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# The Magnetic Susceptibility of Two Coupled Dimers Consisting of S=1/2 Spins

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**Synopsis.** Tetramers consisting of two coupled dimers were classified as (a) linear, (b) cyclic, (c) rhombic, or (d) tetrahedral. The magnetic susceptibility for each tetramer model consisting of S=1/2 spins was obtained as an analytical equation. For the linear tetramer, the susceptibility equation was calculated numerically and compared with the observed values.

It has been found that many compounds have spin-spin interactions among their magnetic ions, so they may be regarded magnetically as composed of clusters such as a dimer and a trimer. Some of them may also have interactions among such clusters.[1–6] These interactions increasing to a certain extent, the compounds may be regarded as composed of larger complicated clusters. While such interactions are weak, the effects can be taken into consideration approximately by modifying the equation of the original cluster—for example, as the magnetic susceptibility of the modified dimer model.[7] Hatfield and Inman, Jr., tried to obtain an exact expression[5] of a tetramer consisting of two coupled dimers, the Hamiltonian of which was:

$$\begin{aligned}\mathscr{H} = & -2J(S_1S_2+S_3S_4)-2J'S_2S_3 \\ & -2J''(S_1S_3+S_2S_4)-2J'''S_1S_4 \qquad (1)\end{aligned}$$

where the $S_i$'s are spin operators, $J$ is the exchange integral of intradimer interaction, and $J'$, $J''$, and $J'''$ are the exchange integrals of the interdimer interactions. The magnetic expression thus obtained, however, was not completely an analytical equation because of the complexity of the problem.

For a tetramer which has interaction between only the adjacent ends of two dimer units, the problem has been simplified; the Hamiltonian appropriate for this problem (Fig. 1a) is:

$$\mathscr{H} = -2J(S_1S_2+S_3S_4+\gamma S_2S_3) \qquad (2)$$

Here $\gamma$ is the ratio of the exchange integrals of the interdimer to the intradimer interactions. This Hamiltonian is, of course, a special case of the first (Eq. 1). Using the same spin functions (products of the eigenfunctions of a dimer system consisting of S=1/2 spins) as in the literature,[5] the elements of an energy matrix are found to be as in Table 1. Diagonalizing this matrix, 6 kinds of eigenvalues (1 quintet, 3 triplets, and 2 singlets) are obtained as:

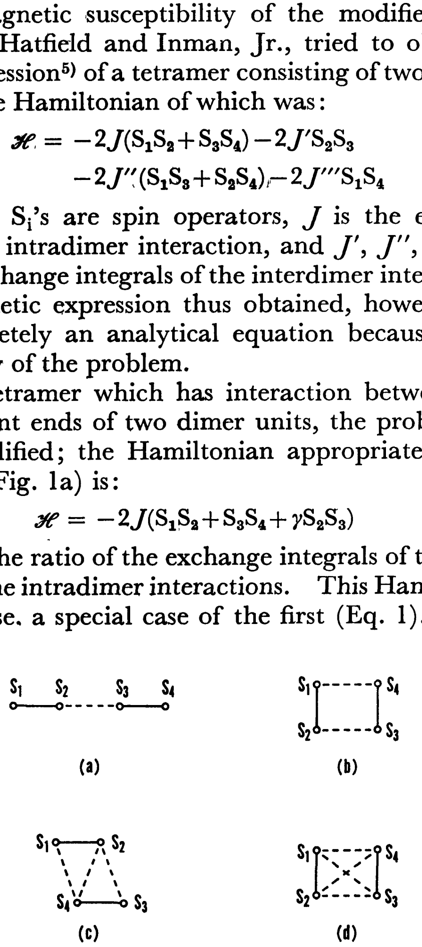

Fig. 1. Schematic representation of the two coupled dimers.
(a): Linear tetramer, (b): cyclic tetramer, (c): rhombic tetramer, (d): tetrahedral tetramer.

Table 1. Non-zero matrix elements

$$\begin{aligned}
(\phi_1\mathscr{H}\phi_1) &= (\phi_{10}\mathscr{H}\phi_{10}) = -J\left(1+\frac{\gamma}{2}\right) \\
(\phi_2\mathscr{H}\phi_2) &= (\phi_3\mathscr{H}\phi_3) = (\phi_7\mathscr{H}\phi_7) = (\phi_8\mathscr{H}\phi_8) = (\phi_9\mathscr{H}\phi_9) \\
&= (\phi_{12}\mathscr{H}\phi_{12}) = (\phi_{13}\mathscr{H}\phi_{13}) = (\phi_{16}\mathscr{H}\phi_{16}) \\
&= -J\gamma/2 \\
(\phi_4\mathscr{H}\phi_4) &= (\phi_5\mathscr{H}\phi_5) = J\left(1-\frac{\gamma}{2}\right) \\
(\phi_6\mathscr{H}\phi_6) &= (\phi_{11}\mathscr{H}\phi_{11}) = (\phi_{14}\mathscr{H}\phi_{14}) = (\phi_{15}\mathscr{H}\phi_{15}) \\
&= 3J\gamma/2 \\
(\phi_2\mathscr{H}\phi_3) &= (\phi_4\mathscr{H}\phi_7) = (\phi_5\mathscr{H}\phi_7) = (\phi_6\mathscr{H}\phi_7) = (\phi_8\mathscr{H}\phi_9) \\
&= (\phi_{11}\mathscr{H}\phi_{12}) = (\phi_{13}\mathscr{H}\phi_{14}) = (\phi_{15}\mathscr{H}\phi_{16}) = -J \\
(\phi_4\mathscr{H}\phi_6) &= (\phi_5\mathscr{H}\phi_6) = J
\end{aligned}$$

$$J\left(-1-\frac{\gamma}{2}\right) \qquad \text{for S} = 2$$

$$J\left(1-\frac{\gamma}{2}\right),\ J\left(\frac{\gamma}{2}+\sqrt{1+\gamma^2}\right),\ J\left(\frac{\gamma}{2}-\sqrt{1+\gamma^2}\right) \qquad \text{for S} = 1$$

$$J\left(1+\frac{\gamma}{2}+\sqrt{4-2\gamma+\gamma^2}\right),\ J\left(1+\frac{\gamma}{2}-\sqrt{4-2\gamma+\gamma^2}\right) \qquad \text{for S} = 0$$

The Van Vleck susceptibility expression yields:

$$\chi = \frac{Ng^2\beta^2}{2kT}\,\frac{\begin{array}{c}5\exp\{J(2+\gamma)/kT\}+\exp(J\gamma/kT)\\ +\exp\{J(1+\sqrt{1+\gamma^2})/kT\}\\ +\exp\{J(1-\sqrt{1+\gamma^2})/kT\}\end{array}}{\begin{array}{c}5\exp\{J(2+\gamma)/kT\}+3\exp(J\gamma/kT)\\ +3\exp\{J(1+\sqrt{1+\gamma^2})/kT\}\\ +3\exp\{J(1-\sqrt{1+\gamma^2})/kT\}\\ +2\cosh(J\sqrt{4-2\gamma+\gamma^2}/kT)\end{array}} \qquad (3)$$

where differences in $g$-value among the 4 spins are neglected.

Figure 2 shows the results of the numerical calculations of the susceptibility for an antiferromagnetically interacting tetramer with $\gamma$=0—2. In the case of $\gamma$=0, this model represents a dimer model. If $\gamma$ increases infinitely, the model tends to indicate an admixture of a dimer and two monomers. Some of the copper(II) alkanoate complexes with *N*-alkylsalicylideneimines (HSal=N–R) have been postulated to have such a linear tetramer structure.[8] The observed susceptibility for the $Cu_2(Sal{=}N{-}CH_3)(OH)(C_2H_5COO)_2$ compound does not show a maximum; perhaps it appears at lower temperatures. However, the differences among various models are already sufficiently clear in the lower part of

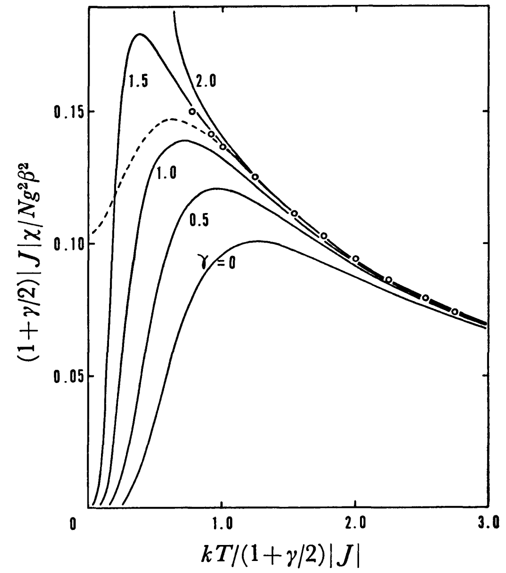

Fig. 2. Magnetic susceptibility of a linear tetramer with $\gamma=0-2$.
Broken curve is drawn for a one-dimensional Heisenberg model. The observed values of $Cu_2(Sal{=}N{-}CH_3)(OH)(C_2H_5COO)_2$ are plotted for the choice of the parameters $J(1+\gamma/2)/k=-100$ K, $g=2.17$, and $N\alpha=60\times10^{-6}$ emu/mol.

this experimental temperature range (77—300 K). The observed values agree well with the equation of a linear tetramer model, but not with that of a dimer model ($\gamma=0$) or a one-dimensional Heisenberg model, the curve of which is extrapolated to a higher temperature than in the literature.[9]

If a linear tetramer has an interaction between the remaining ends as well, a cyclic tetramer (Fig. 1b) will be formed. The Hamiltonian for this problem is:

$$\mathscr{H}=-2J\left(S_1S_2+S_3S_4+\frac{\gamma}{2}S_2S_3+\frac{\gamma}{2}S_1S_4\right) \tag{4}$$

The equation of the magnetic susceptibility can be obtained in a similar manner as for a linear tetramer:

$$\chi=\frac{Ng^2\beta^2}{2kT}\,\frac{5\exp\{J(2+\gamma)/kT\}+1+\exp(J\gamma/kT)+\exp(2J/kT)}{5\exp\{J(2+\gamma)/kT\}+3+3\exp(J\gamma/kT)+3\exp(2J/kT)+2\cosh(J\sqrt{4-2\gamma+\gamma^2}/kT)} \tag{5}$$

Considering a diagonal interaction also in a cyclic tetramer, the problem varies to that of a pseudo-rhombic tetramer (Fig. 1c), the Hamiltonian of which is:

$$\mathscr{H}=-2J\left(S_1S_2+S_3S_4+\frac{\gamma}{3}S_2S_3+\frac{\gamma}{3}S_2S_4+\frac{\gamma}{3}S_1S_4\right) \tag{6}$$

The susceptibility equation obtained in a manner similar to that above is:

$$\chi=\frac{Ng^2\beta^2}{2kT}\,\frac{5\exp\{J(2+\gamma)/kT\}+\exp(J\gamma/3kT)+2\exp\left\{J\left(1+\frac{\gamma}{3}\right)\Big/kT\right\}\times\cosh\left(J\sqrt{1-\frac{2}{3}\gamma+\frac{2}{9}\gamma^2}\Big/kT\right)}{5\exp\{J(2+\gamma)/kT\}+3\exp(J\gamma/3kT)+6\exp\left\{J\left(1+\frac{\gamma}{3}\right)\Big/kT\right\}\times\cosh\left(J\sqrt{1-\frac{2}{3}\gamma+\frac{2}{9}\gamma^2}\Big/kT\right)+2\cosh\left(J\sqrt{4-2\gamma+\frac{1}{3}\gamma^2}\Big/kT\right)} \tag{7}$$

If the ends of a dimer unit interact with either end of the other dimer, the resulting molecule is a pseudo-tetrahedral tetramer (Fig. 1d) with this Hamiltonian:

$$\mathscr{H}=-2J\left(S_1S_2+S_3S_4+\frac{\gamma}{4}S_1S_3+\frac{\gamma}{4}S_2S_4+\frac{\gamma}{4}S_1S_4+\frac{\gamma}{4}S_2S_3\right) \tag{8}$$

The susceptibility equation thus obtained is:

$$\chi=\frac{Ng^2\beta^2}{2kT}\,\frac{5\exp\left\{J\left(1+\frac{\gamma}{2}\right)\Big/kT\right\}+2\exp(-J/kT)+\exp\left\{J\left(1-\frac{\gamma}{2}\right)\Big/kT\right\}}{5\exp\left\{J\left(1+\frac{\gamma}{2}\right)\Big/kT\right\}+6\exp(-J/kT)+3\exp\left\{J\left(1-\frac{\gamma}{2}\right)\Big/kT\right\}+\exp\{J(1-\gamma)/kT\}+\exp(-3J/kT)} \tag{9}$$

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