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Energy levels and exchange interactions of spin clusters

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Résumé . — Nous décrivons d'abord une méthode simple pour diagonaliser l'Hamiltonien d'échange isotrope d'un cluster de N spins dans le cas le plus général où toutes les constantes d'échange sont différentes. La technique, basée sur l'invariance rotationnelle du système, conduit à une réduction considérable de la matrice totale. On donne des expressions simples de l'aimantation et de la susceptibilité et la méthode est appliquée à la détermination des interactions d'échange d'un complexe comprenant cinq ions Cu^{2+} On montre également que pour une assez grande variété de configurations de spins présentes dans les complexes métalliques, on peut résoudre l'Hamiltonien de spin d'échange isotrope dominant de manière directe par des techniques de recouplage. Ceci permet de traiter des clusters jusqu'à neuf spins, ces derniers pouvant avoir des facteurs g différents. Nous poursuivons cette revue par une étude théorique des propriétés magnétiques de spins en interaction sur un anneau avec une étude détaillée d'un complexe oligonucléaire métal-nitroxyde formé de six ions $Mn^{2+}(S = 5/2)$ et de six radicaux libres ($s = 1/2$). Le comportement en fonction de la température de la susceptibilité est interprété à l'aide d'un modèle semi-classique de chaine alternée cyclique. Enfin, nous donnons un procédé pour déterminer les trois constantes d'échange d'un système de trois spins 1/2 couplés par échange isotrope dans le cas non résolu où ces trois constantes sont toutes différentes.

Abstract . — We first describe a simple method for diagonalizing the isotropic exchange Hamiltonian of a cluster of N spins in the most general case where all the exchange constants are different. The technique, based on the rotation invariance of the system, leads to a considerable reduction of the total matrix. Simple expressions of the magnetization and susceptibility are provided and an example of the determination of the exchange constants of a complex with five Cu^{2+} ions is given. It is also shown that for a large variety of spin configurations occuring in metal complexes, it is possible to diagonalize the dominant isotropic exchange spin hamiltonian in a straightforward way by using recoupling techniques. This allows to solve problems up to a nine spin cluster with spins having different g values. This survey is pursued by the theoretical approach of the magnetic properties of interacting spins on a finite ring with a detailed study of an oligonuclear metal nitroxide complex formed by six $Mn^{2+}(S = 5/2)$ and six free radicals ($s = 1/2$). The temperature behaviour of the susceptibility is interpreted with a semi-classical model of a cyclic alternate finite chain. Finally we give a procedure for determining the three exchange constants of three spin 1/2 coupled by isotropic exchange constants in the unsolved case where these constants are all different.

1. Introduction.

There is a considerable interest in the study of magnetic properties of polynuclear complexes where several electronic spins $\mathbf{S}_i$ are coupled with dominant isotropic exchange integrals. An abundant litterature concerns this subject and we will quote only a few examples provided by trinuclear complexes [1(a)], Fe-S compounds [1(b), 2] which play an essential role in biochemistry, chromium complexes [3], and tetra-nuclear complexes of Mn^{2+} ions [4]. Usually, in these systems, because of the low symmetry of their local environment, the individual magnetic ions of the iron group are in singlet orbital electronic ground states which are well separated from the excited orbital states. The same situation occurs for the electron in a free radical. There is no first order contribution of the spin-orbit coupling and to a good approximation the g factors of the various ions can be considered as isotropic and close to the free electron value. The exchange Hamiltonian can be written:

$$\mathcal{H}_0 = -2\sum_{i<j} J_{ij}\mathbf{S}_i \ \ \mathbf{S}_j \tag{1}$$

where the spins $\mathbf{S}_i$ and the exchange constants J_{ij} may be all different. The J_{ij} may have arbitrary signs corresponding to ferro and antiferromagnetic couplings.

In presence of an external magnetic field $\mathbf{H}$, the cluster Hamiltonian becomes:

$$\mathcal{H} = \mathcal{H}_0 + g\mu_{\mathrm{B}}\mathbf{H}\cdot\mathbf{S}_{\mathrm{t}} \tag{2}$$

where $\mathbf{S}_{\mathrm{t}} = \sum_i \mathbf{S}_i$ is the total electronic spin.

The complete cluster Hamiltonian always contains additional anisotropic contributions like the single ion fine structure terms, the antisymmetrical and symmetrical anisotropic exchange interactions and the dipolar coupling [1(a)]. These contributions are small and can be treated, together with the Zeeman effect, as perturbations of the dominant exchange hamiltonian $\mathcal{H}_0$. A technique for diagonalizing the total Hamiltonian including the above contributions as well as any anisotropic part of the Zeeman effect or hyperfine interactions has been developped elsewhere [5], in order to interpret E.P.R. or Mössbauer spectroscopic data. However, except at very low temperatures ($T \sim 1$ or 2 K), the magnetic properties of the cluster such as the temperature dependence of the susceptibility are essentially determined by the spectrum of $\mathcal{H}_0$ and are not sensitive to other perturbing effect. We shall then restrict ourselves to the diagonalization of $\mathcal{H}_0$.

In section 2 we describe a general method for diagonalizing $\mathcal{H}_0$ for N interacting spins. In section 3 we give a much simpler method which is restricted to special geometries but can be used as a first approach of the various problems and has the advantage to deal with spins having different g values. Sections 3 and 4 are concerned with systems which cannot be treated with the above techniques: cyclic alternate chains of spins and three spin 1/2 at the corners of a general triangle.

2. General case.

First, it should be noticed that the dimension of the total spin space of a system of N spins S_i is $d = \prod_{i=1}^{N}(2S_i+1)$. Direct diagonalization of $\mathcal{H}_0$ in the product basis $\prod_{i=1}^{N}|S_i, M_i\rangle$ becomes

hardly tractable when $N \geq 4$ or 5 if $S_i > 1$. For example, in tetranuclear complexes of Mn^{2+} $(S_i = 5/2)$, $d = 1296$. The diagonalization of such a large matrix is usually performed [6] by splitting it into a set of submatrices which are associated to the different values of M_{S_t} of the z component of S_{tz}. In the above example, the maximum order of the submatrices is 146. With the much more efficient method presented below, the maximum order of the submatrices is only 24. The higher that d is, the greater will be the reduction factor of the order of the submatrices.

As $\mathcal{H}_0$ is invariant under the rotation group R_3, each level is associated to an irreducible representation of this group. We denote by $E_0(\alpha, S_t)$ the energy of a multiplet $|\alpha, S_t, M_{S_t}\rangle$, which is associated to the representation $\mathcal{D}_{S_t}$, the index α being necessary in order to take into account the fact that a given representation $\mathcal{D}_{S_t}$ may occur several times. The states $\prod_i |S_i, M_{S_i}\rangle$ form a basis, denoted by $|\prod\rangle$, of the total spin space and generate the reducible product representation $\mathcal{D} = \prod_i \mathcal{D}_{S_i}$ of the double rotation group. $\mathcal{D}$ can be reduced to:

$$\mathcal{D} = \sum_{S_t} n_{S_t} \mathcal{D}_{S_t} \tag{3}$$

so that the index α takes n_{S_t} different values for each value of S_t. According to general results of group theory [7], the calculation of the multiplet energies $E_0(\alpha, S_t)$ and of the associated eigenstates is reduced to a problem of order n_{S_t} for each value of S_t.

In the case of four interacting Mn^{2+} ions, S_t varies from 10 to 0 and the corresponding values of n_{S_t} are (1, 3, 6, 10, 15, 21, 24, 24, 21, 15 and 6) respectively so the highest order of the submatrices is 24.

The above property is easily understood if we remark that the only non vanishing matrix elements of $\mathcal{H}_0$ are $\langle i, S_t, M_{S_t} | \mathcal{H}_0 | j, S_t, M_{S_t}\rangle$, where i and j take n_{S_t} values.

2.1 TECHNICAL PROCEDURE. — We start from the multiplet $S' = \sum_i S_i$, corresponding to the maximal value of S_t which occurs only once in the reduction formula (3) so that the index α can be dropped. We consider the state $|S', -S'\rangle$ corresponding to the minimal value, $-S'$, of M_{S_t} and spanning the subspace $M_{S_t} = -S'$.

Obviously,

$$|S', -S'\rangle = \prod_{i=1}^{N} |S_i, -S_i\rangle . \tag{4}$$

The submatrice of $\mathcal{H}_0$ with respect to the normalized state $|S', -S'\rangle$ is a simple 1×1 matrix $A'_S(\mathcal{H}_0)$ which, according to equation (4) is equal to multiplet energy

$$E_0(S') = -2 \sum_{i<j} J_{ij} S_i S_j \tag{5}$$

Now, we consider the subspace $M_{S_t} = -S' + 1$. By application of the raising operator $S_{t+} = \sum_{i=1}^{N} S_{i+}$ on the state $|S', -S'\rangle$, we easily obtain the normalized state $|S', -S' + 1\rangle$ in the basis $|\prod\rangle$. Then, by an orthogonalization procedure [8] we calculate a set of orthonormal

states $|\beta_1, S'-1, -S'+1\rangle$, belonging to the subspace $M_{S_t} = -S'+1$, orthogonal to the state $|S', -S'+1\rangle$ forming with it a complete orthonormal basis of this subspace, and expressed in the basis $|\prod\rangle$.

To obtain the orthonormal states $|\beta_1, S'-1, -S'+1\rangle$ the Schmidt orthogonalization process is probably the best known method [8]. By construction, these new states are eigenvectors of S_{t_z} for the value $M_{S_t} = -S'+1$ and of $\mathbf{S}_t^2$ for the eigenvalue $(S'-1)\,S'$. The index β_1 runs over a number $g_1 = n_{S'-1}$ of values which is equal to the number of multiplets $S_t = S'-1$. This number g_1 appears automatically in the process of orthogonalization.

The $n_{S'-1} \times n_{S'-1}$ submatrix $A_{S'-1}(\mathcal{H}_0)$ of $\mathcal{H}_0$ in the orthonormal set $|\beta_1, S'-1, -S'+1\rangle$ expressed in the basis $|\prod\rangle$ is a real symmetric matrix. Its diagonalization provides the energies $E_0(\alpha_1, S'-1)$ of the multiplets $S_t = S'-1$, where the index α_1 runs over the same number g_1 of values as β_1. The corresponding eigenstates $|\alpha_1, S'-1, -S'+1\rangle$ can be also obtained from this diagonalization, but they are not useful for computing the magnetic susceptibility of the cluster.

Now, we consider the subspace $M_{S_t} = -S'+2$. By action of the operator S_{t+} on the states $|S', -S'+1\rangle$ and $|\beta_1, S'-1, -S'+1\rangle$, we obtain the orthonormal states $|S',\ -S'+2\rangle$ and $|\beta_1,\ S'-1,\ -S'+2\rangle$ expressed in the basis $|\prod\rangle$. By the same orthogonalization process, we build a set of orthonormal state $|\beta_2,\ S'-2,\ -S'+2\rangle$ belonging to the subspace $M_{S_t} = -S'+2$ orthogonal to the states $|S',\ -S'+2\rangle$ and $|\beta_1,\ S'-1,\ -S'+2\rangle$, forming with them a complete orthonormal basis of this subspace and expressed in the basis $|\prod\rangle$. The index β_2 runs over a number $g_2 = n_{S'-2}$ of values which is equal to the number of multiplets $S_t = S'-2$. Again the energies $E_0\,|\alpha_2,\ S'-2|$ of the multiplets $S_t = S'-2$ are the eigenvalues of the $n_{S'-2} \times n_{S'-2}$ submatrix $A_{S'-2}(\mathcal{H}_0)$ of $\mathcal{H}_0$ in the orthonormal set $|\beta_2,\ S'-2,\ -S'+2\rangle$ and similarly the eigenstates $|\alpha_2,\ S'-2,\ -S'+2\rangle$ could be obtained from the eigen-vectors of this submatrix.

The process of action of S_{t+}, of orthogonalization and of diagonalization of the submatrices $A_{S'-i}(\mathcal{H}_0)$ of $\mathcal{H}_0$ in the successive orthonormal sets $|\beta_i,\ S'-i,\ -S'+i\rangle$ belonging to the subspaces $M_{S_t} = -S'+i$, is carried on until $M_{S_t} = -S''$, where S'' is the minimal value of S_t (usually $S'' = 0$ or $1/2$ for most of the systems considered in magneto chemistry). A Fortran program following this method has been realized in order to determine the unknown J_{ij} constants from the magnetic data.

2.2 MAGNETIC PROPERTIES. — In the presence of an external magnetic field $\mathbf{H}$, the energy levels of the cluster Hamiltonian given by equation (2) are:

$$E(\alpha,\ S_t,\ M_{S_t},\ H) = E_0(\alpha, S) + g\mu_B H\ M_{S_t}. \tag{6}$$

This result is exact and not a first order perturbation approximation because we have assumed that the g factors of all interacting magnetic ions are isotropic and identical, so that the Zeeman term $g\mu_B \mathbf{H}\cdot\mathbf{S}_t$ commutes with $\mathcal{H}_0$. This is a serious limitation for an exact calculation. Otherwise we must use a perturbation treatment [5] and the problem may be extremely complex as there is usually a large number of multiplets $E_0(\alpha, S)$ very close to each other. Then the Zeeman term mixes many multiplets. This situation will be avoided from some special configurations which will be studied in section 3.

Starting from equation (6), the magnetic moment of each Zeeman level is $-g\mu_B\ M_{S_t}$. Introducing

$$x = \frac{g\mu_B H}{2kT}, \tag{7}$$

The average magnetic moment of each cluster is:

$$\mathcal{M} = \frac{g\mu_{\mathrm{B}}}{2} \frac{\sum_{S_t} \{(2S_t+1)\,\mathrm{ch}\,[(2S_t+1)\,x] - \mathrm{sh}\,[(2S_t+1)\,x]\coth x\}\, f(S_t)}{\sum_{S_t} [\mathrm{sh}\,(2S_t+1)\,x]\, f(S_t)} \tag{8a}$$

with

$$f(S_t) = \sum_{\alpha} \exp\left[-E_0(\alpha,\ S_t)/kT\right] \tag{8b}$$

the index α running over all the multiplets with a fixed of S_t. The expression (8b) is a simple generalization of the Brillouin formula.

The molar magnetic susceptibility for a powder or a frozen solution is given by

$$\chi = \frac{\mathcal{N}\,\mu_{\mathrm{B}}^2}{3kT} g^2 \frac{\sum_{S_t} S_t\,(S_t+1)\,(2S_t+1)\, f(S_t)}{\sum_{S_t} (2S_t+1)\, f(S_t)} \tag{9}$$

which generalizes the Curie law.

2.3 EXCHANGE COUPLING IN A PENTACOPPER (II) COMPLEX. — As an illustration of our method we study the interactions between copper in the pentacopper (II) complex involved in biological systems. This complex has been synthetized and its structure determined by X-ray diffraction [9]. In this system we have five Cu^{2+} interacting spins $S_i = 1/2$. Figure 1 describes the structure of this complex. Essentially there are four Cu^{3+} ions at the corner of a rectangle with distances Cu1 – Cu4 = Cu2 – Cu3 = 3.27 Å and Cu1 – Cu2 = Cu3 – Cu4 = 5.77 Å. The fifth Cu5 ion lies on an axis which is perpendicular to the rectangle in its centre. The distance of Cu5 to the four others is 3.46 Å. However, the approximate C_{2v} symmetry of the geometrical figure formed by the five Cu^{2+} cannot be fully used to decrease the number of exchange constants. Indeed, slight distorsions of the molecular complex from this symmetry reduces the point group to identity. In particular the two main exchange constants J_{14} and J_{23} cannot be considered as identical due to a small difference in the Cu O (H) Cu bridge angles. Finally a reasonable form of the exchange Hamiltonian is:

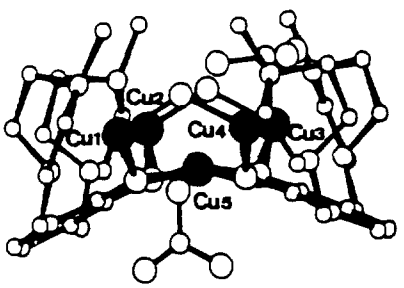

Fig. 1. — Structure of the pentacopper (II) complex.

$$\mathcal{H}_0 = -2J_{14}\mathbf{S}_1 \cdot \mathbf{S}_4 - 2J_{23}\mathbf{S}_2 - \mathbf{S}_3 - 2J_{15}\,(\mathbf{S}_1 + \mathbf{S}_2 + \mathbf{S}_3 + \mathbf{S}_4) \cdot \mathbf{S}_5. \tag{10}$$

Figure 2 illustrates the temperature dependence of the magnetic susceptibility of the complex in the form of the product χT *vs.* T for 5 K $< T <$ 300 K [10]. At low temperature $T <$ 50 K), the product χT is nearly constant at a value 0.38 K cm^3/mol. This corresponds to an isolated spin $S_t = 1/2$ in each complex, which leads to $\chi T = 0.375$ K cm^3/mol. In the upper temperature range χT increases up to 1.5 Kcm^3/mol which shows the presence of antiferromagnetic couplings in the cluster. Our technique was used to determine the values of the exchange parameters. The best fit was obtained with $g = 2.06$, $J_{14} = -161$ cm^{-1}, $J_{23} = -87$ cm^{-1} and $J_{15} = -0.8$ cm^{-1}. This confirms the difference between J_{14} and J_{23} and shows that the coupling of Cu5 with the four other Cu is weak.

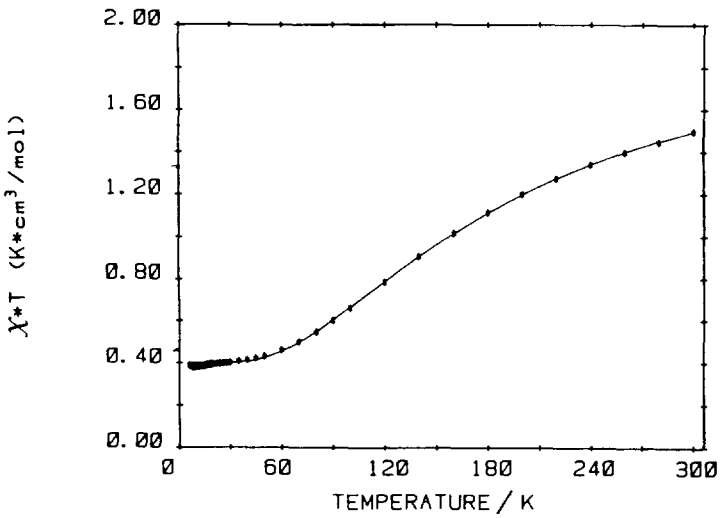

Fig. 2. — Temperature dependence of the magnetic susceptibility (χT *vs.* T) of pentacopper (II) complex. (+) are experimental results and the continuous curve represents the best theoretical fit using the Hamiltonian (2) with $\mathcal{H}_0$ given by equation (10). This fit was obtained with $g = 2.006$, TIP (Temperature Independent Susceptibility) $= 6.26 \times 10^{-4}$ cm^3/mol, $J_{14} = -161$ cm^{-1}, $J_{23} = -87$ cm^{-1}, $J_{15} = -0.8$ cm^{-1}

3. Special geometric configurations.

For a surprinsigly large number of spin configurations occuring in metal complexes where isotropic exchange interactions are dominant, it is possible to diagonalize the Hamiltonian $\mathcal{H}_0$ by simple recoupling techniques. A systematic investigation of soluble problems up to a $n = 9$ spin cluster has been performed. Another advantage of this simple technique is the possibility to treat spins with different g values.

In order to illustrate our purpose we stars with two elementary examples.

3.1 $n = 2$ (FIG. 3.1).

$$\mathcal{H}_0 = -2J_{12}\mathbf{S}_1 \cdot \mathbf{S}_2 = -J_{12}\left[\mathbf{S}_t^2 - \mathbf{S}_1^2 - \mathbf{S}_2^2\right]. \tag{11}$$

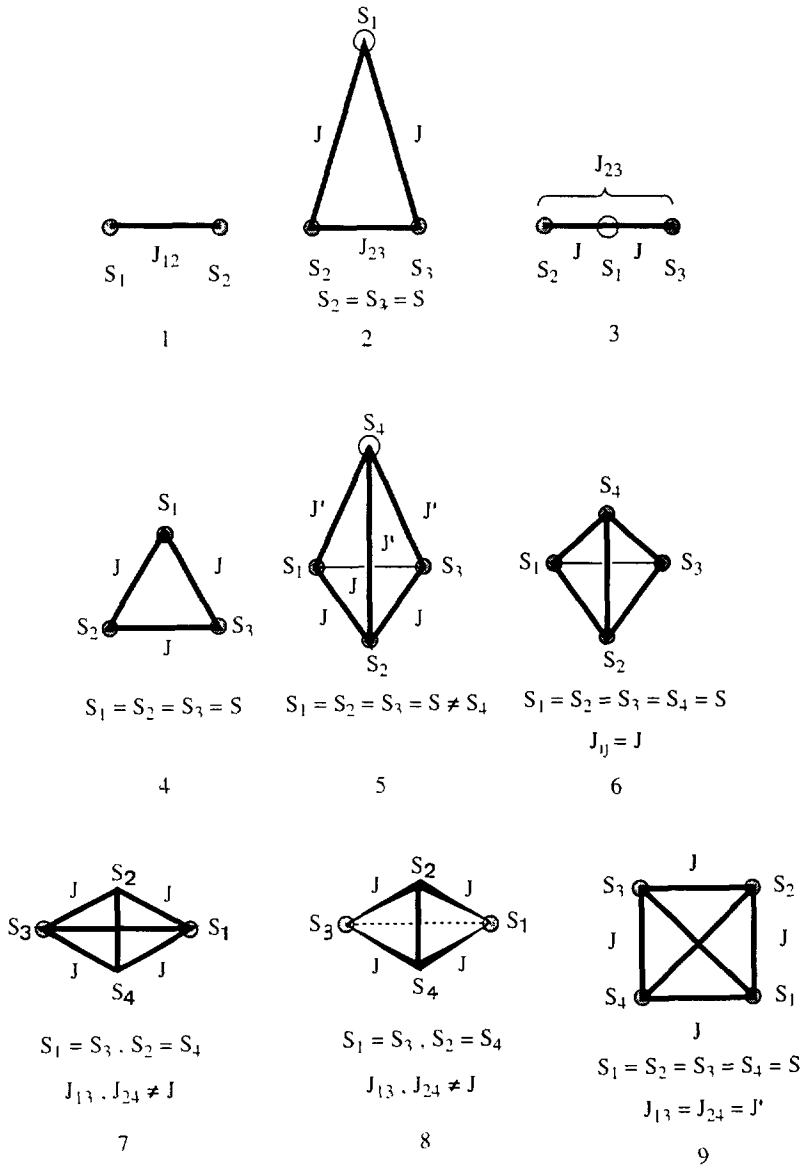

Fig. 3. — Configurations of $n = 2, 3, 4$ spins, with isotropic exchange interactions, for which the energy levels and the corresponding eigenstates can be obtained analytically by vector recoupling techniques.

and the energy multiplets are

$$E(S_t) = -J_{12}S_t(S_t+1) + C$$

with $|S_1 - S_2| \leq S_t \leq S_1 + S_2$ and C is a constant. The corresponding eigenstates are, $|S_1 S_2 S_t M_{S_t}\rangle$. If $\mathbf{S}_1$ and $\mathbf{S}_2$ have respective g_1 and g_2 values, the g factor for any multiplet is given by the simple Landé rule

$$g_{S_t} = \frac{g_1+g_2}{2} + \frac{g_1-g_2}{2}\frac{S_1(S_1+1)-S_2(S_2+1)}{S_t(S_t+1)} \tag{12}$$

Notice that if both g values are anisotropic with $g_{1/\!/}$, $g_{1\perp}$, $g_{2/\!/}$ and $g_{2\perp}$ values for example, at the condition that the principal directions of the g tensors are parallel, equation (12) applies as well for each component [11].

3.2 $n = 3$. — In the general case the solution of the spin Hamiltonian

$$\mathcal{H}_0 = -2J_{12}\mathbf{S}_1\cdot\mathbf{S}_2 - 2J_{23}\mathbf{S}_2\cdot\mathbf{S}_3 - 2J_{13}\mathbf{S}_1\cdot\mathbf{S}_3 \tag{13a}$$

cannot be given explicitely and must be obtained with the help of our general numerical procedure of section 2. The particular case of three spins 1/2 will be discussed later (Sect. 5). However, if two of the exchange constants are equal, $J_{12} = J_{13} = J$, with $S_2 = S_3 = S$ (spins at the corners of an isocele triangle (Fig. 3.2), $\mathcal{H}_0$ reduces to:

$$\mathcal{H}_0 = -2J\mathbf{S}_1\cdot\mathbf{S}_{23} - 2J_{23}\mathbf{S}_2\cdot\mathbf{S}_3. \tag{13b}$$

with $\mathbf{S}_{23} = \mathbf{S}_2 + \mathbf{S}_3$. Then the multiplet energies are apart from an irrelevant constant

$$E(S_{23}, S_t) = -J\ S_t(S_t+1) + (J - J_{23})S_{23}(S_{23}+1). \tag{14}$$

in this equation S_{23} verifies the usual triangle inequality $|S_2 - S_3| \leq S_{23} \leq S_2 + S_3$, and for each value of S_{23}, S_t obeys to $|S_{23} - S_1| \leq S_t \leq S_{23} + S_1$. Clearly, a given value of S_t appears n_{S_t} times according to equation (3). The corresponding eigenstates are [12] $|S_1 S_2 S_3 (S_{23}) S_t M_{S_t}\rangle$ Again if $g_2 = g_3 = g \neq g_1$, the g value of each multiplet is given by equation (12) replacing g_2 and S_2 by g and S_{23}, except if $S_t = 0$ where $g_{S_t} = 0$.

There are numerous examples [13] of trinuclear complexes having this symmetry of the interacting spins like those containing the groupings Cu Co Cu, Cu Mn Cu and Cr Cr Cr. If the three spins lie in the same line (Fig. 3.3) expression (15) is still valid. This is the case of trimeric nickel II acetylacetonate [14] where $S_1 = S_2 = S_3 = 1$, $J = 26$ cm^{-1} and $J_{13} = -7$ cm^{-1} For the special case of three identical spins at the corner of an equilateral triangle ($J_{12} = J_{13} = J_{23} = J$, $S_1 = S_2 = S_3 = S$ (Fig. 3.4), the energy levels are $E(S_{23}, S_t) = -S_t(S_t+1)$.

3.3 $n = 4$. — In this case there are six exchange constants J_{ij} in $\mathcal{H}_0$. The recoupling technique can be used in two cases:

(i) Firstly if $J_{12} = J_{23} = J_{13} = J$ and $J_{14} = J_{24} = J_{34} = J'$.

which corresponds to a tetrahedron (C_{3V} symmetry) with $S_1 = S_2 = S_3 \neq S_4$ (Fig. 3.5), $g_1 = g_2 = g_3 = g \neq g_4$. We easily obtain, with obvious notations, the energy levels:

$$E(S_{123}, S_t) = -J'S_t(S_t+1) + (J' - J)S_{123}(S_{123}+1) \tag{15}$$

and the corresponding eigenstates are $|S_1S_2S_3S_4\,(S_{12})\,(S_{123})\,S_tM_{S_t}\rangle$. The g value of each multiplet is given by equation (12) replacing g_1, g_2, S_1 and S_2 by g, g_4, S_{123} and S_4 respectively. In the particular case of a regular tetrahedron (Fig. 3.6) with $J = J'$, $S_4 = S$ the energy levels are simply $-J\ S_t\,(S_t+1)$. This case was reported for a tetranuclear Manganese (II) complex with $S = 5/2$ [15].

(iii) Secondly if $J_{12} = J_{23} = J_{34} = J_{41} = J$ with different values of J_{13} and J_{24}. This corresponds to various geometrical spin arrangements

— Four spins $\mathbf{S}_i$ with $S_1 = S_3$ and $S_2 = S_4$ at the vertices of a losange with equal interactions along the edges and different diagonal interactions (Fig. 3.7).

— Four spins $\mathbf{S}_i$ with $S_1 = S_3$ and $S_2 = S_4$ at the vertices of two equal isocele triangles 124 and 234 sharing a common edge 24. This arrangement corresponds to an irregular tetrahedron (C_{2V} symmetry. Fig. 3.8) and the losange discussed above is simply the particular case where both isocele triangles are in the same plane.

The energy levels are:

$$E\,(S_{13}, S_{24}, S_t) = -J\ S_t\,(S_t+1) + (J - J_{13})\,S_{13}\,(S_{13}+1) + (J - J_{24})\,S_{24}\,(S_{24}+1) \qquad (16)$$

with eigenstates $|S_1S_2S_3S_4\,(S_{13})\,(S_{24})\,S_tM_{S_t}\rangle$.

Several systems of this kind involving tetranuclear complexes with Mn or Fe ions are reported in the litterature. A more complete review will be given in reference [16]. We just wish to point out that this is the case for the tetranuclear manganese complex $Mn_4O_2\,(O_2 - CCPH_3)_6\,(OEt_2)_2$ consisting of a central planar core of metal atoms (two $Mn^{2+} S_1 = S_3 = 5/2$, two Mn^{3+} $S_2 = S_4 = 2$) bridged by two μ_3–oxo ligands. Susceptibility data was fitted [17] by using equation (16) with $J = -2.8$ cm^{-1}, $J_{24} = -1.5$ cm^{-1} and $J_{13} = 0$, but the fit was obtained with the assumption that all of the spin states have the same g, with an unusually low value $g = 1.47$ which is unrealistic for Mn^{2+} ions. We are reinterpreting these results by assuming that $g_1 = g_3 = 2$ for Mn^{2+} ions and allowing a different value $g_2 = g_4$ for Mn^{3+} ions, a procedure which is possible for this kind of system. Preliminary results provide a more realistic value $g_2 \sim 1.6$ with larger exchange constants $\left(J = -8\ \text{cm}^{-1},\ \ J_{24} = -11.2\ \text{cm}^{-1}\right)$.

The case of four identical spins ($S_1 = S$) arranged in a square with n.n. interactions J and n.n.n. interactions $J_{13} = J_{24} = J'$ (Fig. 3.9) is a particular situation of the above one.

3.4 $n \geq 5$. — The basic configurations which can be solved are, besides a single spin and a pair of spins, three spins on a isocele or equilateral triangle and four spins on a losange or a square. For solving, through a simple angular momentum recoupling, spin cluster with a higher value of n it is necessary to combine in a symmetric way the above basic configurations. For example the configuration represented in figure 3.5 (irregular tetrahedron) is a combination of a single spin $\mathbf{S}_4$ with three equivalent spins on an equilateral triangle.

We can solve systems with $n = 5$ by combining a single spin $\mathbf{S}_5$ with four spins $S_1 = S_2 = S_3 = S_4 = S$ located on a square (C_{4V} symmetry) or by combining three spins $S_1 = S_2 = S_3$ on an equilateral triangle with two spins $S_4 = S_5 = S'$ symmetrically arranged with respect to the triangle (C_{3V} symmetry). In the first case we obtain a pyramid (Fig. 4.1) and in the second case a bitetrahedron (Fig. 4.2). There is no difficulty for obtaining the energy levels of the various multiplets and the corresponding eigenstates and g factors will not be reproduced here for the sake of briefness.

There is another situation involving five spins which is represented in figure 4.3. This is the case of a double isocele triangle which have a common summit (D_2 symmetry if the 5 spins are in the same plane, C_{2V} symmetry otherwise) if we neglect second neighbour interactions.

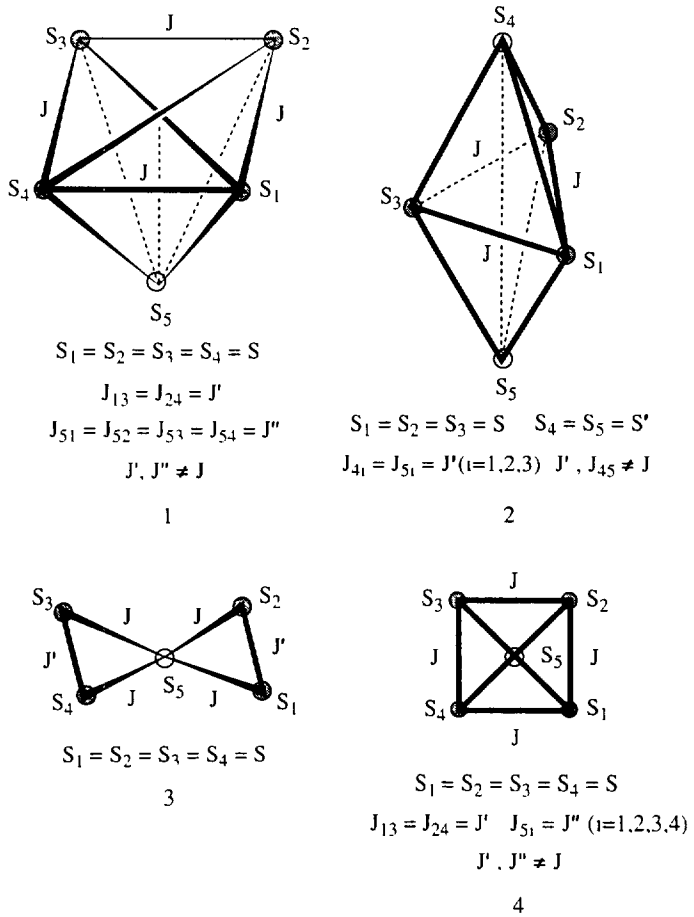

Fig. 4. — Configurations of $n = 5$, 6, 7 spins with an exactly soluble Hamiltonian as in figure 3.

Notice that the case of five spins on a centered square (Fig. 4.4) is a particular case of the pyramid.

A symmetrical array of six spins can be obtained by combining 4 equivalent spins on a square and a pair of equivalent spins on the axis of the square. We obtain an octahedron configuration (Fig. 4.5) for which the regular octahedron (Fig. 4.6) is a particular case.

Configurations with 7 spins are obtained either by considering a centered regular octahedron (Fig. 4.7) or two irregular and equal tetrahedra sharing one common corner (Fig. 4.8). We could also consider the case of figure 4.3 but with three equal isocele triangles sharing a common summit.

Finally the spin configurations with $n = 8$ or 9 are represented in figures 5.1 and 5.2. We shall focus our attention to the last case which is illustrated by a wonderfull example [18], the nomanuclear Oxide-Bridged Manganese Complex. We have 8 Mn^{2+} ions $S_i = 2$ ($i = 1..8$) and a central Mn^{2+} ($S_0 = 5/2$) ion.

Setting $\mathbf{S}_A = \sum_{i=1}^{4} \mathbf{S}_i$ and $\mathbf{S}_B = \sum_{i=5}^{8} S_i$, $\mathbf{S}_{AB} = \mathbf{S}_A + \mathbf{S}_B$

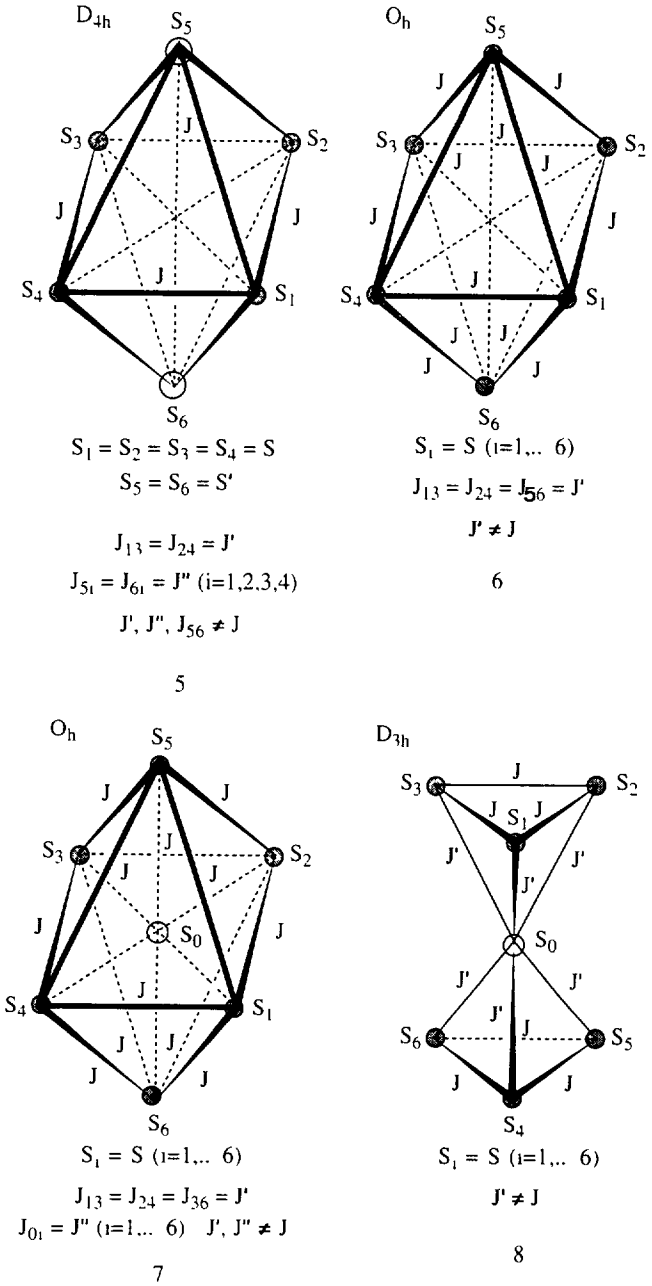

Fig. 4. — *(Continued)*

the energy levels are readily given by:

$$E(S_{13}, S_{24}, S_A, S_{57}, S_{68}, S_B, S_{AB}, S_t) = -J''[S_t(S_t+1) - S_{AB}(S_{AB}+1)]$$
$$-J[S_A(S_A+1) + S_B(S_B+1)] + (J-J')[S_{24}(S_{24}+1) + S_{68}(S_{68}+1) + S_{13}(S_{13}+1)$$
$$+ S_{57}(S_{57}+1)], \tag{17}$$

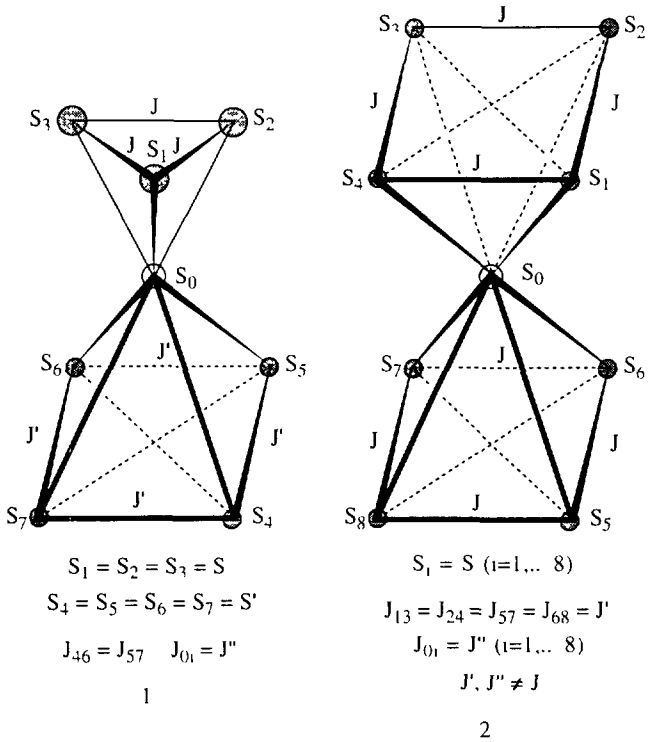

Fig. 5. — Configurations of $n = 8$, 9 spins with an exactly soluble Hamiltonian as in figure 1.

where J, J', J'' correspond to exchange couplings represented in figure 5.2. The magnetic data are very well fitted with $J = -11.2$ cm^{-1}, $J'' = -0.97$ cm^{-1}, $J_{24} = J_{68} = J' = -26.2$ cm^{-1}, $J_{13} = J_{57} = 0$. (With this latter assumption imposed by chemical reasons, the two terms $-J'S_{13}(S_{13}+1)$ and $-J'S_{57}(S_{57}+1)$ in the general formula (17) must be dropped).

Notice that the molar susceptibility for a powder or a frozen solution is, in the general case studied in this section, at the first order of perturbation theory

$$\chi = \frac{\mathcal{N}\mu_{\mathrm{B}}^2}{3kT} \sum_{\alpha, S_t} \frac{g^2(\alpha, S_t)\, S_t(S_t+1)(2S_t+1) \exp\left[-E_{S_t}(\alpha, S_t)/k_{\mathrm{B}}T\right]}{\sum_{S_t}(2S_t+1)\exp\left[-E_{S_t}(\alpha, S_t)/k_{\mathrm{B}}T\right]} \tag{18}$$

which replaces the exact expression (9) when all the g values are equal.

4. Array of spins on a ring.

Much work is currently devoted to the synthesis of molecular ferromagnets [19, 20]. For this purpose the metal nitroxide systems have provided promising results. Indeed, three dimensional ferromagnetic order has been observed in a few systems involving weakly coupled alternate linear chains of nitroxide and metal ions [21]. Besides these compounds presenting long range order, most of the available metal-nitroxide complexes are oligonuclear species.

These limited high spin molecular species are important for the understanding of the magnetic interactions, since they offer simple models allowing a theoretical treatment of the mag-

netic data. However, whereas numerical approaches have been developed for infine unidimensional compounds, the understanding of large but finite oligonuclear species is problematic due to calculation limitations.

Recently [22] such an oligonuclear complex of nitronyl nitroxide with manganese which includes six $S = 5/2$ metal Mn^{2+} spins and six $s = 1/2$ radical spins was synthesized and crystallized (Fig. 6). A complete treatment of such a magnetic system is beyond the possibilities of the most powerful computers and only a lower limit of the metal radical interaction was deduced from the qualitative examination of the magnetic data.

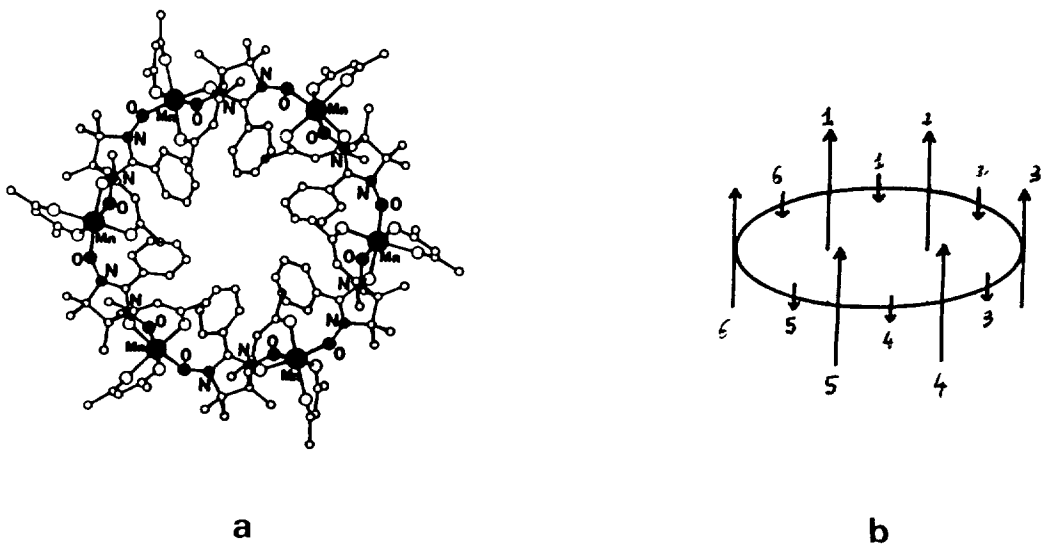

Fig. 6. — (a) View of the cyclic hexanuclear unit of $[Mn(h\ fac)_2Ni\ T\ Ph]_6$. The fluorine atoms of the hexafluoroacethylacetanate ligands have been omitted for clarity. (b) Schematic representation of the magnetic atoms on the ring.

4.1 THE MAGNETIC SYSTEM. LOW TEMPERATURES. — The suceptibility behaviour shown in figure 7 is typical of a paramagnetic system. The antiferromagnetic nature of the manganese-nitroxide interaction is well established. The Hamiltonian of the system is:

$$\mathcal{H} = -2J \sum_{i=1}^{6} Js_i \cdot (\mathbf{S}_i + \mathbf{S}_{i+1}) \tag{19}$$

with $J < 0$ and $\mathbf{S}_7 \equiv \mathbf{S}_1$.

The numerical determination of the energy levels of $\mathcal{H}$ is a very difficult problem because the total dimension of the space is $6^6 \cdot 2^6 = 2\ 985\ 984$. The total spin S_t is a good quantum number

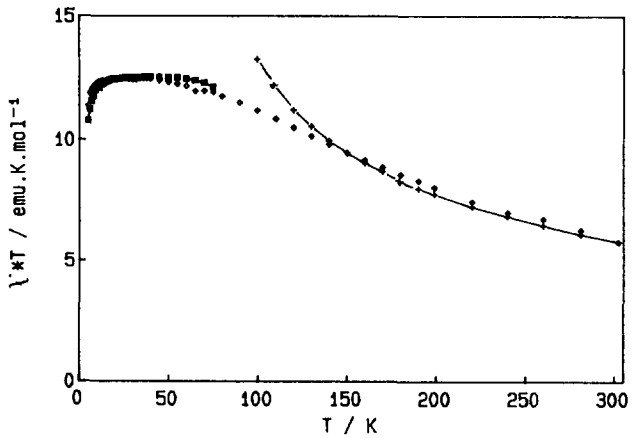

Fig. 7. — Variation of χT with T for a monomeric formula ((◇) experimental, (■) low temperature theoretical behaviour, (+) high temperature theoretical behaviour according to equation (41) with $J/k = -240$ K.

and we have a very large number of multiplets. There is one level $S_t = 18$, 11 levels $S_t = 17$, 60 levels $S_t = 16$ etc... the number of levels of lower multiplicity increasing very fast (36120 levels $S_t = 4$ and a total number of multiplets 267004 !). This precludes any numerical treatment even by taking into account the existence of an approximate sixfold axis of symmetry.

However the presence of a broad plateau at low temperature in the χT *vs.* T curve, corresponding to a value 12.6 uem K mole^{-1} for a Mn = NO pair strongly suggests the presence of a $S_t = 12$ ground state with a gap with the other excited states. Indeed, since both the Mn^{2+} ion ($S = 5/2$) and the radical ($s = 1/2$) have almost isotropic $g = 2$ factors, the total factor will be also close to 2 and the Curie law for a Mn − NO pair gives:

$$\chi T = \frac{\mathcal{N}\mu_B^2}{18\,k} g^2 S_t\,(S_t + 1) = \frac{1}{12} S_t\,(S_t + 1)\,(\text{uem K mol}^{-1})\,. \tag{20}$$

For $S_t = 12$, $\chi T = 13$ in close agreement with the experimental value. Notice that this value of S_t corresponds to the minimal energy of the complex for antiferromagnetic coupling. Indeed each Mn − NO pair has a maximal energy $-5/2\ J$ corresponding to $S_{it} = S_i + s_i = 3$ and a minimal energy $7/2\ J$ corresponding to $S_{it} = 2$. Then the maximal energy of the complex is $-30\ J$ with $S_t = 18$, while its minimal energy has a spin $S_t = 6(S - s) = 12$. This corresponds to a ferrimagnetic like chain with a sublattice $6S$ and a sublattice $6s$. The ground state energy is not known but it must be lower than the classical energy $30\ J$ and higher than the sum of the minimal energy of each pair $42\ J$. We observe at very low temperatures ($T < 10$ K) a strong decrease of the χT value. This is due to saturation effects. The reported experimental susceptibility values on figure 7 are those of M/H. The working field apparatus was $H = 5000$ G. According to the high value of $S_t = 12$ of the ground state $g\mu_B H\ S_t/kT = 8T$ is not much lower than unity at very low temperatures and the Curie law (20) is not applicable. An elementary calculation starting from the expression of the magnetization using the Brillouin function leads to a corrective factor which becomes significant for $T < 10$ K. The theoretical curve in figure 7 including this correction describes correctly the magnetic behaviour at low temperatures.

4.2 HIGH TEMPERATURES. DETERMINATION OF THE EXCHANGE INTEGRAL. — We have shown that for a pair mole Mn – NO, at low temperatures $(\chi T)_{\mathrm{LT}} \sim 13$. At very high temperatures all the spins are independent and $(\chi T)_{\mathrm{HT}} = 4.75$. It is well known [23] that increasing T, χT first decreases, then reaches a minimum and then increases towards its high temperature value. At low temperatures we populate only the ground state (here $S_{\mathrm{t}} = 12$); then increasing T, we populate excited levels with lower values of S_{t} and χT decreases. But when T is high enough we populate the higher levels (the highest being here $S_{\mathrm{t}} = 18$) and χT slightly increases. In this compound, at $T = 300$ K, no minimum is observed and $\chi T = 5.8$ is above the high temperature limit. This makes the problem particularly difficult as it has been shown [23] that for Cu – Ni chains ($S = 1$, $s = 1/2$) there is almost no difference between a finite chain and an infinite chain only above the minimum. However here the Mn^{2+} spin is $S = 5/2$ and it will be shown that the results are different. We shall consider a model in which the Mn spins S are classical spins and the NO spins s are quantum spins. This approach has been used [24] for an infinite chain of antiferromagnetically coupled Mn^{2+} ($S = 5/2$) and Cu^{2+} ($s = 1/2$) spins. *A priori* this model is valid only at high temperatures but it gave good results from high temperatures down to a temperature such that $JS/kT \sim 10$. We shall use the same formalism for our cyclic chain with six $S = 5/2$ spins coupled with six $s = 1/2$ spins.

The g factors for both kinds of spins are assumed to be equal to 2.

According to linear response theorv the susceptibility for a pair Mn – NO is given by:

$$\chi = \frac{\mathcal{N}\mu_{\mathrm{B}}^2 g^2}{6kT} \sum_{ij} \left\langle \left(S_i^z + s_i^z\right)\left(S_j^z + s_j^z\right)\right\rangle . \tag{21}$$

where the symbol $\langle\ \rangle$ means the thermal average. For evaluating the latter we must first calculate the partition function Z and various correlation functions between classical spins $\langle S_i^z S_j^z \rangle$, classical and quantum spins $\langle S_i^z s_j^z \rangle$ and between quantum spins $\langle s_i^z s_j^z \rangle$.

The partition function of the ring is

$$Z = \left(\frac{2S+1}{4\pi}\right)^6 \int \mathrm{d}\Omega_1 .. \mathrm{d}\Omega_6 z_{12} z_{23} z_{34} z_{45} z_{56} z_{61} \tag{22}$$

with

$$z_{i,i+1} = 2\ \mathrm{ch}\left(\frac{J\ S_{i,i+1}}{kT}\right) \tag{23a}$$

where

$$\mathbf{S}_{i,i+1} = \mathbf{S}_i + \mathbf{S}_{i+1} \tag{23b}$$

and

$$S_{i,i+1} = |\mathbf{S}_{i,i+1}| = S\left[2\left(1 + \cos\theta_{i,i+1}\right)\right]$$

$\theta_{i,i+1}$ being the angle between $\mathbf{S}_i$ and $\mathbf{S}_{i+1}$.

Equation (23a) is the quantum partition function of the spin s_i. In equation (22) we have a classical partition function with a sum performed on the classical degrees of freedom of the classical spins: S_i and $\mathrm{d}\Omega_i = \sin\theta_i \mathrm{d}\theta_i \mathrm{d}\varphi_i$.

It is possible to expand $z_{i,i+1}$ in terms of Legendre polynomials

$$z_{i,i+1} = z\left(\theta_{i,i+1}\right) = \sum_{k=0}^{\infty} a_k P_k\left(\cos\theta_{i,i+1}\right) . \tag{24}$$

Using the addition theorem of spherical harmonics, it is easy to show that

$$Z = (2S+1)^6 \sum_{k=0}^{\infty} \frac{a_k^6}{(2k+1)^6}. \tag{25}$$

The coefficients a_k are given by

$$a_k = \frac{2k+1}{2} \int_0^{\pi} z(\theta) P_k(\cos\theta) \sin\theta \, \mathrm{d}\theta. \tag{26}$$

Setting

$$x = -2JS/kT \tag{27}$$

we easily obtain the a_k in terms of x, which is the unique parameter of the problem. For example

$$a_0 = 4x^{-2}(x \operatorname{sh} x - \operatorname{ch} x + 1) \tag{28a}$$

$$a_1 = 12x^{-4}\left[(x^3 + 12x) \operatorname{sh} x - (5x^2 + 12) \operatorname{ch} x - x^2 + 12\right]. \tag{28b}$$

At low temperatures all the a_k have the same order of magnitude $a_k \sim e^x/x$.

At very high temperatures $a_0 = 2$, $a_1 \sim x^2/2$ so only a_0 is relevant. For intermediate temperature ($x = 1$), $a_0 = 2.53$, $a_1 = 0.541$, $a_2 = 9 \times 10^{-3}$

Finally with a good accuracy we can write

$$Z = (2S+1)^6 a_0^6 \left(1 + 3d^6\right) \tag{29a}$$

with

$$d = a_1/3a_0 \tag{29b}$$

Even for $x = 4$, where $d = 0.407$, the corrective term $3d^6$ is only 1% and it is possible to write

$$Z = (2S+1)^6 a_0^6. \tag{30}$$

For an open infinite chain the expression (30) is mathematically rigorous and the limitations of the model arise at low temperatures from the classical treatment of the S spins. Here, for a finite ring, the theory is further limited by neglecting terms in a_1, a_2.. etc. The approximation will become less and valid as x increases but will give reasonable results as long as x is not too large ($x < 8$). We shall perform our calculation of the various correlation functions by limiting ourselves to terms in a_0 and a_1. The classical correlations are given by $\langle S_i^z S_j^z \rangle$ with for example

$$\langle S_1^z S_2^z \rangle = \left(\frac{2S+1}{4\pi}\right)^6 \frac{1}{Z} \int \mathrm{d}\Omega_1 .. \mathrm{d}\Omega_6 z_{12} S \cos\theta_1 z_{23} S \cos\theta_2 z_{34} z_{45} z_{56} z_{61} \tag{31}$$

Using (24) and (30) we obtain

$$\langle S_1^z S_2^z \rangle = \frac{S^2}{3}\left(\mathrm{d} + d^5\right) \tag{31a}$$

$$\langle S_1^z S_3^z \rangle = \frac{S^2}{3}\left(d^2 + d^4\right) \tag{31b}$$

$$\langle S_1^z S_4^z \rangle = \frac{S^2}{3} 2d^3 \tag{31c}$$

where d is defined by (29b).

It should be noticed that a term in d^5 appears in (31a) contrary to the case of the infinite open chain because the spins S_6 and S_2 are the same distance of S_1. Similarly in (31b) and (31c) there are extra terms in d^4 and d^3.

For the autocorrelation function $\langle S_i^z S_i^z \rangle$ we replace its classical value $S^2/3$ by $S(S+1)/3$ which gives the correct behaviour of the susceptibility at very high temperatures.

Now we evaluate the quantum-classical correlation $\langle s_i S_{jz} \rangle$.

we have

$$\langle s_{1z} S_{2z} \rangle = \left(\frac{2S+1}{4\pi}\right)^6 \frac{1}{Z} \int \mathrm{d}\Omega_1 .. \mathrm{d}\Omega_6 y_{12} S \cos\theta_2 z_{23} z_{34} z_{45} z_{56} z_{61} \tag{32}$$

where

$$y_{12} = \mathrm{Tr}\left[s_{1z} \exp\left(\frac{2J\mathbf{s}_1 \cdot \mathbf{S}_{12}}{kT}\right)\right]. \tag{33}$$

After some algebric transformation y_{12} reduces to [23]

$$y_{12} = -2s\left(\cos\theta_1 + \cos\theta_2\right) f\left(\theta_{12}\right) \tag{33a}$$

with

$$f\left(\theta_{12}\right) = \frac{\mathrm{sh}\left[\frac{2JS}{kT}\left(\frac{1+\cos\theta_{12}}{2}\right)^{1/2}\right]}{\left[2\left(1+\cos\theta_{12}\right)\right]^{1/2}}. \tag{33b}$$

Then we expand $f(\theta_{12})$ in terms of Legendre polynomials

$$f(\theta) = \sum_{k=0}^{\infty} b_k P_k(\cos\theta). \tag{34}$$

The coefficients b_k are obtained like the a_k through equation (26), $f(\theta)$ replacing $z(\theta)$. We easily obtain the b_k in terms of x defined by (27):

$$b_0 = x^{-1}(\mathrm{ch}\ x - 1) \tag{35a}$$

$$b_1 = 3x^{-3}\left[(x^2+4)\ \mathrm{ch}\ x - 4\ \mathrm{sh}\ x + x^2 - 4\right] \tag{35b}$$

At low temperatures all the b_k are of the order of e^x/x. At very high temperatures only $b_0 \sim x/2$ is relevant. For intermediate temperatures ($x = 1$) $b_0 = 0.543$, $b_1 = 0.0044$, $b_2 = 10^{-3}$ and we have checked that if x is not too large the expansion (34) can be restricted to b_0 and b_1.

Setting:

$$c = 2\left(\frac{b_1}{3a_0} + \frac{b_0}{a_0}\right) \tag{36}$$

We obtain from (32) to (36)

$$\langle s_1^z S_2^z \rangle = -\frac{sS}{3} c\left(1 + d^5\right) \tag{37a}$$

$$\langle s_1^z S_3^z \rangle = -\frac{sS}{3} c\left(d + d^4\right) \tag{37b}$$

$$\langle s_1^z S_4^z \rangle = -\frac{sS}{3} c\left(d^2 + d^3\right). \tag{37c}$$

For an infinite chain we would not have the terms in d^5, d^4 and d^3 in the above equations. Finally the quantum correlations $\langle s_{iz} s_{jz} \rangle$ are given by:

$$\langle s_1^z s_2^z \rangle = \left(\frac{2S+1}{4\pi}\right)^6 \frac{1}{Z} \int \mathrm{d}\Omega_1 .. \mathrm{d}\Omega_6 y_{12} y_{23} z_{34} z_{45} z_{56} z_{61}, \tag{38}$$

where the y are defined by (33). We obtain:

$$\langle s_1^z s_2^z \rangle = \frac{s^2}{3} c^2 \left(1 + d^4\right) \tag{39a}$$

$$\langle s_1^z s_3^z \rangle = \frac{s^2}{3} c^2 \left(d + d^3\right) \tag{39b}$$

$$\langle s_1^z s_4^z \rangle = \frac{s^2}{3} c^2 \left(2\ d^2\right) \tag{39c}$$

Obviously the autocorrelation function is given by:

$$\langle s_i^z s_i^z \rangle = \frac{s(s+1)}{3} \tag{39d}$$

From the general expression (21) the magnetic susceptibility is given, according to the various correlations functions, (31), (37) and (39) by

$$\chi T = \frac{\mathcal{N}\mu_{\mathrm{B}}^2}{3k} g^2 \left(S(S+1) + 2S^2 \left(d + d^2 + d^3 + d^4 + d^5\right)\right.$$
$$\left. -4sSc\left(1 + d + d^2 + d^3 + d^4 + d^5\right) + s(s+1) + 2s^2c^2 \left(1 + d + d^2 + d^3 + d^4\right)\right] \tag{40}$$

As far as $d \ll 1$, i.e. that the correlation length is short, we find the same result as for an infinite chain.

$$\chi T = \frac{\mathcal{N}\mu_{\mathrm{B}}^2}{3k} g^2 \left[S(S+1) + s(s+1) + \frac{2S^2 d - 4sSc + 2s^2c^2}{1-d}\right], \tag{41}$$

but equation (40) is more appropriate at lower temperature. For $S = 5/2$ and $s = 1/2$ equation (41) rewrites

$$\chi T = 4.75 + \frac{6.25\ d - 2.5\ c + 0.25\ c^2}{1-d}, \tag{42}$$

For $x = 4$, where $d = 0.407$ and $c = 0.818$ the difference between (41) and (42) is only 6×10^{-3}. So we have determined the value of x which is involved in the expressions of c and d in (42) for the highest temperature data i.e. 300 K where $\chi T = 5.8$ (uem K mol^{-1}). We obtained $x = 4.0$, which corresponds to an exchange integral $J = -240$ K. Then we have calculated χT for lower values of T using (41) and the agreement is very good down to $T = 150$ K ($x = 8$) as shown in figure 7. For lower temperatures the theoretical curve increases faster than the experimental one as expected. Indeed the neglected coefficients a_2, b_2 play an increasing role and at low temperatures the spins S cannot be considered as classical spins.

We have also calculated the theoretical position of the minimum of the curve χT *vs.* T for this value of J and we found $x = 1.1$, i.e. $T = 1090$ K with a corresponding value $\chi T = 4.09$. At normal temperatures we are far from the theoretical minimum. However, we have shown that, for $S = 5/2$, there is no great difference between an infinite chain and a ring with 12 spins at normal temperatures i.e. well below the minimum. This was not the case for $S = 1$ and 8 spins [23] for which the minimum is also $x \sim 1$. This shows that the difference between an infinite chain and a finite ring decreases not only with the size of the ring but also with the space dimension i.e. with the number of degrees of freedom of our system.

The general method detailed in this section is applicable to any finite ring of interacting systems in any region where x is not too large.

5. The three spin 1/2 cluster.

We consider a cluster of three spin 1/2, $\mathbf{S}_1$, $\mathbf{S}_1$, $\mathbf{S}_3$ at the corner of a triangle which is not equilateral or isocele, with isotropic exchange interactions.

The Hamiltonian $\mathcal{H}_0$ is written for simplicity, setting $a = -2J_{23}$ etc... as

$$\mathcal{H}_0 = a\mathbf{S}_2 \cdot \mathbf{S}_3 + b\mathbf{S}_1 \cdot \mathbf{S}_3 + c\mathbf{S}_2 \cdot \mathbf{S}_1. \tag{43}$$

This system has three levels $S_t = 3/2$, $S_t = 1/2$ and $S'_t = 1/2$ respectively. From susceptibility measurements we can derive only two independent energy splittings between these levels. But we have three unknown parameters a, b, c. Then, it is obvious that susceptibility experiments cannot provide the exchange parameters of this cluster.

The same problem arises for $n < 6$ exchange coupled spin 1/2. Indeed there are $\dfrac{n(n-1)}{2}$ exchange constants and the number of energy levels is $C^n_{n/2}$ or $C^n_{(n+1)/2}$ according to the parity of n (even or odd respectively). Then the number of energy splittings available are $C^n_{n/2} - 1$ or $C^n_{(n+1)/2} - 1$. It can be easily checked that this number is lower than the number of exchange constants for $n = 3, 4, 5$. This difficulty is not present for higher values of the spin S. Even for $n = 3$, a system of two spins 1/2 coupled with a spin 1 at the corner of a triangle will lead to four levels and consequently to three independent energy splittings allowing the determination of the three exchange parameters.

Coming back to the three spin 1/2 problem, the energy levels are

$$\begin{aligned} E(S = 3/2) &= \frac{a+b+c}{4} \\ E(S = 1/2) &= -\frac{a+b+c}{4} - \frac{K}{2} \\ E(S' = 1/2) &= -\frac{a+b+c}{4} + \frac{K}{2} \end{aligned} \tag{44}$$

with

$$K = \left[a^2 + b^2 + c^2 - (ab + bc + ca)\right]^{1/2} \tag{45}$$

Then susceptibility (or specific heat) experiments only provide the energy splittings

$$\begin{aligned} \Delta_1 &= E(S' = 1/2) - E(S = 1/2) = K \\ \Delta_2 &= E(S = 3/2) - E(S = 1/2) = \frac{a+b+c}{2} + \frac{K}{2}, \end{aligned} \tag{46}$$

i.e. $a + b + c$ and $ab + bc + ca$.

If the three Landé factors g_i associated with the three spins S_i are all equal $g_i = g$, EPR experiments in low fields are of no help since there are five allowed transitions (three within the quartet and one in each doublet), but all of them correspond to the same g value. On the other hand at very high field $g\mu_B H \gg a, b, c$, the problem becomes trivial as from the many allowed transitions it is straightforward to obtain, a, b, c. But when the exchange constants are of the order of 10 cm^{-1} it is very difficult to obtain a much larger Zeeman effect.

This problem of the asymmetric triangle was previously raised by several authors [11, 25] without any simple solution.

Consider now the frequent situation where the three g values are different.

The Hamiltonian of the problem is then:

$$\mathcal{H} = \mathcal{H}_0 + \sum_{i=1}^{3} g_i \mu_B H S_{iz} = \mathcal{H}_0 + 2 \sum_i \varepsilon_i S_{iz} \tag{47}$$

with $\varepsilon_i = 1/2 g_i \mu_B H$.

In high fields the problem is similar to what happens in high resolution NMR spectroscopy. Considering three non-equivalent spin 1/2 nuclei (having different chemical shifts) with indirect isotropic exchange interactions, we obtain the Hamiltonian (47) with $\varepsilon_i = -\gamma_i \hbar H/2$ where γ_i is the gyromagnetic factor of nucleus i. Usually the chemical shifts involved are all large compared with the spin coupling constants. Under these circumstances, the basic product states are good approximations of the eigenstates and the simple first order treatment of $\mathcal{H}_0$ can be applied. The spectrum will then consist of a simple quartet of four equally intense lines for each nucleus and there is no difficulty for determining the modulus of the three exchange constants. This is the well known ABC system [26]. More progress is possible about the determination of the relative signs of the exchange parameters if one of the three nuclei is of a different species or if its signals are well separated from those of the other two nuclei. This is known as an ABX system [26]. A complete solution of the problem in NMR high resolution spectroscopy has been incorporated in a computational scheme [27] but requires the observation of many resonance lines. Corio [27] has discussed in detail the limiting cases of weak and strong coupling which is of interest here. In the latter case he has shown that one observes a central resonance line with two equidistant satellites but this information only provides two additionnal relations $g_1+g_2+g_3$ and an another other complicated expression between the g_i and the three exchange constants from which one can deduce a value of $g_1a+g_2b+g_3c$. As we have added three unknown g factors, we are left with the entire problem.

The solution given below uses simultaneously the susceptibility data which is easy to perform and the EPR spectrum if available.

We assume that the Zeeman effect is a first order perturbation with respect to H_0, which is the usual situation in clusters with electronic spins. The molar susceptibility is easily obtained and is given in cgs units by:

$$\chi T = \frac{3}{32} \frac{g_a^2 + g_b^2 e^{-x_1} + 10 g_c^2 e^{-x_2}}{1 + e^{-x_1} + 2e^{-x_2}} \tag{48a}$$

with

$$x_1 = \frac{\Delta_1}{kT}, \; x_2 = \frac{\Delta_2}{kT} \tag{48b}$$

$$g_a = g(S = 1/2) = g - \frac{1}{K} [(a + b + c)g - J'] \tag{49a}$$

$$g_b = g(S' = 1/2) = g + \frac{1}{K} [(a + b + c)g - J'] \tag{49b}$$

$$g_c = g(S = 3/2) = g \tag{49c}$$

where

$$g = \frac{1}{3} (g_1 + g_2 + g_3) \tag{50}$$

$$J' = g_1 a + g_2 b + g_3 c. \tag{51}$$

The expression (48a) of the susceptibility involves four independent quantities: g, J' defined by (50) and (51) and J, λ defined by

$$J = a + b + c \tag{52}$$

$$\lambda = ab + bc + ca \tag{53}$$

which can easily be determined by a mean square fit.

If EPR is performed on this system, neglecting any hyperfine coupling which can be included in a specific example, we have three intense transitions within each multiplet. The corresponding energy transitions are given by equations (49) and are well separated. Their observation provides a direct determination of g (position of the central line) and the two symmetrical satellite lines give a relation between g, J', J and λ which can be checked with the values obtained from the susceptibility data.

Notice that within the quartet $S = 3/2$, there are 3 coincident transitions with relative intensities (3/4, 1, 3/4) and a total oscillator strength

$$I_c = \frac{5}{2} g^2. \tag{54}$$

We have determined the intensities of the EPR transitions corresponding to the satellite lines g_a and g_b. We obtained:

$$I_a = \frac{1}{4}\left[3g - 2(g_1 + g_2) + \frac{A^2(g_1 + 2g_2 - 3g) + B^2(2g_1 + g_2 - 3g)}{A^2 + B^2 + AB}\right]^2 \tag{55}$$

$$I_b = \frac{1}{4}\left[3g - 2(g_1 + g_2) + \frac{A'^2(g_1 + 2g_2 - 3g) + B'^2(2g_1 + g_2 - 3g)}{A'^2 + B'^2 + A'B'}\right]^2 \tag{56}$$

with

$$\begin{aligned} A &= \lambda - a\left(\sqrt{J^2 - 3\lambda} + J\right) & A' &= \lambda + a\left(\sqrt{J^2 - 3\lambda} - J\right) \\ B &= \lambda - b\left(\sqrt{J^2 - 3\lambda} + J\right) & B' &= \lambda + b\left(\sqrt{J^2 - 3\lambda} - J\right) \end{aligned} \tag{57}$$

A direct observation of the ratios I_a/I_c and I_b/I_c provides two new independent relations between the six unknown parameters g_1, g_2, g_3, a, b, c which must be combined with the four relations (50-53). So combining susceptibility data and E.P.R. measurements in low fields, we can determine all the constants which are characteristic of the system.

For illustrating the method, we consider a simple numerical example in which we have

$$a = 1 \text{ cm}^{-1},\ b = 5 \text{ cm}^{-1},\ c = 6 \text{ cm}^{-1};\ g_1 = 1.9,\ g_2 = 1.8,\ g_3 = 2.3$$

The zero field energy splittings are $\Delta_1 = 4.6$ cm^{-1} and $\Delta_2 = 8.3$ cm^{-1}, the g values corresponding to the central line and the two satellite lines are $g_c = 2$, $g_a = 2.153$, $g_b = 1.847$ and are well separated. At normal temperatures their relative intensities are 10, 1.13 and 0.85.

At low temperatures, the intensities given by $(54-56)$ must be weighted by the respective Boltzmann 10, 1.13 and 0.85 factors which only involve x_1 and x_2 defined by (48b) which are known. According to the values of the exchange constants the relative intensities of the three lines can be greatly modified. In particular if $\Delta_2 > 0$ (antiferromagnetic coupling) and $\Delta_2 \geq kT$, the relative weight of the central line will decrease and the comparison of the line intensities becomes easier. Consequently the accuracy on the determination of the exchange constants will be improved.

We are now experimentally investigating non-centrosymmetric systems including two Cu^{2+} ions coupled with a Nitroxide radical for which this theory can be applied [28].

6. Conclusion.

We described some particular problems which arise in the study of the magnetic properties of spin clusters. Due to the considerable progress in magneto-chemistry techniques a large variety of situations can occur. We have developped general techniques allowing to solve many of these situations. In several cases it is possible to diagonalize the exchange Hamiltonian in an exact way. When the number of interacting spins is increasing approximate methods were developped with particular attention paid to finite ring arrangments.

Undoubtedly new kinds of spin arrangments will be discovered for which the techniques developped in this paper will be useful at least as a first approach.

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