# An Approximate Quantum Theory of the Antiferromagnetic Ground State

P. W. ANDERSON

*Bell Telephone Laboratories, Murray Hill, New Jersey*

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A careful treatment of the zero-point energy of the spin-waves in the Kramers-Heller semiclassical theory of ferromagnetics leads to surprisingly exact results for the properties of the ground state, as shown by Klein and Smith. An analogous treatment of the antiferromagnetic ground state, whose properties were unknown, is here carried out and justified. The results are expected to be valid to order $1/S$ or better, where $S$ is the spin quantum number of the separate atoms.

The energy of the ground state is computed and found to lie within limits found elsewhere on rigorous grounds. For the linear chain, there is no long-range order in the ground state; for the simple cubic and plane square lattices, a finite long-range order in the ground state is found. The fact that this order can be observed experimentally, somewhat puzzling since one knows the ground state to be a singlet, is explained.

## I. INTRODUCTION

KRAMERS and Heller[1] were the first to give a semiclassical derivation of Bloch's spin-wave theory of ferromagnetism.[2] They started with a classical ferromagnetic lattice, with classical spins and the $-J\mathbf{S}_i \cdot \mathbf{S}_j$ Hamiltonian for exchange, found coordinates which represented classically the small vibrations of the system, and quantized these coordinates. In this way they obtained a theory which in principle should be good only to first order in $1/S$ (if the classical results are considered zero'th order) but which actually, perhaps by coincidence, is nearly exact. However, they ignored the zero-point energy of their quantized vibrations without considering its significance very deeply. Klein and Smith[3] have recently pointed out the significance of the zero-point energy, and have shown that only if it is included does one get the correct energy for the ferromagnetic ground state from the Kramers-Heller treatment. That is, the true value of the classical angular momentum $S_c$ which should be used for atoms with spin quantum number $S$ is

$$S_c = (S(S+1))^{\frac{1}{2}}.$$

Therefore, since classically one can expect to be able to set all spins exactly parallel, the energy available from any $-J\mathbf{S}_i \cdot \mathbf{S}_j$ interaction is $-JS_c^2 = -JS(S+1)$. The total zero-point energy of the spin waves turns out to be exactly such as to increase this to $-JS^2$, the correct value.

Hulthén[4] worked out the equivalent quantization problem for small vibrations of simple antiferromagnetic lattices from their classical equilibrium state. Here one has the opposite sign, $+J\mathbf{S}_i \cdot \mathbf{S}_j$, for the nearest neighbor interaction, and the classical expectation is that successive spins will align themselves antiparallel. However, Hulthén ignored the zero-point energy.

Bethe had worked out the exact ground state for the antiferromagnetic linear chain of atoms with spin

one-half.[5,6] The result was so different from what Hulthén had assumed to be true in his spin-wave theory that he considered his former result to be of questionable meaning. Aside from this simplest case, no rigorous treatment of the antiferromagnetic ground state has appeared. For this reason the very basis for the recent theoretical work which has treated antiferromagnetism similarly to ferromagnetism remains in question.[7,8] In particular, since the Bethe-Hulthén ground state is not ordered,[9] it has not been certain whether an ordered state was possible on the basis of simple $\mathbf{S}_i \cdot \mathbf{S}_j$ interactions. The best proof that it is it seems so far to be the experimental results of Shull et al.[10] using neutron diffraction, in which they show that certain substances do have ordered antiparallel spin arrangements. In connection with these experimental results, a theory of the ground state seems also of interest for comparison with observed values of the magnetization of the various sublattices.

In this paper we apply the results of the spin-wave theory[4] to the approximate determination of the ground state energy and wave function in a fashion similar to the work of Klein and Smith,[3] by including the zero-point energy and motion. This can be done for reasonably general lattices (we do explicitly the linear, plane square, and simple cubic lattices) and for arbitrary spin quantum number $S$. The results obtained should be valid to order $1/S$ (or perhaps even $1/ZS$, where $Z$ is the number of nearest neighbors) since the approximations of the so-called "semiclassical" spin-wave theory are valid quantum-mechanical approximations to this order.

We are able to get a result for the ground-state energy in all cases. This energy lies between the rigorous limits which have been derived on the variational

[1] G. Heller and H. A. Kramers, Proc. Roy. Acad. Sci. Amsterdam 37, 378 (1934).
[2] F. Bloch, Z. Physik 61, 206 (1930).
[3] M. J. Klein and R. S. Smith, Phys. Rev. 80, 1111 (1951).
[4] L. Hulthén, Proc. Roy. Acad. Sci. Amsterdam 39, 190 (1936).

[5] L. Hulthén, Arkiv. Mat., Astron. Fysik 26A, No. 1 (1938).
[6] H. A. Bethe, Z. Physik 21, 205 (1931).
[7] J. H. van Vleck, J. Chem. Phys. 9, 85 (1941).
[8] P. W. Anderson, Phys. Rev. 79, 350, 705 (1950); C. Kittel, Phys. Rev. 82, 565 (1951).
[9] This fact has been checked by Kramers and Kasteleijn (Kramers, private communication).
[10] C. G. Shull and J. S. Smart, Phys. Rev. 76, 1256 (1949); also Shull, Wollan, and Strauser, Phys. Rev. 83, 333 (1951).

principle,[11] $-\frac{1}{2}NJZ(S^2)$ and $-\frac{1}{2}NJZ(S^2)(1+1/ZS)$. In fact, it is roughly equal to but slightly lower than $-\frac{1}{2}NJZS^2(1+1/2ZS)$. For the linear chain with $S=\frac{1}{2}$, there is good agreement with the rigorous result of Bethe in spite of the fact that this is the worst possible case for the approximation method, which in fact should break down here, as we shall see.

More interesting results are obtained for the long-range order. The quantity related to long-range order which the theory furnishes directly is $(\bar{S}_z)^1$, the average z-component of the spin in one of the two sublattices into which all the lattices we treat can be subdivided. z is the direction in which we assume the spins of our original unperturbed (i.e., classical) system were pointing. In turns out that the average spin on a given atom is reduced by a small correction factor of order of magnitude $1/2Z$ in the case of 2- and 3-dimensional lattices. This result may be susceptible of experimental verification by accurate neutron diffraction measurements.

In the case of the one-dimensional lattice $(\bar{S}_z)^1$ vanishes: The separate sublattices are on the average in singlet states. A little consideration of the situation for this lattice, in which it requires at most an energy of the order $J$ to break up the long-range order, while $N$ perturbation terms of order $J$ are available to destroy the ordered state, convinces one that this is a reasonable result, and in fact it can be shown to agree with the result for the rigorous ground state derived by Hulthén and Bethe.[5,6,9] Physically, the situation is this: It is known that in the one- and two-dimensional lattices in ferromagnetism only an infinitesimal amount of thermal energy in the spin-waves is necessary to break up long-range order. In ferromagnetism, however, the zero-point energy of the spin waves is not adequate to break up long-range order because the quantized amplitudes of the long-wavelength spin-waves, which are those important in the thermal destruction of order, are small. In the antiferromagnetic case it seems reasonable to expect that the total amount of energy necessary to break up long-range order is again infinitesimal in these two cases; this is certainly true in the classical limit of large $S$. However, here the zero-point energy can do the job, because the large amplitudes of the longest wavelength spin-waves permit a larger proportion of the zero-point energy to go into them as compared to the unimportant short-wavelength waves. This is only true for the one-dimensional case; the two-dimensional case is probably similar to the one- and two-dimensional ferromagnets, having long-range order in the ground state but losing it immediately under thermal excitation.

Another result which has bearing on experiments, while helping to give internal consistency to the theory, can be derived by looking at the properties of the spin-waves of longest wavelength, which actually represent

motion of the transverse components of the total spin of the entire sublattice. The sublattice spin, in the ground state at least, certainly does not maintain a constant, definite direction, since the ground state is a singlet. Therefore, the amplitudes of motion of these transverse components of the total spin show an apparent divergence, indicating that the coupled total spins of the sublattices are indeed compelled to rotate around at will in space. One might think that since the approximate quantization of the spin-waves requires that we assume a constant, large spin for the sublattice, the fact that our theory then tells us that this is not true represents an inconsistency in our reasoning. This objection can be shown to be invalid in several ways, particularly by assuming that a small anisotropy energy is present which holds the spins constant in the z-direction. It then appears that the required anisotropy is actually infinitesimal, so that one can easily go to the limit of zero anisotropy, using the anisotropy merely as a convergence factor. Another way to answer this objection is to assume that our theory really starts out from "wave packets" of states, chosen in such a way that the z-component of the total spin is roughly constant. Inquiry into the properties of the longest wavelength spin-waves shows that the energy required to form such a packet is infinitesimal of order $1/N$, where $N$ is the number of atoms in the lattice. This energy is very small. An equivalent result, of experimental interest, is that the time required for the total spin to drift around from one orientation to another essentially different one, in case we prepared the system originally in a state of definite spin orientation, is of order $N$, and thus extremely large. It is clear that the fact that the neutron diffraction experiments do indicate definite sublattice arrangements, in spite of having been averaged over some finite time, is perfectly reasonable.

This argument, justifying the assumption of a large, constant z-component of spin on the sublattice, is admittedly somewhat circular: We have used the spin-waves, derived on the basis of this assumption, to verify it. However, it is difficult to find any reason why the equation of motion of $(S_z)_{total}$ should change very much if the correction terms of the theory were included. In any case, the argument shows internal consistency. Every other result furnished by the theory is at least not in disagreement with expectations arrived at by other reasoning. For instance, the fact that the sublattice spins are indeterminate in direction agrees with our knowledge of singlet states; the energy values lie between close limits set by a rigorous argument[11]; order does not exist in one dimension, agreeing with the rigorous result,[5,6,9] while it does exist in three dimensions, agreeing with experiment.[10] Further calculations which will be reported later on models for a ferrimagnet, and for an antiferromagnet with next nearest neighbor interaction, again give results whose

[11] P. W. Anderson, Phys. Rev. 83, 1260 (1951).

consistency with one's expectations furnishes further strong confirmation of the theory. Thus, while we cannot claim to have proved rigorously that this picture of the ground state is the correct one, it can be said that the probability is high that it is.

## II. SPIN WAVES IN AN ANTIFERROMAGNET

Hulthen[4] has carried through the quantization of the spin waves in an antiferromagnet, but we shall repeat the derivation here, both for ready reference and because his way of doing it is not easily adapted to our purpose.

The Hamiltonian for an antiferromagnet is taken to be, assuming that the Heisenberg exchange coupling is responsible for the phenomena,

$$H = J \sum_{\langle j, k \rangle} \mathbf{S}_j \cdot \mathbf{S}_k, \tag{1}$$

with $J$ positive. The notation $\sum_{\langle j, k \rangle}$ will be used repeatedly to mean a sum over all pairs $j$ and $k$ of neighboring atoms. $j$ and $k$, of course, represent each a set of $D$ numbers, where $D$ is the dimensionality; they may be thought of as $D$-dimensional vectors. We are assuming nearest neighbor interaction, and also we shall work only with lattices which can be divided into two sublattices with the neighbors of one all on the other and vice versa; the linear, plane square, and simple cubic lattices only will be used as examples. None of these restrictions is essential to carrying out a theory of this general type.

The basic assumption we make in deriving the semiclassical spin waves is that the state of the antiferromagnet is not greatly different from the classical ground state in which the spins of one sublattice all point in one direction (say $+z$), the spins of the other all in the other direction. This is an assumption which must be justified, and which cannot, unfortunately, be justified by external reasoning, as is possible in the ferromagnetic case. We must use for this justification results of the theory itself (as well as its internal consistency and its agreement with other ideas).

Mathematically, we assume

$$S_{zj} \simeq +S, \quad S_{zk} \simeq -S. \tag{2}$$

Here and later, atoms labeled $j$ are always on sublattice (1), while those labeled $k$ are on sublattice (2). For the linear chain, for example, this would mean that $j$ is odd and $k$ is even. Where there is some possibility of confusion, we shall also use a superscript (1) or (2) to denote the sublattice. Now

$$S_z^2 = S_c^2 - (S_x^2 + S_y^2), \tag{3}$$

where $S_c$ is the "classical" total spin of an atom with spin quantum number $S$,

$$S_c = [S(S+1)]^{\frac{1}{2}}. \tag{4}$$

If our fundamental assumption, Eq. (2), is correct, we can use the following binomial theorem expansion for the $z$ components,

$$
\begin{aligned}
S_{zj} &\cong S_c - (S_{xj}^2 + S_{yj}^2)/2S_c, \\
S_{zk} &\cong -S_c + (S_{xk}^2 + S_{yk}^2)/2S_c.
\end{aligned} \tag{5}
$$

Then the Hamiltonian is, by substitution,

$$H = -\tfrac{1}{2}ZNJS_c^2 + \tfrac{1}{2}ZJ\{\sum_j(S_{xj}^2 + S_{yj}^2) + \sum_k(S_{xk}^2 + S_{yk}^2)\}$$
$$+ J\sum_{\langle j, k \rangle} S_{xj}S_{xk} + S_{yj}S_{yk}. \tag{6}$$

This is valid to first order in the small quantities $S_x^2$ and $S_y^2$. We introduce two sets of spin waves, one pair for each sublattice:

$$
\begin{aligned}
S_{xj} &= (2S/N)^{\frac{1}{2}}\sum_\lambda \exp(i\boldsymbol{\lambda} \cdot \mathbf{j})Q_\lambda \\
S_{yj} &= (2S/N)^{\frac{1}{2}}\sum_\lambda \exp(-i\boldsymbol{\lambda} \cdot \mathbf{j})P_\lambda \\
S_{xk} &= (2S/N)^{\frac{1}{2}}\sum_\lambda \exp(-i\boldsymbol{\lambda} \cdot \mathbf{k})R_\lambda \\
S_{yk} &= -(2S/N)^{\frac{1}{2}}\sum_\lambda \exp(i\boldsymbol{\lambda} \cdot \mathbf{k})S_\lambda.
\end{aligned} \tag{7}
$$

Here the wave number $\lambda$ runs only over $N/2$ values from $-\pi$ to $\pi$, giving $2N$ coordinates in all[12]; for example, for the linear chain of length $N$,

$$\lambda = 2\pi n/N, \quad n = -\tfrac{1}{2}N+2, \cdots -2, 0, 2 \cdots \tfrac{1}{2}N. \tag{8}$$

Thus, we have the correct number of degrees of freedom. To show the commutation relations, let us write down the inverse of (7):

$$
\begin{aligned}
Q_\lambda &= (2/NS)^{\frac{1}{2}}\sum_j \exp(-i\boldsymbol{\lambda} \cdot \mathbf{j})S_{jx} \\
P_\lambda &= (2/NS)^{\frac{1}{2}}\sum_j \exp(i\boldsymbol{\lambda} \cdot \mathbf{j})S_{jy} \\
R_\lambda &= (2/NS)^{\frac{1}{2}}\sum_k \exp(i\boldsymbol{\lambda} \cdot \mathbf{k})S_{xk} \\
S_\lambda &= -(2/NS)^{\frac{1}{2}}\sum_k \exp(-i\boldsymbol{\lambda} \cdot \mathbf{k})S_{yk}.
\end{aligned} \tag{7'}
$$

That $Q_\lambda$ commutes with $Q_{\lambda'}$, $R_{\lambda'}$, and $S_{\lambda'}$, etc., is obvious. We need to verify only the following commutation rules:

$$[Q_\lambda, P_{\lambda'}] = \frac{2}{NS}\sum_i \sum_{i'} \exp[-i(\boldsymbol{\lambda} \cdot \mathbf{j} - \boldsymbol{\lambda}' \cdot \mathbf{j}')][S_{xj}, S_{yj'}]$$

$$= \frac{2}{NS}\sum_i \exp[i\mathbf{j} \cdot (\boldsymbol{\lambda} - \boldsymbol{\lambda}')]iS_{zj}.$$

Under our assumption (2) as to the sublattice spins, this gives

$$[Q_\lambda, P_{\lambda'}] = \delta_{\lambda\lambda'}i\sum_j S_{zj}/\tfrac{1}{2}NS \simeq i\delta_{\lambda\lambda'} \tag{9}$$

$$[R_\lambda, S_{\lambda'}] = -(2i/NS)\sum_k \exp[i\mathbf{k} \cdot (\boldsymbol{\lambda} - \boldsymbol{\lambda}')]S_{zk}$$
$$\simeq i\delta_{\lambda\lambda'}. \tag{10}$$

We use the well-known equation

$$\sum \exp[i(\boldsymbol{\lambda} - \boldsymbol{\lambda}') \cdot \mathbf{j}] = \tfrac{1}{2}N\delta_{\lambda\lambda'}. \tag{11}$$

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[12] The use of $\lambda$ as a wave number, or inverse wavelength, for the spin waves, is perhaps unfortunate; it is hoped that no confusion will be caused.

Note that the sign change in $S_\lambda$ comes from the requirement that the two commutators (9) and (10) be equal.

Now we must substitute (7) into the Hamiltonian (6). First we replace $S_{xj}^2$ by $|S_{xj}|^2$, etc., which simplifies the presentation somewhat but does not change the results. Then, of course [using (11)],

$$\sum_j S_{xj}^2 = (2S/N)\sum_\lambda \sum_{\lambda'} \sum_j \exp[i(\lambda-\lambda')\cdot\mathbf{j}]Q_\lambda Q_{\lambda'}$$
$$= S\sum_\lambda Q_\lambda^2,$$

and so forth for the squared terms. The cross-terms are

$$\sum_{\langle j,k\rangle} (S_{xj}S_{xk}+S_{yj}S_{yk})$$

$$= \frac{2S}{N}\sum_{\lambda,\lambda'}\sum_{\langle j,k\rangle} \exp[i(\lambda\cdot\mathbf{j}-\lambda'\cdot\mathbf{k})](Q_\lambda R_{\lambda'}-P_\lambda S_{\lambda'})$$

$$= \frac{2S}{N}\sum_{\lambda,\lambda'}\sum_{\langle k-j\rangle} \exp[i\lambda\cdot(\mathbf{k}-\mathbf{j})](Q_\lambda R_{\lambda'}-P_\lambda S_{\lambda'})$$

$$\times\sum_j \exp[i(\lambda-\lambda')\cdot\mathbf{j}]$$

$$= S\sum_\lambda (Q_\lambda R_\lambda-P_\lambda S_\lambda)\sum_{\langle k-j\rangle} \exp[i\lambda\cdot(\mathbf{k}-\mathbf{j})],$$

again using (11). The sum over $\langle k-j\rangle$, of course, is meant to run only over neighbors. We define

$$2D\gamma_\lambda = \sum_{\langle k-j\rangle} \exp[i\lambda\cdot(\mathbf{k}-\mathbf{j})], \qquad (12)$$

where $D$ is the dimensionality of the lattice. For the three lattices we consider, the linear, plane square, and simple cubic, $\gamma_\lambda$ is

$$\gamma_\lambda = \sum_{i=1}^{D} \frac{\cos\lambda_i}{D}. \qquad (13)$$

(The $\lambda_i$ are the $D$ components of the vector $\lambda$.) Then the total Hamiltonian (6) is, in terms of the spin-wave coordinates (again only for our three lattices):

$$H = -NDJS_c^2 + DJS\sum_\lambda[(P_\lambda^2+Q_\lambda^2+R_\lambda^2+S_\lambda^2 + 2\gamma_\lambda(Q_\lambda R_\lambda - P_\lambda S_\lambda)]. \qquad (14)$$

For our three lattices, of course, $Z=2D$. Similar expressions may obviously be found for other simple lattice types.

$H$ is not quite in normal coordinate form, but a canonical transformation may easily be found to make it so. This transformation is

$$P_\lambda = (p_{1\lambda}+p_{2\lambda})/\sqrt{2}, \quad Q_\lambda = (q_{1\lambda}+q_{2\lambda})/\sqrt{2},$$
$$S_\lambda = (p_{1\lambda}-p_{2\lambda})/\sqrt{2}, \quad R_\lambda = (q_{1\lambda}-q_{2\lambda})/\sqrt{2}. \qquad (15)$$

It leaves the commutation relations unchanged. The Hamiltonian then becomes

$$H = -DJNS_c^2 + DJS\sum_\lambda[q_{1\lambda}^2(1+\gamma_\lambda)+p_{1\lambda}^2(1-\gamma_\lambda) + q_{2\lambda}^2(1-\gamma_\lambda)+p_{2\lambda}^2(1+\gamma_\lambda)]. \qquad (16)$$

The eigenvalues of the harmonic oscillator terms in (16) are easily found. The eigenvalues of

$$H = (p^2/m)+m\omega^2 q^2, \qquad (17)$$

if

$$[q,p]=i,$$

are

$$H = (2n+1)\omega, \qquad (17')$$

so that

$$H = -DJNS_c^2 + DJS\sum_\lambda[(2n_{1\lambda}+1)(1-\gamma_\lambda^2)^{\frac{1}{2}} + (2n_{2\lambda}+1)(1-\gamma_\lambda^2)^{\frac{1}{2}}]. \qquad (18)$$

For the ground state all $n_\lambda=0$, so that

$$E_g = -DJNS_c^2 + 2DJS\sum_\lambda(1-\gamma_\lambda^2)^{\frac{1}{2}}. \qquad (19)$$

The frequencies of the spin waves fall into two identical branches, as we see by (18); using (17), these frequencies are

$$\omega = DJS(1-\gamma_\lambda^2)^{\frac{1}{2}}. \qquad (20)$$

Notice that $\gamma_\lambda\sim1-\frac{1}{2}\lambda^2$, $\lambda\rightarrow0$, so that

$$\omega_\lambda\sim DSJ\lambda, \quad \lambda\rightarrow0. \qquad (21)$$

This dispersion law is quite different from the ferromagnetic case, where $\omega\sim\lambda^2$. The resulting decrease in magnetization of a sublattice, and specific heat, will vary as $T^3$ at low temperatures if this dispersion law is correct. Thus, they will differ from the ferromagnetic case in which these quantities vary as $T^{\frac{3}{2}}$. It is questionable whether this could be observed.

The difference in dispersion laws is not the most important difference between the two types of spin waves; it is the difference in amplitude per quantum of excitation which leads to the more striking effects. Since the potential and kinetic energies of a harmonic oscillator are on the average the same,

$$\langle q_{1\lambda}^2\rangle_{Av}(1+\gamma_\lambda) = \langle p_{1\lambda}^2\rangle_{Av}(1-\gamma_\lambda) = \frac{1}{2}(1-\gamma_\lambda^2)^{\frac{1}{2}},$$

or

$$\langle q_{1\lambda}^2\rangle_{Av} = \frac{1}{2}[(1-\gamma_\lambda)/(1+\gamma_\lambda)]^{\frac{1}{2}},$$
$$\langle p_{1\lambda}^2\rangle_{Av} = \frac{1}{2}[(1+\gamma_\lambda)/(1-\gamma_\lambda)]^{\frac{1}{2}}, \qquad (22)$$

in the ground state. These quantities are also proportional to the extra amplitude per quantum of excitation. Note that, for small $\lambda$,

$$\langle p_{1\lambda}^2\rangle_{Av}\rightarrow 1/(\sqrt{2}\lambda); \qquad (23)$$

the mean amplitude of $p_{1\lambda}^2$ per quantum diverges as $1/\lambda$ (i.e., as the wavelength) for very long wavelengths. This could be predicted from the dispersion law (21), because one expects from analogy with ferromagnetism that it requires only an energy proportional to $\lambda^2$ to create a periodic disturbance in the spins of a certain amplitude and of wavelength $1/\lambda$; since here we require an energy proportional to $\lambda$ per quantum, the amplitude of disturbance per quantum must be as $1/\lambda$.

### III. THE ZERO-POINT ENERGY

We will compute first the energy of the ground state as it is given by (19), assuming for the moment that the basic premise (2) is right. In (19) the sum over $\lambda$ may be replaced by an integral, since the values (8) of $\lambda$ are quite dense. Since there are $\frac{1}{2}N$ values of $\lambda$,

$$\sum_\lambda [(1-\gamma_\lambda^2)]^{\frac{1}{2}} = N/2\langle(1-\gamma_\lambda^2)^{\frac{1}{2}}\rangle_{\text{Av}}$$

$$= (2\pi)^{-D}\frac{N}{2}\int_{-\pi}^{\pi}\int\int d\lambda_1\cdots d\lambda_D$$

$$\times \left[1-\left(D^{-1}\sum_{i=1}^{D}\cos\lambda_i\right)^2\right]^{\frac{1}{2}}, \quad (24)$$

$$\sum_\lambda [(1-\gamma_\lambda^2)]^{\frac{1}{2}} = (\tfrac{1}{2}N)I_D.$$

This equation defines $I_D$. A rough value of $I_D$ may be obtained by expanding the square root in (36) by the binomial theorem and keeping only the first term,

$$I_D \simeq 1 - \left\langle\left(\sum_{i=1}^{D}\cos\lambda_i\right)^2\right\rangle_{\text{Av}}\bigg/ 2D^2 = 1-\langle\cos^2\lambda\rangle_{\text{Av}}/2D,$$

$$I_D \simeq 1-1/4D;$$

since $D=Z/2$, this is equivalent to

$$I_D \simeq 1-1/2Z. \quad (25)$$

This value leads to a rough ground-state energy-value, from (19):

$$E_g \simeq -NDJ[S_c^2-S(1-1/2Z)]$$
$$E_g \simeq -\tfrac{1}{2}NZJS^2(1+1/2ZS). \quad (26)$$

In this approximation, the correction factor for the energy is $1+1/2ZS$, which certainly lies between the rigorous limits 1 and $1+1/ZS$.[11] For most known antiferromagnets this correction is fairly small, as discussed in reference 11.

The approximation (25) for $I_D$ is not very good because of the slow convergence of the series of which (25) is the first two terms. More accurate values of $I_D$ have been computed for $D=1$, 2 and 3.[13] For $D=1$, $I_D$ is,

$$I_1 = \frac{1}{2\pi}\int_{-\pi}^{\pi}|\sin\lambda|\,d\lambda = \frac{2}{\pi}. \quad (27)$$

Thus, the energy for the linear chain is

$$E_g\big|_{D=1} = -NJ[S(S+1)-(2/\pi)S]$$
$$= -NJS^2(1+0.363/S). \quad (28)$$

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[13] I am indebted to Dr. R. W. Hamming for helpful suggestions in connection with the evaluation of these integrals. Dr. J. M. Luttinger has kindly pointed out that one of them, $J_2$, has been shown to be an elliptic integral by G. N. Watson [Quart. J. Math. 10, 266 (1939)]. His more exact value agrees well with our numerical integration.

This is to be compared with the rigorous ground-state energy in the case $S=\frac{1}{2}$ for the linear chain, computed by Bethe,[6]

$$\begin{aligned}(E_g)_{\text{Bethe}} &= -1.77NJS^2,\\(E_g)_{\text{Eq. (28)}} &= -1.73NJS^2.\end{aligned} \quad (29)$$

This agreement is good, which is unexpected, both because $S=\frac{1}{2}$ is a bad case for our assumption that $S$ is large,[14] and because, as we shall see, in this case the basic premise that the sublattice spin is large and nearly equal to $S$, on the average, is incorrect. One can only suppose that the basic premise is fulfilled temporarily over large enough regions of the lattice that the energy parameter is not badly approximated. An interesting comment which might be appended here is that for the antiferromagnet, as for the ferromagnet, the theory gives entirely correct results for the case $N=2$: Two atoms coupled by one exchange interaction. For the antiferromagnetic case, (8) gives $\lambda=\pi$ only, and thus $\gamma_\lambda=-1$, and the zero-point energy vanishes entirely. This is correct: for two spins, the singlet state has energy $-JS(S+1)$. The zero-point motion, however, does not vanish in this case, and as discussed in Sec. V shows us that no directional preferences exist. For the ferromagnetic case one also obtains the correct ground-state energy, $-JS^2$.

The integrals $I_2$ and $I_3$ were evaluated numerically, essentially by computing or approximating higher terms in the binomial series for the square root.[13] The results were

$$I_2 = 1-0.158, \quad I_3 = 1-0.097, \quad (30)$$

so that the energies are

$$(E_g)_{D=2} = -2NJS^2(1+0.158/S), \quad (31)$$
$$(E_g)_{D=3} = -3NJS^2(1+0.097/S). \quad (32)$$

The energies (28), (31), and (32) are all somewhat lower than the rough approximation (26) but lie between the rigorous limits derived on the variational principle.[11]

### IV. THE TOTAL SPIN OF THE SUBLATTICE

A parameter which represents the state of long-range order of the lattice is the total spin of one of the two sublattices. It can easily be shown that the square of this total spin divided by the square of the number of atoms in the sublattice is, except for quantities infinitesimal to order $1/N$, the more usual order parameter

$$\lim_{j-j'\to\infty} \mathbf{S}_j\cdot\mathbf{S}_{j'}.$$

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[14] The direct use of the expansion (5) is rather dubious in case $S=\frac{1}{2}$. One can justify at least the long-wavelength spin-wave approximation on another basis, however: For the long wavelengths one can think that there are relatively large regions of parallel spin, leading to large $S$'s in total so that something like (5) holds. In other words, one sums $S_{zj}S_{zk}$ over fairly large regions first, and then expands into an expression like (5). Since the contribution to the energy is most critical for the long wavelengths, this procedure might well lead to good energy eigenvalues. In other words, for long wavelengths we think more nearly in terms of the phenomenological type of spin-wave theory of C. Herring and C. Kittel [Phys. Rev. 81, 869 (1951)].

The total spin, however, is the more direct physical parameter, since it is what is measured in a neutron diffraction experiment: What is measured is the average spin per atom parallel to the total sublattice spin, which comes directly from the total spin.

The total $z$-component of the spin of a sublattice, which we shall call $(S_z)_{tot}^{(1)}$ (or (2), for the second sublattice) is easily computed, simply by adding up the expressions (5) for the whole sublattice. We shall see later that the $x$ and $y$ components may be neglected; for the time being we shall assume this to be true.

Let us, then, start from (5) and compute

$$(S_z)_{tot}^{(1)} = \sum_j S_{zj} = (\tfrac{1}{2}N)S_c - \sum_j (S_{xj}^2 + S_{yj}^2)/2S_c. \quad (33)$$

By (7),

$$\sum_j S_{xj}^2 + S_{yj}^2 = S\sum_\lambda (Q_\lambda^2 + P_\lambda^2),$$

and by (15)

$$\sum_\lambda (Q_\lambda^2 + P_\lambda^2) = \sum_\lambda \tfrac{1}{2}(q_{1\lambda}^2 + p_{1\lambda}^2 + q_{2\lambda}^2 + p_{2\lambda}^2 + q_{1\lambda}q_{2\lambda} + p_{1\lambda}p_{2\lambda}),$$

so that

$$(S_z)_{tot}^{(1)} = (\tfrac{1}{2}N)S_c - (S/2S_c)\sum_\lambda \tfrac{1}{2}(q_{1\lambda}^2 + p_{1\lambda}^2 + q_{2\lambda}^2 + p_{2\lambda}^2 + q_{1\lambda}q_{2\lambda} + p_{1\lambda}p_{2\lambda}).$$

In the ferromagnetic case, $(S_z)_{tot}$ is a constant of the motion. This is not true for the sublattices here, as could in fact be shown from the original Hamiltonian (1). The sum of $(S_z)^{(1)}$ and $(S_z)^{(2)}$ is, however, a constant of the motion, since this is the $z$-component of total spin. Because of this lack of constancy we must content ourselves with average values,

$$\langle (S_z)_{tot}^{(1)} \rangle_{Av} = \tfrac{1}{2}NS_c - (S/4S_c)\sum_\lambda \langle q_{1\lambda}^2 + p_{1\lambda}^2 + q_{2\lambda}^2 + p_{2\lambda}^2 \rangle_{Av}, \quad (34)$$

since $q_1 q_2$ and $p_1 p_2$ vanish on the average. The average values of the $q$'s and $p$'s are given in (22), so that

$$\langle (S_z)_{tot}^{(1)} \rangle_{Av} = \frac{N}{2}S_c - \frac{S}{4S_c}\sum_\lambda \left\{ \left(\frac{1-\gamma_\lambda}{1+\gamma_\lambda}\right)^{\frac{1}{2}} + \left(\frac{1+\gamma_\lambda}{1-\gamma_\lambda}\right)^{\frac{1}{2}} \right\}$$

$$= \frac{N}{2}S_c - \frac{S}{2S_c}\sum_\lambda \frac{1}{(1-\gamma_\lambda^2)^{\frac{1}{2}}}. \quad (35)$$

Again we can replace the $\lambda$-sum by an integral,

$$\sum_\lambda \frac{1}{(1-\gamma_\lambda^2)^{\frac{1}{2}}} = \frac{N}{2}\frac{1}{(2\pi)^D}\int_{-\pi}^{\pi}\int\int d\lambda_1 \cdots d\lambda_D$$

$$\times \left[ 1 - \left( D^{-1}\sum_{i=1}^{D}\cos\lambda_i \right)^2 \right]^{-\frac{1}{2}}, \quad (36)$$

$$\sum_\lambda \frac{1}{(1-\gamma_\lambda^2)^{\frac{1}{2}}} = \frac{N}{2}J_D.$$

This equation defines $J_D$.

It is obvious that the integral $J_1$ diverges logarithmically. This means that the original assumption that long-range order exists in the one-dimensional case is wrong; no component of the sublattice spin is finite, and the method breaks down. This, as we pointed out in the introduction, is in agreement with the rigorous result of Bethe and Hulthén.[5, 6, 9]

For the other two cases, the integral does not diverge. Because of the slow convergence, however, a rough approximation such as (25) is quite useless, so that it is necessary to use values computed in much the same way as the exact values (30) for $I_2$ and $I_3$.[13] These are

$$J_2 = 1.393, \quad J_3 = 1.156. \quad (37)$$

This leads to the following values for the total $z$-component of spin (in all cases we neglect terms of order $1/S$, so that we set $S_c = S + \tfrac{1}{2}$, etc.):

$$(S_{z\ tot})_{Av}|_{D=2} = \tfrac{1}{2}N(S - 0.197). \quad (38)$$

$$(S_{z\ tot})_{Av}|_{D=3} = \tfrac{1}{2}N(S - 0.078). \quad (39)$$

These corrections to $S$ are small, and one expects them to become smaller as the number of neighbors increases beyond $Z = 6$. Nonetheless, it is entirely possible that this correction term (or the similar term that would be present in more complicated lattices) can eventually be observed by neutron diffraction methods.

The results (38) and (39) cannot immediately be taken at their face values. To see why this is so, let us compute the $x$- and $y$-components of $(S_{tot})^{(1)\ or\ (2)}$. These are given by the particular spin wave coordinates for $\lambda = 0$:

$$\sum_j S_{xj} = (\tfrac{1}{2}NS)^{\frac{1}{2}}Q_0, \quad \sum_k S_{xk} = (\tfrac{1}{2}NS)^{\frac{1}{2}}R_0,$$
$$\sum_j S_{yj} = (\tfrac{1}{2}NS)^{\frac{1}{2}}P_0, \quad \sum_k S_{yk} = -(\tfrac{1}{2}NS)^{\frac{1}{2}}S_0. \quad (40)$$

The two quantities

$$\sum_j S_{xj} + \sum_k S_{xk} = S_{x\ tot} = (NS)^{\frac{1}{2}}q_{10} \quad (41)$$

and

$$\sum_j S_{yj} + \sum_k S_{yk} = S_{y\ tot} = (NS)^{\frac{1}{2}}p_{20}$$

[by (15)] have finite mean squares, as we see by (22); the squares are somewhat smaller than or of order $N$, so that the actual quantities are always very small. This was to be expected from the fact that $S_{tot}$ is a constant of the motion for the Hamiltonian (1). We see that we have, by our basic assumption (2), accidentally limited ourselves exclusively to singlet states or at least states of very low total spin quantum number. This is acceptable; the ground state is certainly a singlet,[5] while actually the majority of all states have very small total spins.

On the other hand, the differences between the two $x$- and $y$-components,

$$\sum_j S_{xj} - \sum_k S_{xk} = (NS)^{\frac{1}{2}}q_{20},$$
$$\sum_j S_{yj} - \sum_k S_{yk} = (NS)^{\frac{1}{2}}p_{10}, \quad (42)$$

have divergent mean square amplitudes, as we saw in

(23). The meaning of this fact is perfectly clear from our basic knowledge of the problem. The ground state of the antiferromagnet is certainly a singlet state, and a singlet state cannot, by general reasoning, show in any way a preference for one direction over another. Therefore, while the spins of the two sublattices can certainly be said to be opposite in direction, in the ground state of the lattice, on an average basis, we cannot define the direction in space of the spin of either one. One may think of the system as similar to the singlet state of two spins, $(\alpha\beta-\beta\alpha)$, in which the spins are certainly opposite but each is directed with equal probability in all directions.

The quantities (42) are the degrees of freedom which represent the rotation of the two oppositely directed sublattices in space. We know that in the ground state, at least, we cannot "pin down" these degrees of freedom in any way; the lattices will rotate around at will in the course of time. The apparently infinite zero-point amplitude of motion is the mathematical result in this theory of this fact, and is therefore not to be thought of as a fault of the theory.

The tendency of the pair of lattices to rotate around is, however, a weak one, as we can show in two ways. One way is more physical: Since every real lattice will certainly have some kind of anisotropy, we introduce in the Hamiltonian (6) an anisotropy of axial symmetry which makes the $z$-axis the preferred direction. It is easily verified that such an anisotropy energy can be expressed by

$$H_{\text{anis}}=K[\sum_j(S_{xj}^2+S_{yj}^2)+\sum_k(S_{xk}^2+S_{yk}^2)],\quad(43)$$

where $K$ is the anisotropy energy constant per atom. (43) can be re-expressed in terms of the spin-waves (7) and is

$$H_{\text{anis}}=KS\sum_\lambda(Q_\lambda^2+R_\lambda^2+P_\lambda^2+S_\lambda^2).\quad(44)$$

Then the total Hamiltonian becomes, instead of (14),

$$\begin{aligned}H=&-NDJS_c^2+DJS\sum_\lambda[(P_\lambda^2+Q_\lambda^2+R_\lambda^2+S_\lambda^2)\\&\times(1+K/DJ)+2\gamma_\lambda(Q_\lambda R_\lambda-P_\lambda S_\lambda)]\\=&-NDJS_c^2+DJS\sum_\lambda[q_{1\lambda}^2(1+K/DJ+\gamma_\lambda)\\&+p_{1\lambda}^2(1+K/DJ-\gamma_\lambda)+q_{2\lambda}^2(1+K/DJ-\gamma_\lambda)\\&+p_{2\lambda}^2(1+K/DJ+\gamma_\lambda)].\quad(45)\end{aligned}$$

The amplitudes (22) become

$$\langle q_{1\lambda}^2\rangle_{\text{Av}}=\langle p_{2\lambda}^2\rangle_{\text{Av}}=\tfrac{1}{2}\left[\frac{1+(K/DJ)-\gamma_\lambda}{1+(K/DJ)+\gamma_\lambda}\right]^{\frac{1}{2}}$$

$$\langle p_{1\lambda}^2\rangle_{\text{Av}}=\langle q_{2\lambda}^2\rangle_{\text{Av}}=\tfrac{1}{2}\left[\frac{1+(K/DJ)+\gamma_\lambda}{1+(K/DJ)-\gamma_\lambda}\right]^{\frac{1}{2}},\quad(46)$$

and, in particular,

$$\langle(\sum_j S_{xj}-\sum_k S_{xk})^2\rangle_{\text{Av}}\cong NS\frac{1}{(2K/DJ)^{\frac{1}{2}}}\quad(47)$$

for very small $K$. This shows us that, unless $K$ is small in the order $1/N$, the root mean square values of $\sum S_{xj}$ or $\sum S_{yj}$ to be expected is reduced from infinity to something of the order $\sqrt{N}$, completely negligible in comparison with the value of $\sum_j S_{zj}$, which is of order $N$. Thus, we may consider an infinitesimal $K$ to be present as a convergence factor, and then the truly interesting physical parameter,

$$[(S_{\text{tot}}^{(1)})^2]^{\frac{1}{2}}=[(S_{x\text{ tot}}^{(1)})^2+(S_{y\text{ tot}}^{(1)})^2+(S_{z\text{ tot}}^{(1)})^2]^{\frac{1}{2}},$$

is simply given by

$$\langle S_{z\text{ tot}}^{(1)}\rangle_{\text{Av}},$$

which is the value computed in (38) or (39).

A second way of clarifying the meaning of the divergence of the amplitudes (42) is the following. Let us return to the consideration of the original Hamiltonian (16):

$$\begin{aligned}H=&-DNJS_c^2+DJS\sum_\lambda[q_{1\lambda}^2(1+\gamma_\lambda)+p_{1\lambda}^2(1-\gamma_\lambda)\\&+q_{2\lambda}^2(1-\gamma_\lambda)+p_{2\lambda}^2(1+\gamma_\lambda)].\end{aligned}$$

For spin waves $\lambda=0$, the energy terms are

$$H_{\lambda=0}=2DJS(q_{10}^2+p_{20}^2).\quad(48)$$

Now besides the ground state of the $\lambda=0$ oscillators, there will be a number of higher states, which happen, since $\omega=0$, to form a continuum. As the first question let us ask: how much energy will it cost to form a wave packet of higher states which, instead of having a large amplitude of $p_{10}$ or $q_{20}$, has a reasonably small one? This is easily answered by means of (48). From the commutation relations it can be derived that

$$p_\lambda=i\partial/\partial q_\lambda,\quad q_\lambda=-i\partial/\partial p_\lambda.\quad(49)$$

Thus, if we limit $q_\lambda$ to some definite range, say $\Delta q_\lambda$, we must contribute a certain amount of $p_\lambda$, given in order of magnitude by

$$\Delta p_\lambda\cong1/\Delta q_\lambda,\quad(50)$$

or vice versa. Thus, to limit $q_{20}$ to a value $\Delta q_{20}$ we require

$$E_{\text{lim}}=2DJS/(\Delta q_{20})^2.\quad(51)$$

Thus

$$\begin{aligned}E_{\text{lim}}=&\frac{2DJS}{[\Delta(\sum S_{xj}-\sum S_{xk})]^2/NS}\\=&\frac{2DJ}{N}\left\{\frac{NS}{\Delta(\sum S_{xj}-\sum S_{xk})}\right\}^2.\quad(52)\end{aligned}$$

From this relation it becomes clear that to limit the rotation of the sublattice spins to a finite angle (this means limiting $\sum S_{xj}$, etc., to a value of order of magnitude $NS$) the excess energy required is only of order of magnitude $1/N$, and thus is extremely small. It is clear that we can even limit $\sum S_{xj}$ to a quantity of order of magnitude $(N)^{\frac{1}{2}+\alpha}$, $\alpha>0$, without requiring any perceptible energy.

An equivalent way of looking at Eq. (52) is this: Suppose the lattice had been looked at at one time (say with neutron diffraction) and it had been determined that the sublattices were pointing in the $+z$ and $-z$ directions, respectively. How long would it then take for them to turn to the $x$-directions under the effects of the Hamiltonian (1)? The answer to this is given by

$$(h \times \text{frequency of rotation}) \simeq E_{\text{lim}};$$
$$\text{Frequency of rotation} \simeq J/hN; \qquad (53)$$
$$\text{Time to rotate} \sim hN/J.$$

This time is of the order of magnitude $10^8$ sec $= 3$ years.

These two arguments based on Eq. (52), I think, show that our original assumption that $S_z$ total$\simeq NS$ is justified, at least according to its own consequences. It seems very difficult indeed to find a reason why, at least in order of magnitude, (52) should not hold even for the rigorous problem. If we assume initially that $(S_z^{(1)})$ is large, the $S_x$, $S_y$ commutation relation tells us that $S_z$ can then be localized easily, and this in turn justifies the entire theory, which tells us then that $S_z$ is large.

This argument also has the consequence that we can definitely predict the result of observing the spins on the two sublattices. The direction of the spins will no doubt in any real case be determined primarily by anisotropy energies. Their magnitude is given to a fair approximation by (39) or the equivalent formula for the lattice under consideration.

## V. SOME CONCLUSIONS

The apparent success of the spin wave theory in elucidating the complications of the ground state of the antiferromagnet leads one to have some confidence in its validity as a description of the higher lying states; thus such things as Bloch wall theory may be capable of being carried over practically unchanged from ferromagnet theory. This is of some practical interest in connection with ferrimagnetism, which will also be discussed in a way similar to the present theory in a later paper. It seems, too, that the "sublattice" picture of antiferromagnetism which has been used in some theoretical papers[6,7] is at least not qualitatively affected by the present picture of the complications of the ground state. This is of importance because these theories have had considerable success in explaining experi-mental results in a semiquantitative way, and because they do lean rather heavily on the assumption that the ground state has order and is not greatly different from what one would naively expect.

The only approximate energies which seem to have been given in the literature for two- and three-dimensional antiferromagnets are the energies of very small aggregates (6 and 8 spins) with periodic boundary conditions, which were computed by Harrison.[15] However, these energies lie even below the rigorous limits computed previously,[11] because of the fact that the aggregates are so small that certain paired electrons can have an over-riding effect (just as in the linear case the binding energy of the two-spin case is far too great). Thus, it does not seem fruitful to make a comparison with Harrison's results.

The conclusions of this paper about long-range order have implications in the theory of metallic binding. If one describes a substance by the Heitler-London model, (1) is at least a fair approximation for the effective spin coupling, unless one has a case such as diamond in which the interatomic exchange integrals may be thought of as over-riding the internal spin-coupling which leads to a total $S$ for the atom. (Of course, such substances as ionic crystals have $S=0$, and we do not treat them.) In most metals, however, and particularly in the single-electron metals such as the alkalis, the description by the Heitler-London model certainly leads to (1). Then, as we have shown, (1) requires a long-range spin order to be present, which is probably not the case in most metals. Thus, we conclude that the Heitler-London model is not even a good qualitative description of metallic binding, in agreement with Schubin and Wonsowski[16] and Mott;[17] the band theory must be used in metals, the Heitler-London theory may be used in insulators.

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