The Magnetic Susceptibility of Spin–Spin Coupled Atoms

BY MARTIN L. SAGE

A high-temperature expansion of the magnetic susceptibility of atoms interacting with indirect spin–spin couplings is evaluated to third order in the coupling. These results are applicable to transition metal compounds which contain several transition metal atoms.

A. Introduction

In recent years a large number of inorganic molecules have been synthesized which contain a number of transition metal atoms. Many of these molecules contain only one transition metal in one oxidation state. If there is no orbital angular momentum, the Hamiltonian which is used to describe the behavior of these compounds in a magnetic field, H, is

$$\mathcal{H} = W + g\beta H S_z \tag{1}$$

where g is the magnetogyric ratio of the electron, β the Bohr magneton, S_z the total spin angular momentum parallel to the magnetic field, and W the isotropic indirect spin–spin coupling.[1] In eq 2 the prime on a summation indicates that we are to sum over distinct i and j. The coupling constants J_{ij} depend on the bonding between atoms i and j.

$$W = -\sum_{i,j}' J_{ij} S_i \cdot S_j \tag{2}$$

Studies of the magnetic susceptibility of the compounds as a function of temperature are one of the standard methods of determining these coupling constants.

In many cases the eigenvalues and their degeneracies of this Hamiltonian can be written down from a knowledge of the rules for addition of angular momentum. From these results the susceptibility is readily obtained. This method has been widely used.[2–4] In other cases the eigenvalue spectrum must be calculated using standard techniques. If there is only a single nonvanishing J[5] or the spin is low,[6] there is little difficulty in finding the eigenvalue spectrum and the susceptibility. If there are a number of distinct nonvanishing J's, these techniques become more cumbersome to apply since the eigenfunctions may depend on the ratio of the coupling constants. We have therefore used a high-temperature expansion technique which will work for the general case provided J_{ij}/kT is not too large. These high-temperature expansion techniques have been widely used in the statistical mechanics of spin systems[7,8] and have been used by Domb and Sykes to calculate the susceptibility of crystals.[9]

B. General Formulation of the Susceptibility

The equivalent susceptibility, $\chi_e(H)$, of a molecule containing n atoms of spin S which has a Hamiltonian given by eq 1 is

$$\chi_e(H) = -N(\partial^2 E/\partial H^2)/2n \tag{3}$$

where N is Avogadro's number and E is the average energy per molecule

$$E = -\partial \ln Z/\partial \gamma \tag{4}$$

where Z is the partition function and $\gamma = 1/kT$. Z is given by

$$Z = \text{Tr}[\exp(-\gamma H)] \tag{5}$$

Since W and S_z commute, we can write

$$\exp(-\gamma \mathcal{H}) = \exp(-\gamma g\beta H S_z) \exp(-\gamma W)$$

If we are interested in the susceptibility for weak fields, we need only consider the first several terms in the expansion of the last exponential

$$Z = Z_w[1 + \gamma^2 g^2 \beta^2 H^2 \langle S_z^2 \rangle_w/2 + \gamma^4 g^4 \beta^4 H^4 \langle S_z^4 \rangle_w/4! + \cdots] \tag{6}$$

where

$$Z_w = \text{Tr}[\exp(-\gamma W)] \tag{7}$$

is the zero-field partition function. For any operator A

$$\langle A \rangle_w = \text{Tr}(A)[\exp(-\gamma W)]/Z_w \tag{8}$$

is the zero-field average. We have made use of the fact that $\langle S_z^{2l+1} \rangle_w = 0$. Substitution into eq 3 and 4 leads to

$$\chi_e(H) = \chi_e + \chi_e'' H^2/2 + \cdots \tag{9}$$

with

$$\chi_e = (N\gamma g^2 \beta^2/n)\{\langle S_z^2 \rangle_w - \gamma[\langle W S_z^2 \rangle_w - \langle W \rangle_w \langle S_z^2 \rangle_w]/2\} \tag{10}$$

and

$$\chi_e'' = (N\gamma^3 g^4 \beta^4 H^2/n)\{4[\langle S_z^4 \rangle_w - 3\langle S_z^2 \rangle_w^2] - \gamma[\langle W S_z^4 \rangle_w - 6\langle W S_z^2 \rangle_w \langle S_z^2 \rangle_w - \langle W \rangle_w \langle S_z^4 \rangle_w + 6\langle W \rangle_w \langle S_z^2 \rangle_w^2]\} \tag{11}$$

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TABLE I

$\chi_e/N\gamma g^2\beta^2$ FOR TWO PARTICLES OF SPIN $^1/_2$ [$W = -2JS_1 \cdot S_2$; HIGH-TEMPERATURE EXPANSION INCLUDING $(1/T)^{m-1}$ TERMS]

$J\gamma$	Exact	1	2	3	4
0	0.25000000	0.25000000	0.25000000	0.25000000	0.25000000
0.01	0.25186247	0.25000000	0.25187500	0.25186250	0.25186248
0.03	0.25551185	0.25000000	0.25562500	0.25551250	0.25551180
0.05	0.25905971	0.25000000	0.25937500	0.25906250	0.25905925
0.1	0.26748150	0.25000000	0.26875000	0.26750000	0.26747396
0.3	0.29485727	0.25000000	0.30625000	0.29500000	0.29429688
0.5	0.31313943	0.25000000	0.34375000	0.31250000	0.30924480
1	0.33271227	0.25000000	0.43750000	0.31250000	0.28645834
3	0.33388303	0.25000000	0.81250000	-0.31250000	-1.01562482
5	0.33335350	0.25000000	1.18750000	-1.93750000	-5.19270750
-0.01	0.24811252	0.25000000	0.24812500	0.24811250	0.24811252
-0.03	0.24426326	0.25000000	0.24437500	0.24426250	0.24426320
-0.05	0.24031624	0.25000000	0.24062500	0.24031250	0.24031575
-0.1	0.23003405	0.25000000	0.23125000	0.23000000	0.23002604
-0.3	0.18386935	0.25000000	0.19375000	0.18250000	0.18320312
-0.5	0.13331216	0.25000000	0.15625000	0.12500000	0.12825520
-1	0.02779515	0.25000000	0.06250000	-0.06250000	-0.03645834
-3	-0.00486641	0.25000000	-0.31250000	-1.43750000	-0.73437518
-5	-0.00018152	0.25000000	-0.68750000	-3.81250000	-0.55729250

Ordinarily only χ_e is important and we can ignore saturation effects.

C. High-Temperature Expansion

When the spin–spin interaction energy is small compared to kT, we can expand $\exp(-\gamma W)$ in a power series and retain only the first several terms. Thermal averages may then be expressed in terms of averages taken assuming $\gamma W = 0$

$$\langle A\rangle_w = \langle A\rangle_0 - \gamma\langle WA\rangle_0 + (\gamma^2/2)[\langle W^2 A\rangle_0 -$$
$$\langle W^2\rangle_0\langle A\rangle_0] - (\gamma^3/3!)[\langle W^3 A\rangle_0 - 3\langle W^2\rangle_0\langle WA\rangle_0 -$$
$$\langle W^3\rangle_0\langle A\rangle_0] + \cdots \quad (12)$$

where

$$\langle A\rangle_0 = \text{Tr}(A)/(2S + 1)^n \quad (13)$$

We have used the fact that $\langle W\rangle_0 = 0$ and we have obtained

$$\chi_e = (N\gamma g^2\beta^2/n)\{\langle S_z^2\rangle_0 - (3\gamma/2)\langle WS_z^2\rangle_0 +$$
$$\gamma^2[\langle W^2 S_z^2\rangle_0 - \langle W^2\rangle_0\langle S_z^2\rangle_0] - (\gamma^3/12)[5\langle W^3 S_z^2\rangle_0 -$$
$$15\langle W^2\rangle_0\langle WS_z^2\rangle_0 - 5\langle W^3\rangle_0\langle S_z^2\rangle_0] + \cdots\} \quad (14)$$

and

$$\chi_e'' = (N\gamma^3 g^4\beta^4/n)\{4[\langle S_z^4\rangle_0 - 3\langle S_z^2\rangle_0^2] - 5\gamma[\langle WS_z^4\rangle_0 -$$
$$6\langle WS_z^2\rangle_0\langle S_z^2\rangle_0] + \cdots\} \quad (15)$$

The susceptibility is expressed in terms of the trace of operators of the type $W^m S_z^{2l}$. The calculation of these traces is sketched in the Appendix where the results are also tabulated.

D. Results

Table I lists $\chi_e/N\gamma g^2\beta^2$ as a function of $J\gamma$ for two spin $^1/_2$ atoms. The exact result and approximations using up to four terms in the high-temperature expansion are given. For $|J\gamma| < 0.1$ a linear relation in $1/T$ is sufficient for 0.5% accuracy. J is proportional to the slope. Quadratic deviations are sufficient for 1% accu-

racy for $|J\gamma| < 0.5$. The coefficient of the quadratic term is proportional to J^2.

For ferromagnetic coupling $(J > 0)$ $\chi_e T$ has changed 20% of the total change from its high-temperature to its low-temperature value for $J\gamma = 0.1$. For $J\gamma = 0.5$ the change is 75%. For the antiferromagnetic case $(J < 0)$ the change is 10 and 50% for $J\gamma = -0.1$ and -0.5, respectively.

Table II shows $\chi_e/N\gamma g^2\beta^2$ for three spin $^1/_2$ atoms interacting with two equal coupling constants J and one unequal constant J' as a function of $J\gamma$ and $J'\gamma$ for $J' = J$, $J' = 0$, and $J' = -J$. Again deviations from linearity are small for $|J\gamma| < 0.1$ and from a quadratic relationship for $|J\gamma| < 0.5$. The limiting slope depends on $(2J + J')/3$ which is the average coupling constant. The coefficient of the quadratic terms depends on products of two coupling constants. If we can determine the limiting slope and the quadratic coefficients, we can determine J and J'.

For larger values of spin our linear and quadratic expressions will become inaccurate at smaller values of $|J\gamma|$ because of the larger value of the energy levels. They will remain accurate for comparable changes in temperature times susceptibility.

E. Conclusions

Expressions have been given for temperature times susceptibility in a power series in $1/T$. The intercept depends only on spin, the limiting slope depends on the average spin–spin coupling constant, and the quadratic term depends on an average of products of two coupling constants. From an experimental determination of slope and quadratic deviations, we are able to determine some averages of the coupling constants. If there are only two distinct ones, we can determine them. If there are more than two we can only put limits on them. These limits will prove helpful in trying to fit the susceptibility using the exact quantum statistical

TABLE II

$\chi_e / N\gamma g^2 \beta^2$ FOR THREE PARTICLES OF SPIN $\frac{1}{2}$ [$W = -2J(S_1 \cdot S_2 + S_1 \cdot S_3) - 2J'S_2 \cdot S_3$; HIGH-TEMPERATURE EXPANSION INCLUDING $(1/T)^{m-1}$ TERMS]

			m			
$J\gamma$	$J'\gamma$	Exact	1	2	3	4
0	0	0.25000000	0.25000000	0.25000000	0.25000000	0.25000000
0.01	0	0.25249152	0.25000000	0.25250000	0.25249167	0.25249514
0.03	0	0.25742137	0.25000000	0.25750000	0.25742500	0.25742125
0.05	0	0.26227522	0.25000000	0.26250000	0.26229167	0.26227431
0.1	0	0.27404263	0.25000000	0.27500000	0.27416667	0.27402779
0.3	0	0.31494040	0.25000000	0.32500000	0.31750000	0.31375000
0.5	0	0.34549135	0.25000000	0.37500000	0.35416667	0.33680556
1	0	0.38857837	0.25000000	0.50000000	0.16666667	0.02777778
3	0	0.42048693	0.25000000	1.00000000	0.25000000	−3.50000000
5	0	0.41833643	0.25000000	1.50000000	−0.58333333	−17.94444444
−0.01	0	0.24749180	0.25000000	0.24750000	0.24749167	0.24749180
−0.03	0	0.24242886	0.25000000	0.24250000	0.24242500	0.24242875
−0.05	0	0.23730993	0.25000000	0.23750000	0.23729167	0.23730903
−0.1	0	0.22431958	0.25000000	0.22500000	0.22416667	0.22430555
−0.3	0	0.17222582	0.25000000	0.17500000	0.16750000	0.17125000
−0.5	0	0.12727411	0.25000000	0.12500000	0.10416667	0.12152778
−1	0	0.07299273	0.25000000	0.00000000	−0.08333333	0.05555555
−3	0	0.08304687	0.25000000	−0.50000000	−1.25000000	2.50000000
−5	0	0.08333192	0.25000000	−1.00000000	−3.08333333	14.27777778
0.01	0.01	0.25374953	0.25000000	0.25375000	0.25375000	0.25374953
0.03	0.03	0.26123736	0.25000000	0.26125000	0.26125000	0.26123734
0.05	0.05	0.26869159	0.25000000	0.26875000	0.26875000	0.26869140
0.1	0.1	0.28703708	0.25000000	0.28750000	0.28750000	0.28703125
0.3	0.3	0.35114154	0.25000000	0.36250000	0.36250000	0.34984374
0.5	0.5	0.39314476	0.25000000	0.43750000	0.43750000	0.37890624
1	1	0.42344639	0.25000000	0.62500000	0.62500000	0.15625000
3	3	0.41681059	0.25000000	1.37500000	1.37500000	−11.28124988
5	5	0.41666734	0.25000000	2.12500000	2.12500000	−56.46874943
−0.01	−0.01	0.24625046	0.25000000	0.24625000	0.24625000	0.24625046
−0.03	−0.03	0.23876262	0.25000000	0.23875000	0.23875000	0.23876265
−0.05	−0.05	0.23130839	0.25000000	0.23125000	0.23125000	0.23130859
−0.1	−0.1	0.21296289	0.25000000	0.21250000	0.21250000	0.21296875
−0.3	−0.3	0.14885844	0.25000000	0.13750000	0.13750000	0.15015625
−0.5	−0.5	0.10685521	0.25000000	0.06250000	0.06250000	0.12109375
−1	−1	0.07655362	0.25000000	−0.12500000	−0.12500000	0.34375000
−3	−3	0.08318939	0.25000000	−0.87500000	−0.87500000	11.78125000
−5	−5	0.08333267	0.25000000	−1.62500000	−1.62500000	56.96875000
0.01	−0.01	0.25121664	0.25000000	0.25125000	0.25121667	0.25121665
0.03	−0.03	0.25344988	0.25000000	0.25375000	0.25345000	0.25344954
0.05	−0.05	0.25541722	0.25000000	0.25625000	0.25541667	0.25541450
0.1	−0.1	0.25919190	0.25000000	0.26250000	0.25916667	0.25914931
0.3	−0.3	0.25988451	0.25000000	0.28750000	0.25750000	0.25703125
0.5	−0.5	0.24462842	0.25000000	0.31250000	0.22916667	0.22699654
1	−1	0.18364103	0.25000000	0.37500000	0.04166667	0.02430556
3	−3	0.07234184	0.25000000	0.62500000	−2.37500000	−2.84375000
5	−5	0.07683231	0.25000000	0.87500000	−7.45833333	−9.62847221
−0.01	0.01	0.24871668	0.25000000	0.24875000	0.24871667	0.24871668
−0.03	0.03	0.24595085	0.25000000	0.24625000	0.24595000	0.24595046
−0.05	0.05	0.24292181	0.25000000	0.24375000	0.24391667	0.24291884
−0.1	0.1	0.23423230	0.25000000	0.23750000	0.23416667	0.23418403
−0.3	0.3	0.18698327	0.25000000	0.21250000	0.18250000	0.18296875
−0.5	0.5	0.13479783	0.25000000	0.18750000	0.10416667	0.10633680
−1	1	0.07342773	0.25000000	0.12500000	−0.20833333	−0.19097222
−3	3	0.08300441	0.25000000	−0.12500000	−3.12500000	−2.65625000
−5	5	0.08333201	0.25000000	−0.37500000	−8.70833333	−6.53819445

results since we have reduced the number of unknown parameters.

The approximate treatment is applicable to situations in which the exact susceptibility cannot be calculated which is the case for molecules containing several coupled atoms which have additional intermolecular couplings.

Further work is in progress to determine how the susceptibility changes with slight changes in some of the coupling constants.

Appendix. Evaluation of $\langle W^m S_z^{2l} \rangle_0$

We shall illustrate our methods using $\langle W^2 S_z^2 \rangle_0$ and merely tabulate the results for other terms. The types of expressions which occur in W^2 are $(S_1 \cdot S_2)^2$, $(S_1 \cdot S_2) \cdot (S_1 \cdot S_3)$, and $(S_1 \cdot S_2)(S_3 \cdot S_4)$. All computations shall be done using a basis in which each S_{zi} is diagonal.

$(S_1 \cdot S_2)^2$ can be multiplied by $S_{1z}{}^2$, $S_{3z}{}^2$, $S_{1z}S_{2z}$, $S_{1z}S_{3z}$, and $S_{3z}S_{4z}$. The last two terms will have vanishing expectation values as will all terms which are linear in a spin operator for one of the atoms. The first two are equal to $S(S+1)\langle(S_1 \cdot S_2)^2\rangle_0/3$ since $\langle(S_1 \cdot S_2)^2 S_{1z}{}^2\rangle_0 = \langle(S_1 \cdot S_2)^2 S_{1x}{}^2\rangle_0 = \langle(S_1 \cdot S_2)^2 S_{1y}{}^2\rangle_0 = \langle(S_1 \cdot S_2)^2 S_1{}^2\rangle_0/3$. In our basis the diagonal part of $(S_1 \cdot S_2)^2$ is

$$S_{1z}{}^2 S_{2z}{}^2 + (S_{1+}S_{1-}S_{2-}S_{2+} + S_{1-}S_{1+}S_{2+}S_{2-})/4 =$$
$$S_{1z}{}^2 S_{2z}{}^2 + [S^2(S+1)^2 - S(S+1)(S_{1z}{}^2 + S_{2z}{}^2) +$$
$$S_{1z}{}^2 S_{2z}{}^2 - S_{1z}S_{2z}]/2$$

We now see

$$\langle(S_1 \cdot S_2)^2 S_{1z}{}^2\rangle_0 = \langle(S_1 \cdot S_2)^2 S_{3z}{}^2\rangle_0 = S^3(S+1)^3/9$$

which could also be determined from symmetry considerations. The diagonal part of $(S_1 \cdot S_2)^2$ also allows us to determine

$$\langle(S_1 \cdot S_2)^2 S_{1z}S_{2z}\rangle_0 = -S^2(S+1)^2/18$$

The only remaining contributions from $W^2 S_z{}^2$ are from

$$\langle(S_1 \cdot S_2)(S_1 \cdot S_3)S_{2z}S_{3z}\rangle_0 = \langle S_{1z}{}^2 S_{2z}{}^2 S_{3z}{}^2\rangle = S^3(S+1)^3/27$$

By similar considerations we find the results

$$\langle S_z{}^2\rangle_0 = nS(S+1)/3$$

$$\langle S_z{}^4\rangle_0 = (5n-2)nS^2(S+1)^2/15 - nS(S+1)/15$$

$$\langle W\rangle_0 = 0$$

$$\langle WS_z{}^2\rangle_0 = -2S^2(S+1)^2 \Sigma' J_{ij}/9$$

$$\langle WS_z{}^4\rangle_0 = -[4(5n-4)S^3(S+1)^3 - 8S^2(S+1)^2]\Sigma' J_{ij}/45$$

$$\langle W^2\rangle_0 = 2S^2(S+1)^2\Sigma' J_{ij}{}^2/3$$

$$\langle W^2 S_z{}^2\rangle_0 = 2S^2(S+1)^2[nS(S+1) - 1]\Sigma' J_{ij}{}^2/9 + 8S^3(S+1)^3\Sigma' J_{ij}J_{ik}/27$$

$$\langle W^3\rangle_0 = 2S^2(S+1)^2 \Sigma' J_{ij}{}^3/3 - 8S^3(S+1)\Sigma' J_{ij}J_{ik}J_{jk}/9$$

$$\langle W^3 S_z{}^2\rangle_0 = -4[2S^4(S+1)^4/15 - (4/45 + n/18) \times S^3(S+1)^3 + 4S^2(S+1)^2/45]\Sigma' J_{ij}{}^3 -$$
$$8[2S^4(S+1)^4 - S^3(S+1)^3]\Sigma' J_{ij}{}^2 J_{ik}/9 -$$
$$8[nS^4(S+1)^4 - S^3(S+1)^3]/27\Sigma' J_{ij}J_{ik}J_{ki} -$$
$$4\Sigma' J_{ij}{}^2 J_{kl}S^4(S+1)^4/9 -$$
$$8\Sigma' J_{ij}J_{jk}J_{kl}S^4(S+1)^4/27$$

Four-, Five-, and Six-Coordinate Metal Complexes of Di(2-pyridyl) Disulfide and 1,2-Di(2'-pyridyl)ethane. Further Studies of the Infrared Spectra of Pyridine–Metal Complexes

BY M. KEETON AND A. B. P. LEVER*

Complexes of cobalt(II), nickel(II), zinc(II), and mercury(II) with the ligands di(2-pyridyl) disulfide and 1,2-di(2'-pyridyl)-ethane are described. The cobalt complexes are tetrahedral, while tetrahedral, square-planar, and five-coordinate complexes of nickel are characterized. Utilization is made of electronic spectra, vibrational spectra (conventional and far-infrared), and magnetism in structural diagnosis. A detailed comparison of the bonding characteristics of the two closely related ligands is made. It is shown that in the five-coordinate complexes, the ligands span equatorial and axial sites. The sulfur atoms of the disulfide ligand are not involved in coordination except in the mercury complex.

There has been extensive interest[1] in the chemistry of ligands formed by the linkage of two pyridine residues, in the ortho position, by various groups such as $-CH_2-$, $-NH-$, $-CH_2NHCH_2-$, $-CO-$, $-S-$, $-CH{=}CH-$, $-SO_2-$, $-CH_2CH_2XCH_2CH_2-$ (X = S, NH), $-N{=}N-$, etc.

In most cases the bridging atom(s) is (are) not involved in coordination to the metal and the ligand behaves essentially as a sterically hindered 2-substituted pyridine. When coordination by the bridging group does occur, as for example with $-CH_2CH_2SCH_2CH_2-{}^2$ or with $-N{=}N-,{}^3$ complexes of interesting stereochemistry are obtained.

The complexing ability of di(2-pyridyl) disulfide (LS) was investigated in the hope that this very simple ligand would give rise to five-coordinate complexes. This in fact it does although, surprisingly, the sulfur atoms are not involved.

As a model for comparison purposes, the pyridine analog of ethylenediamine, 1,2-di(2'-pyridyl)ethane (LE) was also studied.

LN

LS   LE
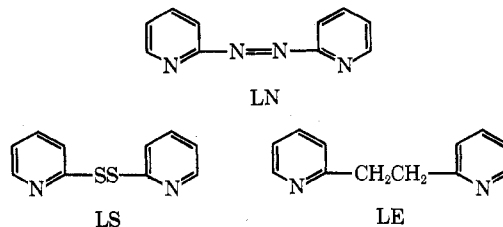
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