIGENVALUES FOR GENERAL CASE OF TRINUCLEAR COMPLEX WITH (*a*) $S_1 = S_2 = S_3 = \frac{1}{2}$ AND (*b*) $S_1 = S_M$, $S_2 = S_3 = \frac{1}{2}$

Total spin S_T	*Eigenvalues $E(S_T)$*	
	General case	*Case where* $J_{12} = J_{13} = J$, $J_{23} = J_{CuCu}$
(*a*)		
$\frac{3}{2}$	$-\frac{1}{2}(J_{12}+J_{13}+J_{23})$	
$\frac{1}{2}$	$\frac{1}{2}(J_{12}+J_{13}+J_{23})+X$	$\frac{3}{2}J_{CuCu}$
$\frac{1}{2}$	$\frac{1}{2}(J_{12}+J_{13}+J_{23})-X$	$2J-\frac{1}{2}J_{CuCu}$
(*b*)		
S_M+1	$-(S_MJ_{12}+S_MJ_{13}-\frac{1}{2}J_{23})$	$(2-m)J+\frac{1}{2}J_{CuCu}$
S_M	$\frac{1}{2}(J_{12}+J_{13}+J_{23})+Y$	$\frac{3}{2}J_{CuCu}$
S_M	$\frac{1}{2}(J_{12}+J_{13}+J_{23})-Y$	$2J-\frac{1}{2}J_{CuCu}$
S_M-1	$(S_M+1)J_{12}-\frac{1}{2}J_{23}+(S_M+1)J_{13}$	$mJ-\frac{1}{2}J_{CuCu}$

$X = (J_{12}{}^2+J_{23}{}^2+J_{13}{}^2-J_{12}J_{13}-J_{12}J_{23}-J_{13}J_{23})^{\frac{1}{2}}$ $m = 2S_M+2$
$Y = (aJ_{12}{}^2+J_{23}{}^2+aJ_{13}{}^2-J_{12}J_{23}-bJ_{12}J_{13}-J_{23}J_{13})^{\frac{1}{2}}$ $a = (S_M+\frac{1}{2})^2$ $b = 2a-1.$

$$\mu_{eff} = \frac{g}{2}\left[(e^{-A+B}+e^{-A-B}+10e^{A})/(e^{-A+B}+e^{-A-B}+2e^{A})\right]^{\frac{1}{2}} \qquad (25)$$

where $A = (J_{12}+J_{23}+J_{13})/2kT$, $B = X/kT$, X is defined in Table 2, and μ_{eff} is related to χ_M by Eqn. 26:

$$\mu_{eff}{}^2 = \frac{3kT}{N\beta^2}\chi_M = 7.994\,\chi_M T \tag{26}$$

Eqn. 25 is the general equation[23,51,53] describing the magnetic properties of various kinds of trinuclear complexes[51-55,129]. The same calculation for $S_1 = S_M$ (which may have any value) and $S_2 = S_3 = \frac{1}{2}$ yields a similar set of eigenvalues, also listed in Table 2. As before there are off-diagonal elements between two wavefunctions corresponding to two identical values of S_T ($S_T = S_M$), and between the analogous wavefunctions obtained when M_{S_T} is negative. In each case, if two of the J_{ij} are held equal, the $E(S_T)$ values are the same as those previously obtained from Eqn. 12 or 16[51-55].

When $n = 3$ and $S_1 = S_2 = S_3 = 1$, this calculation gives the eigenvalues listed in Table 3. If we equate two of the exchange integrals, $J_{12} = J_{23}$, we obtain the eigenvalue previously calculated for trinuclear nickel(II) acetylacetonate[17,41]. The extension of any other system containing three interacting paramagnetic atoms is now trivial.

TABLE 3

EIGENVALUES AND EIGENFUNCTIONS FOR THE GENERAL CASE OF TRINUCLEAR COMPLEXES WITH $S_1 = S_2 = S_3 = 1$

Eigenfunctions	*Eigenvalues*	
(S_T, M_{ST})	*General Case*	*Case where* $J_{12} = J_{13} = J$, $J_{23} = J'$
$(3, M_{ST})$	$E_3 = -2(J_{12}+J_{13}+J_{23})$	$-4J-2J'$
$(2, M_{ST}, a)$	$E_2{}^a = -2(J_{12}{}^2+J_{13}{}^2+J_{23}{}^2-J_{12}J_{13}-J_{13}J_{23}-J_{12}J_{23})^{\frac{1}{2}}$	$-2J+2J'$
$(2, M_{ST}, b)$	$E_2{}^b = 2(J_{12}{}^2+J_{13}{}^2+J_{23}{}^2-J_{12}J_{13}-J_{13}J_{23}-J_{12}J_{23})^{\frac{1}{2}}$	$2J-2J'$
$(1, M_{ST}, \alpha)$	$E_1{}^\alpha$ (* see footnote)	$4J'$
$(1, M_{ST}, \beta)$	$E_1{}^\beta$ (* see footnote)	$2J+2J'$
$(1, M_{ST}, \delta)$	$E_1{}^\delta$ (* see footnote)	$6J-2J'$
$(0, 0)$	$E_0 = 2(J_{12}+J_{13}+J_{23})$	$4J+2J'$

* $E_1{}^\alpha$, $E_1{}^\beta$, $E_1{}^\delta$ are given by the three roots of the equation $-E^3+4(J_{12}+J_{13}+J_{23})E^2+$ $+4(J_{12}{}^2+J_{13}{}^2+J_{23}{}^2-5J_{12}J_{13}-5J_{12}J_{23}-5J_{13}J_{23})E+16(-J_{12}{}^3-J_{13}{}^3-J_{23}{}^3+J_{12}{}^2J_{13}+$ $+J_{12}J_{23}{}^2+J_{12}{}^2J_{23}+J_{13}J_{23}{}^2+J_{13}{}^2J_{23}+J_{12}J_{13}{}^2+J_{12}J_{13}J_{23}) = 0$

The same calculation for the tetranuclear case ($n = 4$) where $S_1 = S_2 = S_3 = S_4 = \frac{1}{2}$, yields the eigenvalues listed in Table 4. These eigenvalues are readily checked by equating appropriate J_{ij} values to each other to permit comparison with the special cases, Eqns. 21–23. The results of a calculation of this type[51,53] for the case $S_1 = S_2 = S_3 = S_4 = \frac{1}{2}$ with the simplifications $J_{13} = J_{24}$ and $J_{23} = J_{14}$, have been given recently[130], but its applicability to the system under consideration[68,131] remains to be demonstrated, and will be discussed below.

TABLE 4

EIGENVALUES AND EIGENFUNCTIONS FOR THE GENERAL CASE OF TETRANUCLEAR COMPLEXES WITH $S_1=S_2=S_3=S_4=\frac{1}{2}$

Eigenfunctions	*Eigenvalues*
$(2, M_{S_T})$	$E_2 = -\frac{1}{2} \sum_{j>i=1}^{4} J_{ij}$
$(1, M_{S_T}, a)$	$E_1{}^a$ (*see footnote)
$(1, M_{S_T}, b)$	$E_1{}^b$ (* see footnote)
$(1, M_{S_T}, c)$	$E_1{}^c$ (* see footnote)
$(0, 0, \alpha)$	$E_0{}^\alpha = \frac{1}{2}(J_{13}+J_{23}+J_{14}+J_{24})+\frac{1}{2}X$
$(0, 0, \beta)$	$E_0{}^\beta = \frac{1}{2}(J_{13}+J_{23}+J_{14}+J_{24})-\frac{1}{2}X$

$X = (J_{12}-J_{13}-J_{23}-J_{24}+J_{34})^2-2(J_{13}-J_{23}-J_{14}+J_{24})^2$

*$E_1{}^a$, $E_1{}^b$, $E_1{}^c$ are given by the three roots of the equation

$$-E^3+aE^2+bE+c = 0$$

where

$$a = \frac{1}{2} \sum_{j>i=1}^{4} J_{ij}$$

$$b = \frac{5}{4} \sum_{j>i=1}^{4} J_{ij}{}^2 - \frac{1}{2} \sum_{j>i=1}^{4} \sum_{k>j=2}^{4} J_{ij}J_{jk} + \sum_{j>i=1}^{4} \sum_{\substack{k>i=2 \\ k>j}}^{4} J_{ij}J_{ik}$$
$$+ \sum_{j>i=1}^{4} \sum_{\substack{j>k=2 \\ k>i}}^{4} J_{ij}J_{kj} - \frac{3}{2} \sum_{\substack{j>i=1 \\ k>i}}^{4} l \sum_{\substack{>k=2 \\ l\neq j}}^{4} J_{ij}J_{kl}$$

$$c = \frac{3}{8} \sum_{j>i=1}^{4} J_{ij}{}^3 - \frac{3}{8} \sum_{j=2}^{4} l \sum_{>k=2}^{4} (J_{ij}J_{kl}{}^2+J_{ij}^2J_{kl})$$
$$-\frac{3}{8} \sum_{k>j>i=1}^{4} (J_{ij}J_{jk}{}^2+J_{ij}{}^2J_{jk}+J_{ij}J_{ik}{}^2+J_{ij}{}^2{}^{\tau}{}_{ik}+J_{ik}J_{jk}{}^2+J_{ik}{}^2J_{jk})$$
$$+\frac{7}{4} \sum_{j,k,l\neq i=1}^{4} J_{ij}J_{ik}J_{il}$$
$$-\frac{9}{4} \sum_{j\neq i=1}^{2} \sum_{k>j=2}^{4} (J_{ij}J_{ik}J_{jk}) + \frac{5}{4} \underbrace{\sum_{i=1}^{2} \sum_{j=2}^{4} \sum_{k=3}^{4} \sum_{l=1}^{3}}_{\substack{i,\,l \text{ not both } = 1 \\ j,\,k \text{ not both } = 4 \\ \text{if } j = i \text{ or } k,\ l \neq j}} J_{1j}J_{ik}J_{l4}$$

It is apparent that the expressions rapidly become more cumbersome with increasing complexity of the system under consideration. For systems more complicated than that in Table 4, it is preferable to give the spin–spin interaction matrix rather than the eigenvalues, and to obtain the eigenvalues numerically from the matrix via computor methods. Fig. 4 gives the energy level diagram, obtained from Eqn. 19 for a particular set of values of the J_{ij} in the case $S_1 =$

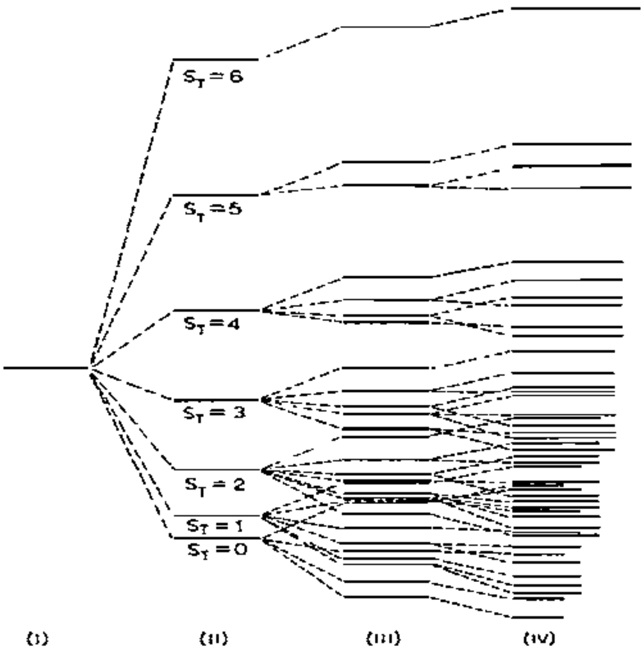


Fig 4 Energy levels resulting from antiferromagnetic interaction in a cluster of four interacting paramagnetic atoms, each with spin $S = \frac{3}{2}$. (i) Zero interaction. (ii) Equal interaction, all $J_{ij} = J$, as for a tetrahedral array, Eqn. 21 (iii) Two different interactions, $J_{12} = J_{23} = J_{34} = J_{14} = J$ and $J_{13} = J_{24} = J'$, as in a square or D_{2d} array, Eqn 22. (iv) More general case leading to a complete removal of degeneracy in the energy level, $J_{12} = J_{34} \neq J_{13} = J_{24} \neq J_{14} \neq J_{23}$ For clarity, the levels (iv) are shown in increasing length from $S_T = 0$ to $S_T = 6$ Each of the levels (iv) splits into $2S_T+1$ equally spaced levels under the influence of an external magnetic field.

$S_2 = S_3 = S_4 = \frac{3}{2}$, which is probably applicable to tetranuclear cobalt(II) acetylacetonate[17,132,133] and tetranuclear cobalt(II) oxypivalate[134].

It is now clear that the interaction matrix can be set up and solved for any conceivable finite interacting system. Given the structure of an interacting cluster of paramagnetic atoms, suitable J values can be chosen and the possible types of magnetic properties may be predicted (and the magnetic properties that are impossible may be delineated). Alternatively, given any experimental χ_M or μ_{eff} *vs.* T curve, we can reproduce it theoretically from a calculation of the type outlined above, using suitable J curves. In fact the danger now is one of overparameterisation. Given a free choice of n, the number of interacting paramagnetic atoms in a discrete cluster, and the magnitudes of the J_{ij} it is often too easy to obtain fits to experimental data on an *unknown* system. For some types of experimental magnetic curves there is no finite limit to the number of combinations of J values that can be used to fit the data. This is especially true when experimental data show no characteristic features, such as when an unknown system shows little deviation within experimental error from a Curie–Weiss law value over the temperature range of measurement (usually 80 °K and above).

Thus structural postulates, based on the fit of experimental magnetic data to values calculated from the theory, are often of doubtful validity unless other evidence is available to eliminate some of the possibilities. It is very important that the extent of applicability and the limitations of the theory, and the kinds of approximations made, are well understood before the theory is applied. Unfortunately, this has been ignored in a large number of cases already.

F. LIMITATIONS AND APPLICABILITY

(i) *Orbital contribution*

The Hamiltonian (24) specifically excluded a spin–orbit coupling term, as indeed have most discussions of antiferromagnetic interactions. Thus Eqn 12, combined with the appropriate $E(S_T)$ values, for interacting clusters of paramagnetic metals, is equivalent to a Curie law (Section D) value of the magnetic moment

$$\mu_{\text{eff}} = g\sqrt{S(S+1)} \tag{27}$$

for a mononuclear complex. This seems very incongruous when most calculations of magnetic properties of mononuclear complexes of the same paramagnetic metals incorporate spin–orbit coupling, and (27) is considered inaccurate in many cases[16,21,22]. There is abundant evidence that the approximations used in considering exchange interactions lead to satisfactory agreement anyway, but the question of why it works is relevant and important enough to be asked at this stage. The answer is two-fold Firstly the relative magnitudes of the effect of exchange interactions and spin–orbit coupling are often such that only the interaction matters. For orbitally non-degenerate states [for octahedral (O_h) and tetrahedral (T_d) this includes A_1, A_2 and E states, *i e.* O_h: d^3, high spin d^4 and d^5, low spin d^6, d^7, d^8, d^9; T_d: d^1, d^2, low spin d^3 and d^4, high spin d^6, d^7; for D_{2d} this includes A_1, A_2, B_1 and B_2 states] the magnetic moment can be represented by Eqn. 27 so that Eqn. 12 may be applied immediately to interactions between paramagnetic atoms with such ground states. In such cases, the constant g, calculated from first principles, incorporates the orbital contribution. If g is not calculated it should be measured independently, or, if used as an experimental parameter to fit experimental magnetic data, constrained to values that are realistic for the system under consideration. It is clear that this has not been done in general (*e g.* some refs. given in Ref. 15). For orbitally degenerate states spin–orbit coupling is more important; one such case is shown schematically in Fig 5 where a ground state with a temperature-dependent moment (an orbitally degenerate state) is considered together with the temperature dependence expected if a metal with this ground state forms part of a binuclear interacting system. This would

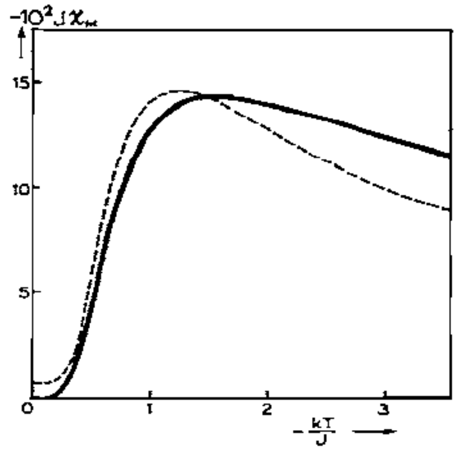


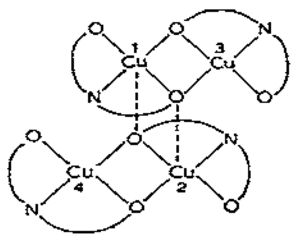
Fig 5 Temperature dependence of molar susceptibilities for interacting pairs of ions with orbitally degenerate ground states, using $2J = \zeta/5$ ($2J$ = singlet triplet separation) The curve shape differs significantly from that of the regular Bleaney–Bowers type, indicated by the broken curve. The difference is here maximised because no account has been taken of distortion from cubic symmetry or of metal–ligand bonding effects In a real system the effect is generally expected to be smaller than suggested by the figure

apply specifically to interaction between two tetrahedral copper(II) or octahedral iron(III) atoms, but the extension to other more complicated systems is obvious. In the region where the effect of the exchange interactions is significant, the orbitally degenerate state is only partly occupied, thereby further reducing the importance of orbital contribution. The exact importance could be calculated using terms $\Sigma l_i \cdot s_i$ added to Hamiltonian (24) and operating on the wavefunctions diagonalised for electrostatic and crystal field interactions, but the figure indicates approximately what effect this has, and it is clear that deviations due to spin–orbit coupling are generally relatifely small Detailed calculations of this effect are being carried out[135].

The second reason why orbital contributions can often be ignored in interacting clusters is that the very nature of a discrete polynuclear complex implies distortion from the perfect nominal symmetry (*e.g.* octahedral or tetrahedral) that might otherwise be expected to exist around the metal atoms. Even in apparently symmetrical complexes such as cobalt(II) acetylacetonate in which the desire for octahedral symmetry about the metal appears to be the driving force for the formation of the cluster, single crystal X-ray studies indicate considerable distortion from octahedral symmetry[133]. Distortions from formal symmetries have been considered in some detail[7,16,21,22,66,135–143], and could be incorporated in an exact calculation by adding a term $\varepsilon_{\parallel} l_z^2 + \varepsilon_{\perp}(l_x^2 + l_y^2)$ to the Hamiltonian. In most cases, even in mononuclear complexes, not enough is known about the detailed electronic structure to put very useful values on $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$. The general effect of such distortion is to reduce the temperature dependence, thereby bringing the moments of the orbitally degenerate states closer to $g\sqrt{S(S+1)}$, where the entire orbital contribution is represented by the deviation of g from 2.00. Thus the temperature dependence of the moment is mainly due to the interaction. Similar conclusions can be drawn in a case that parallels the present one very closely: the high spin–low spin crossover, where the effects of orbital contribution are relatively minor compared with the main effect, the crossover[51,84,144–146].

In temperature ranges where the effect of exchange interactions is unimportant (*i e.* when $J \ll kT$), orbital contribution may have the greater effect on the temperature dependence of the magnetic moments. This is likely to be the case in $Cu_4OL_4X_6$ complexes (structure 5): $[Cu_4OBr_6(C_5H_5N)_4]$[84] and $[Cu_4OCl_6\{OP(C_6H_5)_3\}_4]$[17] have room temperature moments (in B.M.) of 1.90 and 1.87 respectively, rising to maxima of 2.15 (70 °K) and 2.12 (54 °K) and falling sharply to 1.0 (5 °K) and 0.76 (1.5 °K)[17,84]. The decrease in the moments at low temperatures is likely to be the result of weak antiferromagnetic interactions, while the values at higher temperatures are quite consistent with those expected and found in five-coordinated and pseudo-tetrahedral complexes[16,147].

Thus, keeping in mind the limitations always imposed by experimental error, we can frequently ignore the effect of orbital contribution for transition metal complexes, except in the form of a constant g-value, and still expect to get good agreement with experiment. However, both the approximations used in the theory and the experimental error must be taken into account. In a recent calculation[130] the copper(II) complex of acetylacetone (*o*-hydroxyanil), a weakly linked tetramer (with Cu–O = 2.64 Å between adjacent molecules) 9[68,131], was treated as a tetranuclear instead of the original binuclear model[68]. Strong interactions were postulated between the pairs of copper atoms 1–2, 1–4 and 2–3, but there is no precedent for interactions between coppers linked by such weak Cu–O–Cu bonds[148]. Moreover, little support for the postulate is offered by experiment because the improvement in the fit of the theory to experiment afforded by the tetranuclear model over the binuclear does not seem significant within the limits set by experimental error and the approximations implicit in the treatment. The copper atoms in this complex are likely to be in an orbitally degenerate ground state so that orbital contribution alone is likely to impose a temperature dependence on the magnetism at least as great as the difference in magnetism predicted



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by the two models. Using the tetranuclear model, strong ferromagnetic couplings ($J = 134$ cm^{-1}) must be postulated between atoms 1 and 4, and between 2 and 3. Although there is good evidence favouring the existence of discrete ferromagnetic interactions in various systems, direct evidence is required before such a postulate can reasonably be made in this case[149].

(ii) Temperature independent paramagnetism

A further correction frequently made to some interacting systems is the temperature independent paramagnetism, $N\alpha$. When second order Zeeman splitting lowers the thermally populated levels by a constant amount, the expected susceptibility is increased by a constant amount. When calculated empirically, or constrained to a reasonable value, $N\alpha$ is a useful correction to the magnetic susceptibility equation, but it should not be used as a variable parameter, as has frequently been done. This constant can be added to all the magnetic susceptibility equations described here

(iii) Various J values

With the limitations just discussed, we can use the method of Section E to describe the magnetic properties of an interacting paramagnetic cluster of known structure. A good example is the theory for tetranuclear cobalt(II) acetylacetonate, of known structure[132,133], which cannot be handled by an extended Kambe theory. The magnetic properties of this complex have been published in part ($\mu_{\text{eff}} = 5.11$ B.M. at 295 °K, 5.56 B.M. at 96 °K (max.), and 2.49 B.M. at 1.5 °K), and the possibility of competing ferromagnetic and antiferromagnetic interactions has been raised[17]. The maximum moment of 5.56 B.M. seems too high for any coordinated cobalt(II) complex, even in extremely weak crystal fields, and is therefore indicative of a ferromagnetic interaction. The sharp drop in μ_{eff} at lower temperatures suggests an antiferromagnetic interaction. Calculations show that a combination of positive and negative J values can reproduce the observed results.

Determinations of an unknown structure from magnetic interactions requires more care. Often the temperature dependence of the magnetism of an interacting binuclear complex is sufficient to establish its structure[15–17,19,20,68,131,149,150,151,152] if the temptation to use all of J, g and $N\alpha$ as parameters is overcome. In conjunction with other evidence, trinuclear and tetranuclear structures have also been correctly predicted[17,18,32,35,48,49,109,110]. In general, as the complexity of a multinuclear complex increases, the supporting evidence must become increasingly specific. Where possible, molecular weight measurements are highly desirable. It has been noted that the magnetic properties of some chromium(III) methoxide complexes $\text{Cr(OMe)Cl}_2 \cdot n\text{S}$ (where S is solvent) are described equally well by a dimeric and a trimeric model over the temperature range available to measurement[50]. The magnetic properties of the complexes of proposed structure **7** are similar, and show no characteristic features such as maxima, minima or points of inflection. Simple calculations show that the results can be fitted by an endless variety of structures other than **6** or **7**, but which are still compatible with the other observed properties of the complexes. In such cases, other data, and measurements over a wider range of temperatures (*e g.* down to liquid helium temperature) are highly desirable.

(iv) Other errors due to Hamiltonian (6)

Within the limitations already discussed the treatment given here can adequately describe all discrete interacting clusters that have so far been reported in detail. However, the assumptions of complete isotropy of the exchange, and complete quantisation of the total spin of each paramagnetic atom, implicit in Hamiltonian (6) need not be exactly true, although they appear to be good approximations. This should be kept in mind when attempts are made to attribute deep theoretical significance to small differences in magnetic properties or J-values.

The treatment of anisotropic exchange interactions in discrete systems was described at the beginning of this section together with the necessary precautions in using it. There is considerable evidence, at least in a number of infinite systems, for an essentially isotropic exchange [γ nearly 1 in Hamiltonian (5)][29,153–156] and although other results can be interpreted in terms of anisotropic or isotropic interactions, the isotropic model was not ruled out[23,25,156–158]. The significance of anisotropic interactions can only be estimated if the significance of the various other effects, such as spin–orbit coupling, are known. To this end, more data (*e g.* as single crystal magnetic susceptibility, ESR) will be required than are at present available

We now consider a possible non-quantised exchange system. Hamiltonian (6) represents interactions between paramagnetic atoms i, j each with strongly quantised spin S_i, S_j. In the special case of some dimeric dithiolene complexes such as $[Fe_4S_4C_4(CF_4)_4]_2$, it has been suggested[103] that Hamiltonian (6) is inappropriate and that a model incorporating interactions between each pair of the extensively delocalised unpaired electrons of the molecule gives better agreement with the experimental results. The detailed results are not yet available but the postulate is in agreement with the conclusions that the most energetic valence electrons are highly delocalised in such dithiolene complexes[159,160]. This means that the Kambe approach fails to apply even in simple cases, and the general treatment (Section E) must be used, with S_i replacing s_i. Although the delocalisation is singularly high in dithiolenes (so much so that conventional oxidation numbers are inapplicable), the effect of the smaller delocalisation in most interacting paramagnetic clusters may still make a finite contribution to the errors expected from the use of Hamiltonian (6).

Another factor that is usually ignored is the possibility that J may have at least a slight temperature dependence

G. EXCHANGE INTEGRAL

Since mathematically J is in the form of an orbital overlap, we would expect to be able to get some information from the J values if the sizes, shapes and orientations of say the d-orbitals of interacting transition metals are known. In real situations, these things are usually quite unknown and the theory is necessarily somewhat qualitative and *ad hoc* at this stage Nevertheless, it has been possible to make some generalisations and predictions about various types of exchange. A lucid account of the present state of the theory has been given by Martin[17], and the discussion here will be confined to some contraversial points about exchange.

It has been suggested that linear M–O–M bridges lead to strong antiferromagnetic interactions, while non-linear bridges, such as in $\mathrm{M}\genfrac{<}{>}{0pt}{}{\mathrm{O}}{\mathrm{O}}\mathrm{M}$ linkages, do not[161]. This would explain the absence of any detectable antiferromagnetism (Refs. 56, 161) down to 80 °K in the dimeric N,N'-ethylenebis(salicylaldimine)-copper(II)[161]. However, the latter complex is very weakly dimeric (intermolecular Cu–O distances are 2.41 Å compared with intramolecular distances of 2.0 Å)[148] and it has been pointed out[56] that such weak Cu–O–Cu linkages have never been found to lead to appreciable antiferromagnetic interactions, while strong non-linear $\mathrm{M}\genfrac{<}{>}{0pt}{}{\mathrm{O}}{\mathrm{O}}\mathrm{M}$ linkages are responsible for strong interactions in many complexes[15,17,54]. Thus, although linear linkages do result in strong interactions in some complexes, *e.g.* Ru–O–Ru in $K_4[Ru_2OCl_{10}] \cdot H_2O$[162] and Fe–O–Fe[77,80,163,164], the comment is by no means general.

(i) δ-Bond

There has been much discussion on the relative importance of two mechanisms for exchange, direct metal–metal bonding and superexchange, in copper(II) acetate monohydrate, and hence in other related systems. Postulates have varied from a weak δ-bond[165–168] or superexchange interactions (*via* the ligands) between isolated copper atoms[19,169], to a strong σ-bond[170], or a strong δ-bonding[171] interaction, but there now appears to be general agreement that there is *no direct metal–metal interaction*, and the exchange interaction probably works through a superexchange mechanism, while a weak δ-bond is also likely to be present, though the relative importance of each can probably not be determined exactly[15,17,62,170,172–174]. It is interesting to recall that when the δ-bond was first hypothesised it was considered that "the bond is so weak that the configuration of the binuclear molecule can only be maintained by the four bridging acetate groups"[165]. High pressure susceptibility measurements indicate that the metal–metal interaction is not strong, again leaving a δ-bond and superexchange as possibilities[172]. However, recently this approach has again been critised and a strong metal–metal bond again postulated[175], on the basis of the metal–metal distance (2.64 Å). Using a model described previously[176] Jotham and Kettle[175] obtained Eqn. 28

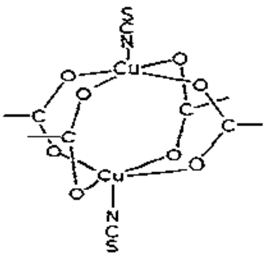
$$\mu^2_{\mathrm{dimer}} = 6g^2[3+\mathrm{e}^{-2J/kT}+2\mathrm{e}^{-2J/4kT}\cosh(2\gamma/kT)]^{-1} \tag{28}$$

which is claimed to give a better fit to the experimental data than the Bleaney–Bowers equation

$$\mu^2_{\mathrm{dimer}} = 6g^2[3+\mathrm{e}^{-2J/kT}]^{-1} \tag{29}$$

However, the improved agreement with experiment, the main argument in favour of the model, is not significant within experimental error. The "much better fit at low temperatures" claimed for Eqn. 28 over Eqn. 29 seems incongruous, since with the values used in Eqn. 28 ($J = 327$ cm^{-1}, $2\gamma = 381$ cm^{-1})[175] and in Eqn. 29 ($J = -283$ cm^{-1})[163], the two equations should tend to similar values of $\mu^2_{\mathrm{dimer}} \doteqdot 6g^2[3+\mathrm{e}^{300/kT}]^{-1}$ at low temperatures. In any case, the fit at low temperatures is not a good criterion for the validity of a model with a $S = 0$ ground state, since the magnetism, and hence the experimental precision, are minimal at low temperatures, while the effect of paramagnetic impurities is highest, so that even small traces of paramagnetic impurities can drastically alter the results[177–179]. Other unsatisfactory features of the discussion of Eqn. 28 are the claim that no "best fit" procedure was needed to fit the results (*cf.* Ref 115) although γ and J were obtained from the fit to an experimental Néel point, itself a best-fit procedure, and the failure to mention Dubicki and Martin's[62] proposal from spectral data that each of the two electrons involved in the exchange is essentially localised on its own copper atom. This is diametrically opposed to the strong metal–metal bonding implied in Eqn. 28 and cannot be dismissed without discussion.

Still more recently, Goodgame *et al.*[180] have obtained direct experimental evidence against the significance of metal–metal bonding in binuclear copper(II) alkanoates and hence against Eqn. 28, from a study of $[\mathrm{N(CH_3)_4}][\mathrm{Cu(HCOO)_2(NCS)_2}]$ and $[\mathrm{N(CH_3)_4}][\mathrm{Cu(CH_3\cdot COO)_2(NCS)_2}]$, **10**, which are both structurally



analogous to copper(II) acetate monohydrate[20], with NCS groups replacing H_2O. The formate complex exhibits a stronger interaction ($-2J = 485$ cm^{-1}) than the acetate ($-2J = 305$ cm^{-1}), yet it has a greater copper–copper separation (2.716 Å, *cf.* acetate 2.643 Å), a failure of J to correlate with metal–metal distance, which weakens the argument for the importance of metal–metal bonding. On the other hand, the total bond lengths (the "superexchange pathway") via the briding ligands is shorter for the formate, and this may be responsible for the relative magnitudes of J. Metal–metal bonding must be of even lesser importance in complexes containing a $\mathrm{Cu}\langle{}^{\mathrm{O}}_{\mathrm{O}}\rangle\mathrm{Cu}$ bridge[26,44,51–63 68,69,109,110,131,150,151], where larger metal–metal distances are observed, *e g.* 3 00 Å in the copper complex of acetylacetone(*o*-hydroxyanil)[68,131] and 3.245 Å for the copper chloride complex of pyridine *N*-oxide[151]. Rather similar considerations can be applied to other polynuclear complexes.

(ii) Temperature dependence of J

We have considered the effect of orbital contribution, which in certain cases effectively results in a slight temperature dependence of g in the magnetic equations (5), (12), (25), (28), (29) Another factor that must be kept in mind is the possibility that the exchange integrals may not be entirely independent of temperature[19,181, 182]. Although any temperature dependence is not expected to be very great, and agreement with experimental results indicates that any such dependence is not very important, the possibility adds to the approximations already inherent in the theory. The more closely the exchange integral is examined, the more refinement appears to be desirable. Thus, even when the use of a constant g value is justified, before using small discrepancies between calculated and experimental magnetic data to support more complicated models such as those described above and in Section F, the extent to which our approximate picture of the exchange integral leads to such discrepancies should first be estimated.

(iii) Magnitude of J

We noted above that the strength of exchange interactions does not depend on the metal–metal distances in a number of related complexes, and that direct bonding between the metals is not important for such complexes. However, direct metal–metal bonding is important in (diamagnetic) complexes with very short distances between the metals. Examples of this are the diamagnetic alkanoates of molybdenum(II)[183–185], rhenium(III)[186–188] and rhodium(II)[17,191] in which the short metal–metal distances (usually shorter than in the pure metals) are indicative of multiple metal–metal bonds[17,183–191]. Strong metal–metal bonds are also found in binuclear halide complexes of these metals and of technetium (Refs. 190–192). The ligand diazoaminobenzene forms binuclear complexes of the first row transition elements with very short metal–metal separations. In the nickel(II) and copper(I) complexes, these separations are shorter than in the metals[193], and it is not surprising therefore that the copper(II) complex is diamagnetic[194]. On the other hand, the diamagnetism[195] of binuclear chromium(II) acetate[196] (with the same metal–metal separation as its copper(II) analogue) is considered to result from favourable orientation of the metal d_{xy}-orbitals for overlap with the ligand π-orbitals, rather than strong direct bonding[17,62].

Systematic variations in J values in related complexes have been used to examine electronic effects, especially in binuclear molecules[15,17,65,66,152], but, in view of the limitations discussed above, a much greater range of data seems desirable to evaluate the significance of the variations in J to build up a complete picture of the exchange mechanism. In some cases, trends have only been observed in the room temperature moments[65,66], and measurements over a temperature range are desirable before conclusions can be drawn with certainty.

(iv) Limiting J-values

If $-J$ is greater than about 600 cm^{-1} in the Bleaney–Bowers equation (29), the magnetism is negligible at room temperature. For a trinuclear copper(II) complex, it is found that if one of the J_{ij} is about -600 cm^{-1} or if two of the J_{ij} are about half this magnitude, the lower limiting magnetic moment for antiferromagnetic interactions in such a system ($\mu_{\text{eff}} = g/2$ B.M.) is observed at room temperature[23,51]. For a multinuclear cluster, the general effect of the various exchange interactions is additive, as would be expected: several small J_{ij} values have as great an effect on the magnetism as a few larger ones.

If all J_{ij} are equal, Eqn. 12 can be expanded further for small J or large T, giving a linear limiting relation of χT with $1/T$, the gradient of which depends on J. For several J_{ij}, such a plot would be less useful since the gradient would depend on an averaged J-value.

(v) Positive J-values

Ferromagnetic interactions in discrete paramagnetic clusters are probably quite common[17,23,44–46,52,113,123–124], but could not be definitely established until recently[45] because usually such interactions only alter the magnetic properties significantly at very low temperatures, where the moment tends to the upper limiting moment for the system ($\mu_{\text{eff}} = g\sqrt{S_{T_m}(S_{T_m}+1)}$, where S_{T_m} is the maximum allowed value of S_T for the system). Thus, in many cases the existence of ferromagnetism is very difficult to verify experimentally, as in complex **9**[130] where the situation is complicated by the presence of known antiferromagnetic interactions. In the presumed binuclear complex [(4-nitroquinoline N-oxide)CuCl$_2$]$_2$ (Ref. 197), J and g values of 200 cm^{-1} and 2.13 respectively lead to calculated moments in B.M. of 2.14 (77 °K), 2.13 (196 °K) and 2.12 (300 °K) which compare well with the observed values of 2.14, 2.12 and 2.13 at the same temperatures[23].

H. OTHER MEASUREMENTS

The theory and experimental data discussed in the preceding sections has pertained largely to magnetic susceptibilities, but exchange interactions in discrete systems can also be examined by other techniques, such as ESR[19,156,157,174,198,208] and the Mössbauer effect[76,209–212]. The same Hamiltonian (24) is added to those normally used for the calculation of ESR and Mössbauer spectra[22,213]. ESR data have been interpreted using a similar approximation to that used for Fig 5, the Hamiltonian being the sum of the Hamiltonians of the individual magnetic atoms added to (24) and a magnetic dipole–dipole interaction term between pairs of atoms. This approximation is reasonable in view of the other inherent approximations (Section E), and discussions have been given of the cases where the exchange interaction is large compared with the dipole–dipole interaction[19,202] and where it is small[203,204].

Mössbauer spectra can help to distinguish between possible ground states of interacting metals, although the limited information contained in powder spectrum of a complex, whose structure is unknown, requires that studies be done over a wide temperature range (*e g.* down to 4 °K). Single crystal studies where possible are desirable. Thus it should be possible to select the best model for a variety of linearly bridged iron(III) Fe–O–Fe complexes with $\mu_{\text{eff}} < 2$ B.M. at 300 °K, which has been interpreted in terms of interacting pairs of $S = \frac{1}{2}$, $S = \frac{3}{2}$ and $S = \frac{5}{2}$ atoms[73–80,163,164,209,210,215–220]. The $S = \frac{5}{2}$ and $S = \frac{3}{2}$ models require strong interactions, so that with pure spin models (Eqn 12) the highest attainable temperatures (below decomposition point) will significantly populate only the lowest $E(S_T)$ levels, which are the same for both models. Thus no choice can be made from magnetic data[107,216]. For an accurate calculation the pure spin model is quite adequate for $S = \frac{5}{2}$ ($^6A_1$) centres, but is less so for $S = \frac{3}{2}$ and $S = \frac{1}{2}$, where the effect of spin–orbit coupling should be considered (together with that of distortion from octahedral symmetry, orbital reduction, *etc.*). Thus magnetic data allow no choice of S in general, although a g-value > 2.8 required to fit the magnetic data for $[\text{Fe}_2(\text{terpy})_2\text{O}](\text{NO}_3)_4 \cdot \text{H}_2\text{O}$ using the $S = \frac{1}{2}$ model is unrealistic and suggests that the $S = \frac{1}{2}$ model is inapplicable. For orbitally non-degenerate ground states only asymmetry of bonding (different values of the orbital reduction factor for different metal *d*-orbitals) about the metal lead to Mössbauer quadrupole splitting, ΔE_Q, so that the splittings are expected to be smaller for $S = \frac{5}{2}$ centres than for $S = \frac{3}{2}$ or $S = \frac{1}{2}$[122,160,209–212,214,221–224]. The observed ΔE_Q values are in keeping with the asymmetry expected in the Fe–O–Fe complexes[209,210] if $S = \frac{5}{2}$, but mostly seem too large for $S = \frac{3}{2}$ or $S = \frac{1}{2}$ centres, although it has been pointed out that the $S = \frac{3}{2}$ model could still explain the results[209]. Single crystal Mössbauer (and other) studies could be more conclusive and are desirable, but it seems a safe prediction that the $S = \frac{5}{2}$ will be found correct.

A series of binuclear ferric complexes[104–107,163,164] with $\mathrm{Fe}\langle\begin{smallmatrix}\mathrm{O}\\\mathrm{O}\end{smallmatrix}\rangle\mathrm{Fe}$ bridges $(\mathrm{FeLX})_2$ (L is a tetradentate Schiff base, X a halide or similar group) again have ΔE_Q values in keeping with the expected asymmetry, but the interaction is weak ($J \sim 10\ \mathrm{cm}^{-1}$) and the magnetic data leave no doubt that the interaction is between $S = \frac{5}{2}$ centres[84,210–212]. These complexes exhibit an asymmetric quadrupole doublet with equal areas under the two peaks at liquid nitrogen temperature[84,210–212], where the $S_T = 1,2,3$ states are populated. This is attributed to spin–spin relaxation[211,212 225–227], [a fluctuating hyperfine magnetic field with an electric correlation time comparable with the nuclear precession time for $|\frac{3}{2}, \pm\frac{1}{2}> \rightarrow |\frac{3}{2}, \pm\frac{3}{2}>$ (notation $|I, M_I>$ for nuclear spin states of ^{57}Fe) transitions, and fast enough for nuclei undergoing transitions to the $|\frac{3}{2}, \pm\frac{1}{2}>$ excited states to experience a zero average magnetic field]. At 4.2 °K where only $S_T = 0$ is appreciably populated, a sharp symmetrical doublet is obtained as expected, while at room temperature, the doublet still has its expected asymmetry but the areas under the peaks are no longer the same. The loss in area of the broader peak is attributed to the Karagin effect[211,212,228–230]. Single crystal Mossbauer studies are also being carried out on these systems.

Intercomparison of results from various techniques will undoubtedly become of increasing importance in magnetically interacting systems.

I. CONCLUSION

Despite the preoccupation above with limitations of the treatment, it is possible to conclude on an optimistic note: we have shown that magnetic exchange interactions in discrete systems can be represented by sound models which can be treated easily and exactly, unlike interactions in infinite lattices. It is merely necessary to keep in mind the limitations imposed by the approximations made and by experimental error. For fundamental investigations of the nature of exchange interactions, therefore, the discrete paramagnetic cluster should generally be a much more useful object of study than the lattice ferro or antiferromagnet.

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