PHYSICAL REVIEW VOLUME 163, NUMBER 2 10 NOVEMBER 1967

# High-Temperature Susceptibility of an Exchange-Interaction Model of Ferromagnetism

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(Received 26 June 1967)

The Schrödinger exchange interaction for arbitrary spin is used to construct a Hamiltonian for a nearest-neighbor model of ferromagnetism. The general high-temperature series for the low-field susceptibility is developed, and the first three terms of the series, for arbitrary crystal lattices, are calculated. The Curie temperature obtained from setting $\chi^{-1}=0$ and taking the first two terms (molecular-field theory) or three terms ("Heisenberg Gaussian" approximation), is given by

$$(2S+1)k_BT_C/J=z \quad \text{or} \quad 4/[1-(1-8/z)^{1/2}],$$

respectively. The functional dependence on $z$ (number of nearest neighbors) of the latter result, for arbitrary $S$, is exactly the same as originally obtained by Heisenberg for $S=\frac{1}{2}$. In general, the exchange model appears to disorder at a lower temperature than the Heisenberg model, as could be anticipated from the higher degeneracy of the ground state of a pair of spins interacting with the exchange Hamiltonian compared to the Heisenberg Hamiltonian.

## I. INTRODUCTION

CONSIDER an operator $\mathbf{P}_{ij}$ which has the property that it exchanges, or permutes, the spin coordinates of two electrons, labelled $i$ and $j$; this operator is called the exchange-interaction operator. The connection between this operator and spin was first extablished for spin $\frac{1}{2}$ by Dirac[1] and later generalized to the case of arbitrary spin $S$ by Schrödinger,[2] who showed that

$$\mathbf{P}_{ij}=\sum_{n=0}^{2S} A_n(\mathbf{S}_i\cdot\mathbf{S}_j)^n, \tag{1}$$

where the coefficients $A_n$ typically have the values

$$\begin{aligned}
&A_0=\tfrac{1}{2}, \quad A_1=2, && \text{for } S=\tfrac{1}{2}\\
&A_0=-1, \quad A_1=1, \quad A_2=1, && \text{for } S=1\\
&A_0=-67/32, \quad A_1=-9/8, &&\\
&A_2=11/18, \quad A_3=2/9, && \text{for } S=\tfrac{3}{2}.
\end{aligned} \tag{2}$$

The general formula[2] from which the $A_n$ may be obtained is given in the Appendix.

The operator $\mathbf{P}_{ij}$ may be used to construct an interaction Hamiltonian. For the case $S=\frac{1}{2}$ this Hamiltonian is identical in form to that used in the Heisenberg model of ferromagnetism.[3] The connection between the exchange-interaction operator and spin for this case was first utilized by Baker *et al.*,[4] by Domb and Wood,[5] and by Baker *et al.*,[6] in conjunction with powerful group-theoretic techniques to obtain a large number of terms (10) in the low-field, high-temperature susceptibility series for the nearest-neighbor Heisenberg ferromagnet. More recently, Allan and Betts,[7] using similar group-theoretic techniques, have considered the case $S=1$ for a face-centered cubic (fcc) lattice and obtained the first eight terms in the high-temperature susceptibility series. The Hamiltonian in this situation is a special case of the biquadratic Hamiltonian considered by Joseph.[8] As pointed out in Ref. 7, the physical relevance of such a Hamiltonian constructed from $\mathbf{P}_{ij}$ (for $S>\frac{1}{2}$) is limited. The calculations, however, give added insight into the question of the nature of the behavior of the susceptibility in the vicinity of the critical temperature.

The calculations discussed in Refs. 4–7, while giving large numbers of terms in the susceptibility series, are restricted to special values of the spin and to specific crystal lattices. The present calculation, while restricted to only the first few terms in the series, is for arbitrary spin and crystal lattices. It is hoped that some added insight into the nature of series results will be obtained.

## II. THEORY

We consider a system consisting of a lattice of $N$ sites containing atoms of spin $S$ and gyromagnetic ratio $g$, each atom having $z$ nearest neighbors. The Hamiltonian for the system in the presence of an external magnetic field in the $z$ direction $H$ is taken to be

$$\mathcal{H}=-J\sum_{n=1}^{2S} A_n\mathbf{P}_n-g\mu H\mathbf{Q}, \tag{3}$$

where

$$\mathbf{P}_n=\sum_{\langle i,j\rangle}(\mathbf{S}_i\cdot\mathbf{S}_j)^n \tag{4}$$

and

$$\mathbf{Q}=\sum_k S_{kz}. \tag{5}$$

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[1] P. A. M. Dirac, *The Principles of Quantum Mechanics* (Clarendon Press, Oxford, England, 1958), Sec. 58.

[2] E. Schrödinger, Proc. Roy. Irish Acad. **47**, 39 (1941).

[3] W. Heisenberg, Z. Physik **49**, 619 (1928).

[4] G. A. Baker, G. S. Rusbrooke, and H. E. Gilbert, Phys. Rev. **135**, A1272 (1964).

[5] C. Domb and D. W. Wood, Proc. Phys. Soc. (London) **B86**, 1 (1965).

[6] G. A. Baker, H. E. Gilbert, J. Eve, and G. S. Rusbrooke, Phys. Letters **20**, 146 (1966).

[7] G. A. T. Allan and D. D. Betts (to be published).

[8] R. I. Joseph, Phys. Rev. **138**, A1441 (1965). We take this opportunity to point out an error in this paper. Equation (7) should read: $b_{02}=-Xz(-4X^2+5X-3)/9$.

Here $J$ is the magnitude of a nearest-neighbor exchange interaction and $\mu$ is the Bohr magneton. $-g\mu H\mathbf{Q}$ is the Zeeman-energy operator for the entire lattice, while $\mathbf{P}_n$ is the sum for all first-neighbor pairs of the operator $(\mathbf{S}_i\cdot\mathbf{S}_j)$ raised to the power $n$. The operator $\mathbf{Q}$ commutes with all of the $\mathbf{P}_n$, but the $\mathbf{P}_n$ for various $n(\leq 2S)$ do not commute among themselves. Typical values of the $A_n$ were given in Eq. (2), as obtained from the formulas given in the Appendix.[2] The formal derivation of the susceptibility series is similar to the generalization of the Rusbrooke-Wood[9] result as discussed previously by Wojtowicz and Joseph[10] and by Joseph.[8] The low-field susceptibility is given by the following $2S$-fold series:

$$\chi=(C/T)\Big[1+\sideset{}{'}\sum_{m_1,\cdots,m_{2S}=0} a_{m_1\cdots m_{2S}}\prod_{i=1}^{2S}(\beta JA_i)^{m_i}\Big], \tag{6}$$

where

$$a_{m_1\cdots m_{2S}}=\Big[3/NS(S+1)\Big(\sum_{i=1}^{2S}m_i\Big)!\Big]\sum_{\text{perm}}\Gamma_N\Big\langle\prod_{i=1}^{2S}\mathbf{P}_i^{m_i}\mathbf{Q}^2\Big\rangle, \tag{7}$$

and

$$C=Ng^2\mu^2S(S+1)/3k_B, \tag{8}$$

with

$$\beta=1/k_BT. \tag{9}$$

Here $C$ is the Curie constant, $k_B$ is the Boltzmann constant, and $T$ is the thermodynamic temperature. $\langle\mathbf{O}\rangle$ stands for the normalized trace of the $(2S+1)^N$-dimensional direct-product-matrix representation of the operator $\mathbf{O}$ and the symbol $\Gamma_N f$ means "that part of $f$ which is proportional to $N$". $\sum_{\text{perm}}$ denotes the sum over all permutations in the order of appearance of the operators $\mathbf{P}_1$ through $\mathbf{P}_{2S}$ and arises from their noncommunitivity. The prime on the summations excludes the term $m_1=\cdots=m_{2S}=0$. The first term of Eq. (6) is Curie's law for noninteracting spins, while succeeding terms represent increasing orders of the statistical-mechanical perturbation of the nearest-neighbor exchange on the free-ion paramagnetism. The reciprocal susceptibility may also be written as a $2S$-fold series.

The general diagrammatic technique developed by Rusbrooke and Wood[9] for the usual Heisenberg Hamiltonian (for arbitrary $S$) may be extended in a manner analogous to that discussed in Refs. 8 and 10 to evaluate the present coefficients. The details of the evaluation of the coefficients will not be presented here. In what follows, results obtained from using the Hamiltonian given by Eqs. (3)–(5) will be referred to as results of the *exchange-interaction* model. These are to be contrasted to any results obtained from the usual Hamiltonian

$$\mathcal{H}=-2J\sum_{\langle i,j\rangle}\mathbf{S}_i\cdot\mathbf{S}_j-g\mu H\sum_k S_{kz}, \tag{10}$$

for arbitrary $S$, which will be referred to as the *Heisenberg model.* For $S=\frac{1}{2}$ the two model are, of course, identical.

We have explicitely evaluated the first two correction terms in the susceptibility series for the exchange-interaction model. The susceptibility is thus given by

$$\chi=(C/T)[1+z\{J/k_BT(2S+1)\}$$
$$+z(z-2)\{J/k_BT(2S+1)\}^2+\cdots], \tag{11}$$

or equivalently,

$$\chi^{-1}=(T/C)[1-z\{J/k_BT(2S+1)\}$$
$$+2z\{J/k_BT(2S+1)\}^2+\cdots]. \tag{12}$$

The present results agree exactly with the results given in Refs. 4–9 when the proper values of the spin, lattice, and exchange parameters are substituted.

## III. DISCUSSION

It is interesting to note that as far as the present calculations go, one may define a reduced expansion coefficient

$$\mathcal{J}\equiv J/k_BT(2S+1) \tag{13}$$

such that the coefficients in the $\chi$- or $\chi^{-1}$-versus-$T$ series are explicitly independent of the spin $S$. The results of the exchange-interaction model [Eqs. (11) or (12)] are to be compared to the comparable results for the Heisenberg model[9]:

$$\chi=(C/T)[1+z\{2JS(S+1)/3k_BT\}$$
$$+z[z-\langle 1+3/4S(S+1)\rangle]\{2JS(S+1)/3k_BT\}^2$$
$$+\cdots] \tag{14}$$

or

$$\chi^{-1}=(T/C)[1-z\{2JS(S+1)/3k_BT\}$$
$$+z[1+3/4S(S+1)]\{2JS(S+1)/3k_BT\}^2+\cdots]. \tag{15}$$

No such reduced expansion coefficient as given by Eq. (13) may be defined in this case.

The result of a "molecular-field" treatment is equivalent to retaining only the first correction term in the susceptibility series. In this approximation we then find that

$$\chi^{-1}=(T-T_C)/C, \tag{16}$$

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[9] G. S. Rusbrooke and P. J. Wood, Mol. Phys. 1, 257 (1958).

[10] P. J. Wojtowicz and R. I. Joseph, Phys. Rev. 135, A1314 (1964).

where

$$T_C = zJ/k_B(2S+1), \tag{17}$$

for the exchange-interaction model, which is to be contrasted to the usual Heisenberg-model result

$$T_C = 2zJS(S+1)/3k_B. \tag{18}$$

If one uses the "enlarged" susceptibility series (enlarged to include the term $T^{-3}$), the critical temperature obtained from setting $\chi^{-1}=0$ is given by

$$T_C = [4J/k_B(2S+1)]/[1-(1-8/z)^{1/2}] \tag{19}$$

for the exchange-interaction model and

$$T_C = \frac{J[1+\frac{4}{3}S(S+1)]/k_B}{1-(1-[4+3/S(S+1)]/z)^{1/2}} \tag{20}$$

for the Heisenberg model. The result for the exchange-interaction model [Eq. (19)] is identical in its dependence upon $z$, for arbitrary $S$, to the result originally obtained by Heisenberg for the case $S=\frac{1}{2}$ based upon his Gaussian approximation to the energy levels of the system.[3] That is, the exchange-interaction model differs only by a spin-scaling factor from the original Heisenberg Gaussian result for $S=\frac{1}{2}$ and hence, for arbitrary $S$, suffers from the same flaw that result did, namely, failure to predict a real Curie temperature for $z<8$. For $S\neq\frac{1}{2}$ the Heisenberg-model result [Eq. (20)] does not have this flaw, i.e., it does predict a real Curie temperature for all three-dimensional lattices. Comparison of Eqs. (17) and (18) [since,

$$1 \leq \tfrac{2}{3}S(S+1)(2S+1)]$$

and/or Eqs. (19) and (20) [since,

$$3-2S \leq \tfrac{4}{3}S(S+1)(2S+1)$$

and $1 \leq \frac{4}{3}S(S+1)$] shows that

$$T_C(\text{exchange}) \leq T_C(\text{Heisenberg}), \tag{21}$$

that is, the exchange model is expected to disorder at a lower temperature than the Heisenberg model. This could have been anticipated from the higher degeneracy of the ground state of a pair of spins interacting with the exchange Hamiltonian compared to the Heisenberg Hamiltonian. This result is in agreement with the conclusion of Ref. 7 based upon many more terms in the series (for $S=1$ and a fcc lattice). In the "classical" limit, that is for $S\rightarrow\infty$, the exchange model predicts that

$$T_C \sim 1/S \rightarrow 0, \tag{22}$$

which is to be contrasted to the Heisenberg model which predicts that

$$T_C \sim S^2 \rightarrow \infty. \tag{23}$$

TABLE I. Comparison of calculated values of $k_BT_C/J$ based on the exchange and Heisenberg models, for a fcc lattice. The numbers in parentheses are the percentage difference between that value of $k_BT_C/J$ and the relevant "exact" value.

| | $k_BT_C/J$ | | |
|---|---|---|---|
| | $S=\frac{1}{2}$ Exchange or Heisenberg | $S=1$ Heisenberg | Exchange |
| Molecular-field theory ($n=1$) | 6.00 | 16.0 | 4.00 |
| | (47%) | (33%) | (30%) |
| Gaussian approximation | 4.73 | 13.9 | 3.15 |
| ($n=2$) | (16%) | (16%) | (2.6%) |
| "Exact" | 4.07 | 12.0 | 3.07 |

These results can be anticipated from the general form of the respective Hamiltonians.

It is interesting now to compare the numerical values predicted for $T_C$ based upon the first few terms of the series with the extrapolation results obtained from the much lengthier series. This is done in Table I for the fcc lattice ($z=12$) and for $S=\frac{1}{2}$ and 1. For the exchange model, the values of $k_BT_C/J$ seem to approach the "exact" result more rapidly than for the Heisenberg model, and, within the context of the exchange model, this approach seems to be more rapid as $S$ increases. Indeed, if for the exchange model one plots $k_BT_C/J$ versus $S$ for $n=1$ and for $n=2$ and compares it to the exact result (for $S=\frac{1}{2}$ and 1), a smoothed curve through the exact points and the curve for $n=2$ appear to be indistinguishable for $S \gtrsim \frac{3}{2}$.

Let us assume that $T_C$ is rigorously given by Eq. (19). We can then solve this equation for $z$ in terms of $T_C$, i.e.,

$$z^{-1} = \mathcal{J}_C(1-2\mathcal{J}_C), \tag{24}$$

where $\mathcal{J}_C$ is defined by Eq. (13) but with $T$ replaced by $T_C$. Substituting this into Eq. (12), we then find that

$$\chi^{-1} \cong (T/C)[1-(1-2\mathcal{J}_C)^{-1}(\mathcal{J}/\mathcal{J}_C)+\cdots]. \tag{25}$$

Denote the coefficient of $\mathcal{J}/\mathcal{J}_C$ in Eq. (25) by $\tilde{\gamma}$,

$$\chi^{-1} \cong (T/C)[1-\tilde{\gamma}(\mathcal{J}/\mathcal{J}_C)+\cdots] = (T/C)[1-\tilde{\gamma}(T_C/T)+\cdots]. \tag{26}$$

In general,

$$\tilde{\gamma} = T_M/T_C, \tag{27}$$

where $T_M$ is the Curie temperature predicted by a molecular-field treatment and $T_C$ is the "exact" Curie

Table II. Comparison of numerical values of $\gamma$ [Eq. (29)] and $\tilde{\gamma}$ [Eq. (27)] for both the exchange and Heisenberg models for the fcc lattice for various values of spin.

| | Exchange | | | Heisenberg | | |
|---|---|---|---|---|---|---|
| $S$ | $\tilde{\gamma}$ | $\gamma$ | $\tilde{\gamma}-\gamma$ | $\tilde{\gamma}$ | $\gamma$ | $\tilde{\gamma}-\gamma$ |
| $\frac{1}{2}$ | 1.47 | 1.43 | +0.04 | 1.47 | 1.43 | +0.04 |
| 1 | 1.30<br>(1.27[a]) | 1.27 | +0.03 | 1.33 | 1.38 | −0.05 |
| $\frac{3}{2}$ | | | | 1.30 | 1.36 | −0.06 |
| ... | | | | | | |
| $\infty$ | 1.27[a](?) | | | 1.27 | 1.33 | −0.06 |

[a] Based on Gaussian approximation for $T_C$; $1.27 \cong 3-\sqrt{3}$.

temperature. For the present situation we have

$$\tilde{\gamma}=(1-2\mathcal{J}_C)^{-1}=\tfrac{1}{4}z[1-(1-8/z)^{1/2}], \qquad (28)$$

which is independent of $S$, but not of the lattice. Substituting $z=12$ for the fcc lattice into Eq. (28), we have $\tilde{\gamma}=3-\sqrt{3}\cong 1.27$, which is *identical* to the value of $\gamma$, defined by

$$\chi^{-1}\sim(1-T_C/T)^{\gamma} \quad \text{for} \quad T\to T_C^{+}, \qquad (29)$$

obtained by Allen and Betts[7] for the exchange model ($S=1$, fcc lattice). Whether this numerical agreement is pure coincidence or has real significance, we cannot say.

In Table II we compare the computed and known values of $\gamma$ and $\tilde{\gamma}$[9,11] for the fcc lattice and various spin values for both the exchange and Heisenberg models. We see that when the "exact" value of $T_C$ for $S=1$ for the former model is used, the equality between $\gamma$ and $\tilde{\gamma}$ disappears. A reasonable estimate for the infinite spin value of $\tilde{\gamma}$ for this model is 1.27 (if the Gaussian approximation gets to be asymptotically better as $S\to\infty$). It is then interesting to note that this would agree quite closely with the corresponding quantity for the Heisenberg model which was obtained by using either the Rushbrooke-Wood[9] mnemonic formula for $T_C$ (in this case, $1.27\cong 768/605$) or from the more recent results of Stanley[11] ($\cong 1/0.792$). Results comparable to those shown in Table II can also be given for the Ising model.[12]

Finally, if we write the susceptibility in the form

$$\chi=\frac{C}{T}\Big[1+\sum_{n=1}^{\infty}a_n(J/k_BT)^n\Big], \qquad (30)$$

it can be shown[11,13] that if $\chi$ is to diverage with a power law as $T\to T_C^{+}$, then for *large n*,

$$a_n/a_1a_{n-1}\cong\tilde{\gamma}^{-1}[1+(\gamma-1)/n]. \qquad (31)$$

If we *naively* set $n=1$ into Eq. (31) [$a_0\equiv 1$], we find that $\tilde{\gamma}=\gamma$, which is certainly not *too far* from the truth.

## ACKNOWLEDGMENTS

I wish to thank Dr. Peter J. Wojtowicz for his many helpful comments and Dr. G. A. T. Allan and Dr. D. D. Betts for a copy of their paper prior to publication.

## APPENDIX: THE COEFFICIENTS $A_n$

From Schrödinger[2] we have

$$\begin{aligned}\mathbf{P}_{ij}=&[(2S)!]^{-2}[M-(2S-1)2S]\\ &\times[M-(2S-2)(2S-1)]\cdots[M-2]M\\ &-[(2S-1)!]^{-2}[M-(2S-2)(2S-1)]\cdots[M-2]M\\ &+[(2S-2)!]^{-2}[M-(2S-3)(2S-2)]\cdots[M-2]M\\ &+\cdots+(-1)^{2S-1}M+(-1)^{2S}, \qquad (A1)\end{aligned}$$

where

$$M=(\mathbf{S}_i+\mathbf{S}_j)^2\doteq 2[S(S+1)+\mathbf{S}_i\cdot\mathbf{S}_j]. \qquad (A2)$$

For any particular value of $S$, the coefficients $A_n$ may be directly obtained by substituting Eq. (A2) into Eq. (A1), expanding, and comparing the coefficients of the various powers of $(\mathbf{S}_i\cdot\mathbf{S}_j)$ with Eq. (1).

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[11] H. E. Stanley and T. A. Kaplan, J. Appl. Phys. **38**, 977 (1967); H. E. Stanley, Phys. Rev. **158**, 546 (1967).

[12] M. E. Fisher, J. Math. Phys. **4**, 278 (1963). Note that $\tilde{\gamma}\equiv\theta_c^{-1}$ in the notation of this paper.

[13] C. Domb and M. F. Sykes, J. Math. Phys. **2**, 63 (1961).

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# Erratum

**Spin-$\frac{3}{2}$ Iron Ferromagnet: Its Mossbauer and Magnetic Properties,** H. H. Wickham, A. M. Trozzolo, H. J. Williams, G. W. Hull, and F. R. Merritt [Phys. Rev. **155**, 563 (1967)]. A line of type was inadvertently omitted in the final copy. The missing fourth line of the second paragraph is: "Fe(diEt-DTC)$_2$Cl. The crystal structure determina-."