THE RELATION BETWEEN ANTIFERROMAGNETISM AND INDETERMINACY OF MULTIPLICITY

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The problem of the ground state of antiferromagnetism is considered from the viewpoint of establishing the relation between antiferromagnetic ordering and multiplicity indeterminacy. It is shown that realization of an antiferromagnetic state in a system consisting of an even number of atomic carriers of the magnetic moment with identical spins requires indeterminacy of multiplicity. The failure of attempts to explain antiferromagnetism in electron systems with an isotropic Heisenberg Hamiltonian is due to the fact that the Hamiltonian describes a spin system with a definite multiplicity. Of the various types of subsidiary (anisotropic) Hamiltonians that are usually introduced for stabilization of the antiferromagnetic state, the only Hamiltonians that describe states with indefinite multiplicity possess this property. It should be noted, however, that if the Hamiltonian commutes with the time-reversal operator the antiferromagnetic state cannot be realized in the degenerate state of a system with integer spin. We therefore consider antiferromagnetism in a system in which the Hamiltonian does not commute with the time-reversal operator. If the Hamiltonian describing a state with indefinite multiplicity commutes with the time-reversal operator, then the stabilized ground antiferromagnetic state is degenerate.

1. THE PROBLEM OF STABILIZATION OF THE ANTIFERROMAGNETIC STATE

In earlier papers[1-3] we established the connection between the change in the multiplicity and the antisymmetrical exchange interaction. At the same time, we clarified the role played by the multiplicity change in the stabilization of the weak-ferromagnetism state. In the present article we consider the role of the indeterminacy of the multiplicity in the mechanism of antiferromagnetic-state stabilization, first proposed by Neel[4] and Landau[5].

In the study of antiferromagnetism it is usually assumed that the principal role is played by exchange interaction, described by a Heisenberg Hamiltonian

$$\mathcal{H}_0 = I \sum_{\langle j,k \rangle} S_j S_k, \tag{1}$$

where I is the exchange integral, $\langle j, k\rangle$ are pairs of neighboring sites of the crystal lattice, and S_j is the spin-vector operator of the j-th site. It has however been noticed long ago that the Hamiltonian (1), with the aid of which it is possible to describe the ferromagnetic state when $I < 0$, does not make it possible to describe the antiferromagnetic state satisfactorily following a simple reversal of the sign of the parameter I ($I > 0$). The complexity of the quantum-mechanical treatment of the ground antiferromagnetic state is connected with the fact that the wave function

$$\Psi = \prod_i \psi_i(+S) \prod_j \psi_j(-S), \tag{2}$$

corresponding to two sublattices with sites i and j and antiparallel z-projection of their resultant spins +S and −S is not an eigenfunction of the Hamiltonian (1) (see, for example,[6]). It is therefore usually assumed that although the ground state of the antiferromagnetic system does not coincide with the state described by the function (2), nevertheless it does not differ very strongly from the latter, so that the function (2) can serve as the starting point for the application of the spin-wave method[7,8] (or other methods[9]) in an approximate analysis of the antiferromagnetic state. This basic assumption was not proved, so that the validity of the theory (using this assumption) is frequently assessed only on the basis of its self-consistency. There is certainly no such self-consistency if we confine ourselves to an analysis of the Hamiltonian (1). The latter is due to the fact that functions differing slightly from (2) presuppose the presence of a large z-projection of the resultant spin of each sublattice, whereas the Hamiltonian (1) leads to "rotation" of the sublattice spins in space (which is formally expressed in the divergence of the amplitudes of motion of the transverse components S_x and S_y of the resultant spin of the sublattices,[6,7]).

The foregoing circumstance has made it necessary to introduce into consideration, besides the operator (1), additional Hamiltonians $\mathcal{H}_1$, which are usually connected with the energy of the magnetic anisotropy of the crystal. For example, the following expression was used for $\mathcal{H}_1$ in[7] (see also[10,11] and elsewhere)

$$\mathcal{H}_{1K} = K\left[\sum_j (S_{xj}^2 + S_{yj}^2) + \sum_k (S_{xk}^2 + S_{yk}^2)\right] \tag{3}$$

for the energy of magnetic anisotropy with axial symmetry. It was concluded there that even small values of the parameter K (compared with I) eliminate the divergence of the transverse spin components, making it possible by the same token to regard K as a convergence factor that ensures stability of the antiferromagnetic ground state.

A similar result was obtained also in[8], where the anisotropy energy operator was chosen in the form

$$\mathcal{H}_{1A} = -\sum_k g\mu_B S_{zk} H_A \exp(iWR_k),$$

where $\exp(iWR_k)$ reverses sign on going from one lattice site to the neighboring one, so that the effective internal magnetic field H_A is directed in each site parallel to the spin projection in the state (2), μ_B is the Bohr magneton, and g is the Lande factor.

Thus, allowance for the anisotropy energy makes it possible to obtain, as it were, self consistency of a theory based on the aforementioned main assumption that the ground-state function is close in form to (2). However, one must not overestimate the significance of this conclusion, since, as noted in[12], the satisfactory final result obtained when using anisotropic additions, which leads to stability of the antiferromagnetism, may be simply the consequence of the aforementioned main assumption, and not a confirmation of its correctness. In addition, a weak spot of the spin-wave theory is the introduction of a large number of fictitious states. All this makes it advantageous to return to a consideration of the problem of the ground state of an antiferromagnet without using the aforementioned main assumption and without using the spin-wave method.

It will be shown below that realization of antiferromagnetism in a system made up of an even number of atomic carriers of magnetic movement with identical spins calls for an indeterminacy of its multiplicity. From the point of view of this criterion, the insufficiency of the Hamiltonian (1) for the description of the antiferromagnetic state is due to the fact that the eigenfunctions of the Hamiltonian (1) describes states with definite multiplicity. In addition, it turns out that the additional anisotropic Hamiltonians of the type (3) and (4) have different values for the stabilization of the antiferromagnetism. Namely, inasmuch as the Hamiltonian (3) commutes with the time-reversal operator, its addition to the Hamiltonian (1), which has a nondegenerate ground state, cannot lead to antiferromagnetism. The opposite conclusion obtained in[7] is due to the use in it of the main assumption, which in this case takes the form

$$\begin{gathered} S_{zj} \approx S_c - (2S_c)^{-1}(S_{xj}^2 + S_{yj}^2), \\ S_{zk} \approx -S_c + (2S_c)^{-1}(S_{xk}^2 + S_{yk}^2), \quad S_c = [S(S+1)]^{1/2} \end{gathered} \tag{5}$$

and in which one postulates essentially that the deviation of the antiferromagnetic state from the state described by the function (2) is small. This conclusion is thus a simple consequence of this assumption, which remains unproved.

The Hamiltonian (4) does not commute with the time-reversal operator, and can therefore lead, independently of the main assumption (5), to stabilization of the antiferromagnetic ground state. However, the opinion advanced for example in[8,13], that the operator (4) plays only an auxiliary role and that an appreciable z-projection of the resultant spin of each sublattice remains in the system when the magnetic field H_A tends to zero, is incorrect. It can be stated, however, that actually when $H_A \to 0$ the magnetization of the sublattice vanishes, and therefore no antiferromagnetism is produced in this case. The opposite result obtained in[8,13] is again due to the use of the main assumption (5). In this connection, we discuss in Sec. 6 of the present paper the possible appearance of a Hamiltonian of the form (4) in the crystal. It can also be shown that in a classical Neél antiferromagnetic state (2), which is an eigenstate of the Hamiltonian of the type (4), the indeterminacy of the multiplicity is equal to the largest possible spin value in the system.

2. CONNECTION BETWEEN ANTIFERROMAGNETISM AND MULTIPLICITY INDETERMINACY

To establish the connection between the antiferromagnetism and the multiplicity indeterminacy, let us consider a crystal with two sublattices I and II, the total spin-vector operator of which S is determined by the sum

$$S = S_I + S_{II}, \tag{6}$$

where S_I and S_{II} are the spin-vector operators of the first and second sublattices. If the crystal is in an antiferromagnetic state, then the resultant spontaneous mechanization is equal to zero in the absence of an external magnetic field, but the magnetizations of the sublattices (determined by the mean values of the z projection of the sublattice spins $\langle S_{I,z}\rangle$ and $\langle S_{II,z}\rangle$) differ from zero in the region of temperatures below the Neel point. Therefore, in the absence of an external field and below the Neel point, the antiferromagnetic state is characterized by simultaneous satisfaction of the following relations:

$$\langle S_z\rangle = 0, \tag{7}$$

$$\langle S_{I,z}\rangle \neq 0, \quad \langle S_{II,z}\rangle \neq 0. \tag{8}$$

It follows from (6)—(8) that $\langle S_{I,z}\rangle = -\langle S_{II,z}\rangle$, i.e., the nonvanishing sublattice magnetizations are equal in magnitude and opposite in sign. We introduce the antisymmetric operator

$$A = S_I - S_{II}, \tag{9}$$

which is a generalization of the operator $A_{12} = S_1 - S_2$, which was introduced by us in[1] and used in[2,3], to include the case of two centers. From (6) and (9) it follows that the sublattice spin operators S_I and S_{II} are connected with the operators S and A by the equations

$$S_I = {}^1/_2(S + A), \quad S_{II} = {}^1/_2(S - A). \tag{10}$$

It follows from (10) and (7) that the following relations hold in the antiferromagnetic state

$$\langle S_{I,z}\rangle = {}^1/_2\langle A_z\rangle, \quad \langle S_{II,z}\rangle = -{}^1/_2\langle A_z\rangle. \tag{11}$$

Comparing relations (11) with inequalities (8), we see that in the antiferromagnetic state there should be satisfied the inequality

$$\langle A_z\rangle \neq 0. \tag{12}$$

This inequality is the necessary condition for the realization of the antiferromagnetic state, determined by relations (7) and (8), which reduces to the requirement that the mean value of the z projection of the antisymmetrical operator (9) be different from zero. In this case, according to (11), the sublattice magnetizations are determined by the mean value of $\langle A_z\rangle$.

To explain the physical meaning of the necessary condition (12), we take into account the fact that, in

analogy with the case considered by us in[2,3], the antisymmetrical vector operator A can transform the state of a crystal with spin S only into a state with a spin S′, satisfying the conditions

$$S' = S + 1, \tag{13}$$

$$S' = S. \tag{14}$$

In the case of (14), the following equality takes place (see, for example,[14])

$$\langle S, S_z | A_z | S, S_z \rangle = A_S^S S_z, \tag{15}$$

where the coefficient A_S^S does not depend on S_Z. Equation (15) can be used to consider states in which S and S_Z have definite values. We shall therefore assume at first that in the antiferromagnetic state S and S_Z have definite values (there is no indeterminacy of the multiplicity). In this case it follows from (10) that

$$S_z = 0. \tag{16}$$

Substituting (16) in (15), we obtain $\langle A_Z \rangle = 0$, thus violating the necessary condition (12). It follows therefore that it is impossible to realize antiferromagnetism in a state with definite multiplicity and with a value $S_Z = 0$.

This result suffices to demonstrate the inconsistency of theories in which antiferromagnetism is considered as a state with a definite spin and with a value $S_Z = 0$. Such are, for example, papers in which it is stated that antiferromagnetism is a singlet state (for example it is stated in[7] that the "ground state of an antiferromagnet is indeed a singlet state"). Since S and S_Z have definite values in the singlet state, namely zero values, it follows from (16), (15), and (12) that there is not antiferromagnetism in this state.

Let us assume now that for some reasons inherent in the crystal S_Z has no definite value. In this more general case, Eq. (16) does not follow from the condition (7). If, however, S has a definite value, then the following equality obtains

$$\langle S | A_z | S \rangle = \sum_{S_z} |\langle S, S_z | S \rangle|^2 \langle S, S_z | A_z | S, S_z \rangle, \tag{17}$$

where $\langle S, S_Z | S \rangle$ are the coefficients in the expansion of the state $|S\rangle$ in the states $|S, S_Z\rangle$. We have shown in[2,3] that in the case of a system made up of two centers with identical spins $S_1 = S_2$ (not necessarily equal to $\frac{1}{2}$) the matrix elements entering in the right side of (17) vanish at all possible values of S_Z. The same statement remains in force for a system of any even number of centers with identical spins. Moreover, for this purpose it suffices to require that the system under consideration consist of a pair of centers with spins of equal value.

Indeed, the operator A, defined in (9), is additive with respect to the indicated pairs, so that we get the equality

$$A_z = \sum_{\alpha=1}^{N/2} A_{z,\alpha}, \tag{18}$$

where α(jk) is the number of pair of sites with identical spins $S_j = S_k$, and $A_{z,\alpha} = S_{zj} - S_{zk}$. In (18), each index j from the subsystem I is encountered only with a single index k from the subsystem II, so that there are N/2 terms, where N is the number of centers. It follows from (18) that

$$\langle S, S_z | A_z | S, S_z \rangle = \sum_{\alpha} \langle S, S_z | A_{z,\alpha} | S, S_z \rangle. \tag{19}$$

To consider the matrix elements in the right side of (19), we represent the state $|S, S_Z\rangle$ in the form of the sum

$$|S, S_z\rangle = \sum_{S_{z,\alpha}, S_{z,\beta}}{}' (S_\alpha, S_\beta, S_{z,\alpha}, S_{z,\beta} | S, S_z) | S_\alpha, S_{z,\alpha} \rangle | S_\beta, S_{z,\beta} \rangle$$

$$(S_{z,\alpha} + S_{z,\beta} = S_z), \tag{20}$$

where α is a system of a pair of spins S_j and S_k; β is a system made up of all the remaining N − 2 spins, and $(S_\alpha, S_\beta, S_{Z,\alpha}, S_{Z,\beta} | S, S_Z)$ are Wigner coefficients. It follows from (20) that

$$\langle S, S_z | A_{z,\alpha} | S, S_z \rangle$$

$$= \sum_{S_{z\,\alpha}, S_{z,\beta}}{}' |(S_\alpha, S_\beta, S_{z,\alpha}, S_{z,\beta} | S, S_z)|^2 \langle S_\alpha, S_{z,\alpha} | A_{z,\alpha} | S_\alpha, S_{z,\alpha} \rangle, \tag{21}$$

where account is taken of the fact that the operator $A_{Z,\alpha}$ does not act on the system β. But according to[2,3] all the matrix elements in the right side of (21) are equal to zero, since the system α consists of two identical spins. We then obtain accordingly from (19) and (21)

$$\langle S, S_z | A_z | S, S_z \rangle = 0. \tag{22}$$

From (22) and (17) it follows that

$$\langle S | A_z | S \rangle = 0. \tag{23}$$

By the same token we have demonstrated that if the system consists of an even number of centers with identical spins or if the system consists of pairs of centers with identical spins, then, regardless of the definiteness of the projection S_Z, the condition (14) is excluded, so that the operator A_Z is the operator of the excitation of the multiplicity of such a system. From a comparison of (23) with (12) it follows that in a system made up of an even number of sites with identical spins antiferromagnetism is possible only in states having an indeterminate multiplicity.

3. PROOF OF UNSUITABILITY OF THE ISOTROPIC-EXCHANGE HAMILTONIAN FOR THE DESCRIPTION OF ANTIFERROMAGNETISM

We shall use the conclusion derived in Sec. 2 to analyze the properties of Hamiltonian (1). This Hamiltonian commutes with the operator S^2 and consequently describes a state with definite multiplicity. According to[10,15], the ground state of the Hamiltonian (1) is singlet when $I > 0$. As noted in Sec. 2, in this case the antiferromagnetism cannot be realized. This also explains the impossibility of describing antiferromagnetism with the aid of the Heisenberg Hamiltonian (1).

It can be shown that in the case of a singlet state there is another possible proof, not derived from formula (15), of the absence of antiferromagnetism. The point is that the singlet state is a nondegenerate state with an integer spin value. We shall show that if the Hamiltonian of the system commutes with the time-reversal operator Θ, then $\langle A_Z \rangle = 0$ in any nondegenerate state with integer spin.

Indeed, let Ψ be the eigenstate of the energy operator of the system. Then, according to formula (26.8) of[16], the following equality holds

$$\langle A_z\rangle = \langle\Psi|A_z|\Psi\rangle = \langle\Theta A_z\Psi|\Theta\Psi\rangle. \quad (24)$$

It follows from the definition (9) that the operator A_z anticommutes with the operator Θ, and therefore

$$\langle A_z\rangle = -\langle\Theta\Psi|A_z|\Theta\Psi\rangle, \quad (25)$$

where, in addition, account is taken of the fact that A_z is a self-adjoint operator. According to the condition assumed above, the Hamiltonian commutes with the time-reversal operator Θ. Consequently, the functions $\Theta\Psi$ and Ψ correspond to the same energy. Since this energy level is nondegenerate in accordance with our initial assumption, the following equality holds true

$$\Theta\Psi = e^{i\gamma}\Psi, \quad (26)$$

where γ is the phase, so that $\Theta^2 = 1$, as should be the case for a state with integer spin. Substituting (26) in (25) we get $\langle A_z\rangle = -\langle A_z\rangle$, from which it follows that $\langle A_z\rangle = 0$. The latter, according to the condition (12), denotes absence of antiferromagnetism. The conclusion that there is no long-range antiferromagnetic order defined by the quantity $\langle S_{I,z}\rangle$ in a nondegenerate ground state of the Hamiltonian that is invariant against time reversal, was qualitatively obtained in a paper by Pratt[19].[1)]

We have thus shown that if the Hamiltonian of the system commutes with the time reversal operator, then no antiferromagnetism can be realized in a nondegenerate state with an integer spin. The result is an application to the antiferromagnetism problem of the well known theorem that the mean value of any time-odd operator vanishes in a state that is "invariant" with respect to Θ (see, for example,[17]). From this point of view, the inadequacy of the attempts (undertaken in[7] and elsewhere) to "correct" the Hamiltonian (1) by adding to it an magnetic-anisotropy energy operator of the type (3) becomes clear. A more detailed analysis of the properties of the Hamiltonian (3) is presented below.

4. INSUFFICIENCY OF THE ANISOTROPIC PERTURBATION FOR THE STABILIZATION OF THE ANTIFERROMAGNETIC STATE

Let us consider now the Hamiltonian

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_{1K} = I\sum_{(j,k)} S_jS_k + K\left[\sum_j (S_{xj}^2 + S_{yj}^2) + \sum_k (S_{xk}^2 + S_{yk}^2)\right], \quad (27)$$

where $I > 0$. The Hamiltonian $\mathcal{H}_{1K}$ differs from a constant only if the spins of the magnetism carriers at the crystal-lattice sites are larger than 1/2. This Hamiltonian does not commute in this case with the operator S^2, and consequently its eigenstates can have an indeterminant multiplicity. If, however, in accordance with[7], we regard the coefficient K as a "convergence factor," called upon to ensure stability of the antiferromagnetism, then it is easily seen that the Hamiltonian $\mathcal{H}_{1K}$ does not possess this property. Indeed, if $\mathcal{H}_{1K}$ is a small perturbation, then the ground state of the Hamiltonian $\mathcal{H}_0$ is shifted, but the new ground state of the operator (7), resulting from the singlet, remains nondegenerate. Since the Hamiltonians $\mathcal{H}_0$ and $\mathcal{H}_{1K}$ commute with the time-reversal operator Θ, it follows therefore, in accordance with the result obtained in Sec. 3, that $\langle A_z\rangle = 0$ in the ground state of the Hamiltonian (27), and consequently no antiferromagnetism is realized.

The question may arise of how the opposite conclusion, that the antiferromagnetic state is stable when an anisotropic operator (3) is added to the Hamiltonian (1), was reached in[7] (and elsewhere). The answer becomes clear if it is recalled that in these papers they use, besides the Hamiltonian (3), also the "main assumption" in the form of formulas (5). The latter makes it possible to transform the Hamiltonian (3) into

$$\mathcal{H}_{1K} = 2KNS_c^2 + 2S_cK\left(\sum_k S_{zk} - \sum_j S_{zj}\right), \quad (28)$$

or

$$\mathcal{H}_{1K} = 2KNS_c^2 + 2S_cKA_z. \quad (29)$$

It becomes obvious from (28) and (29) that the assumption (5) changes the character of the symmetry of $\mathcal{H}_{1K}$ relative to the time reversal, and formally transforms the Hamiltonian (3) into a Hamiltonian of the type (4). It follows therefore that the addition of the anisotropic perturbation of the type (3) to the Hamiltonian (1) does not lead by itself to stability of the antiferromagnetic state. The opposite result obtained in[7] is a consequence of the additional assumption (5). In other words, the antiferromagnetism was obtained in (7) because it was postulated from the very outset.

5. ROLE PLAYED IN THE STABILIZATION OF THE ANTIFERROMAGNETIC STATE BY A HAMILTONIAN THAT IS ODD WITH RESPECT TO TIME REVERSAL

We now consider a spin-system Hamiltonian in the form

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_{1A} = I\sum_{(jk)} S_jS_k + pA_z, \quad (30)$$

where $p = |g\mu_B H_A \exp(iWR_k)|$ and $I > 0$. This Hamiltonian contains from the very outset an operator A_z which is odd with respect to time reversal. If, however, we apply to (3) a "main assumption" of the type (5), as is done in the spin-wave theory[8,13], then the difference between $\mathcal{H}_{1A}$ and $\mathcal{H}_{1K}$ with respect to their commutation properties with the time-reversal operator vanishes formally. This has led to the conclusion drawn in[8,13] that the coefficient p also plays the role of the "convergence factor," and that even in the limit as $p \to 0$ the lattice is spontaneously antiferromagnetic, and the magnetization of each sublattice is close to saturation. We shall now show that this conclusion, based on the assumption (5), is incorrect and that actually the magnetization of the sublattices tends to zero when $p \to 0$.

Let E and Ψ be respectively the eigenvalue and the eigenfunction of the Hamiltonian (30). Then for the aver-

[1)] Mention should also be made that in another paper [20] the long-range antiferromagnetic order is characterized by the quantity $R_{jk} = \frac{1}{2}(S_{jx}S_{kx} + S_{jy}S_{ky})$, where j and k are the numbers of the lattice sites. Obviously, the operator R_{jk}, which is even in the spins, is invariant against the time reversal, and therefore we cannot use the proof given in the text for the vanishing of the mean value $\langle R_{jk}\rangle$. However, one can hardly regard the quantity $\langle R_{jk}\rangle$ as an adequate measure of the long-range antiferromagnetic order, since, for example in the case of a system consisting of a pair of sites with spin 1/2, this quantity differs from zero both in the singlet and in the triplet states (i.e., at both possible signs of the exchange integral).

age value of the operator A_z we have the equality

$$\langle A_z\rangle = \langle\Psi|A_z|\Psi\rangle = \partial E / \partial p. \tag{31}$$

Regarding pA_z as a perturbation, we obtain for E the expression

$$E = E_0 + p\langle\Psi_0|A_z|\Psi_0\rangle + p^2 \sum_m{}' \frac{|\langle\Psi_m{}^0|A_z|\Psi_0\rangle|^2}{E_0 - E_m{}^0} + \ldots, \tag{32}$$

where Ψ_m^0 and E_m^0 ($m \neq 0$) are the eigenfunctions and eigenvalues of the Hamiltonian $\mathcal{H}_0$, and E_0 is the energy of the singlet and consequently nondegenerate state of Ψ_0, while the prime of the summation sign denotes elimination of the term with m = 0. The second term in the right side of (32), which is linear in p, vanishes because of the absence of transitions between the states with S = 0[14]. It therefore follows from (31) and (32)

$$\langle A_z\rangle = 2p \sum_m{}' \frac{|\langle\Psi_m{}^0|A_z|\Psi_0\rangle|^2}{E_0 - E_m{}^0} + \ldots \tag{33}$$

Putting p = 0, we obtain from (33) $\langle A_z\rangle = 0$, which denotes, in accordance with (11), that the sublattice magnetizations are equal to zero and there is no antiferromagnetism.

The same result can be obtained also without using perturbation theory. To this end we take into account the fact that the Hamiltonian (30) satisfies the commutation relation

$$S^+\mathcal{H} - \mathcal{H}S^+ = -pA^+, \tag{34}$$

where

$$S^\pm = S_x \pm iS_y, \quad A^\pm = A_x \pm iA_y.$$

On the other hand

$$S^+A^- - A^-S^+ = 2A_z. \tag{35}$$

It follows from (34) that

$$\langle\Psi_n|S^+|\Psi_m\rangle(E_n - E_m) = p\langle\Psi_n|A^+|\Psi_m\rangle, \tag{36}$$

inasmuch as Ψ_n and Ψ_m are eigenfunctions of the Hamiltonian (30), while E_n and E_m are the corresponding energies. On the other hand, according to (35)

$$(A_z)_{nn} = \langle\Psi_n|A_z|\Psi_n\rangle$$
$$= \tfrac{1}{2}\sum_m[\langle\Psi_n|S^+|\Psi_m\rangle\langle\Psi_m|A^-|\Psi_n\rangle - \langle\Psi_n|A^-|\Psi_m\rangle\langle\Psi_m|S^+|\Psi_n\rangle]. \tag{37}$$

It follows from (37) and (36) that

$$(A_z)_{nn} = -\frac{p}{2}\sum_m \frac{|\langle\Psi_m|A^-|\Psi_n\rangle|^2 + |\langle\Psi_m|A^+|\Psi_n\rangle|^2}{E_m - E_n}. \tag{38}$$

Putting in (38) p = 0 and noting that, by virtue of (36), the terms with $E_m = E_n$ make no contribution to $(A_z)_{nn}$, and when $E_m \neq E_n$ the denominators on the right side of (38) are determined in the case when $p \to 0$ from (30) by the nonvanishing exchange integral I, we get $(A_z)_{nn} = 0$, which means that there is no antiferromagnetism. Thus, the coefficient p, which is connected with the field H_A, cannot be regarded as a convergence factor that vanishes in the limit. Only finite values of p can lead to a finite magnetization of each of the sublattices and consequently to antiferromagnetism. We note also that from (38) there follows a "sum rule"

$$\sum_n (A_z)_{nn} = 0. \tag{39}$$

This means that the mean value $(A_z)_{nn}$ is positive for some states and negative for others.

In the ground state (n = 0) we get for the energy E_0 the inequality $E_m - E_0 > 0$ at all values $m \neq 0$. Therefore (38) leads to

$$\text{sign}\,(A_z)_{00} = -\text{sign}\,p, \tag{40}$$

which is understandable, for in this case the contribution of pA_z to the energy, i.e., to the eigenvalue of the Hamiltonian (30), is negative. From (40) and (11) it follows that when $p > 0$ the magnetization of the sublattice I is directed against the z axis, and that of sublattice II along the z axis. When $p < 0$ the magnetization of the sublattices have the opposite directions.

6. POSSIBLE CAUSES OF APPEARANCE OF STABILIZING FACTORS

The foregoing analysis shows that the presence in the Hamiltonian of an antisymmetrical spin operator A_z connected with the change of the multiplicity can lead to the stabilization of the antiferromagnetism. Yet in[8,13], where they introduced and used the Hamiltonian (4) which is equivalent, as shown above, to the operator pA_z, its origin was not explained. In this connection it is of interest to discuss the possible causes of the appearance of a term of the type pA_z in the spin-system Hamiltonian.

One of the possible and natural causes of the appearance of an antisymmetrical spin operator A_z in the Hamiltonian is, in our opinion, the spin-orbit interaction. Indeed, the Hamiltonian of the spin-orbit coupling of two particles with spins S_1 and S_2 and orbital angular momenta l_1 and l_2 can be represented in the form

$$\zeta(l_1S_1 + l_2S_2) = \tfrac{1}{2}\zeta(l_1 + l_2)S + \tfrac{1}{2}\zeta(l_1 - l_2)A, \tag{41}$$

where ζ is the parameter of the spin-orbit interaction, $S = S_1 + S_2$, and $A = S_1 - S_2$. The appearance in (41) of the operator A connected with the change of the multiplicity does indeed show that the spin-orbit interaction can play an important role in the stabilization of the antiferromagnetic state. It must be taken into account, however, that in the case of (21) the vector parameter $p = \frac{1}{2}\zeta(l_1 - l_2)$ is a function of the orbital angular momenta, so that in this case the product pA as a whole is invariant against time reversal. According to the theorem proved in Sec. 3, this means that the condition $\langle A_z\rangle \neq 0$ can be satisfied only for the degenerate state. Consequently, the stabilized antiferromagnetic state of which spin-orbit interaction can lead is degenerate. This is understandable, for in the case $p_z = \frac{1}{2}\zeta(l_1^z - l_2^z)$, for a specified z axis, it is impossible to speak of a definite sign of p_z, and consequently the two possible sublattice magnetization directions are connected with a single energy. This degeneracy with respect to direction can be lifted (just as in the case of ferromagnetism) with a magnetic field. It is therefore advantageous to consider from the very beginning the case of exchange interaction in the presence of local magnetic fields.

Let us consider for simplicity two centers with spins $S_1 = \frac{1}{2}$ and $S_2 = \frac{1}{2}$ in magnetic fields H_{1z} and H_{2z}. The Hamiltonian of this system

$$\mathcal{H} = I(S_1S_2) + \mu_B(S_{1z}H_{1z} + S_{2z}H_{2z}) \tag{42}$$

has the following eigenvalues, eigenfunctions, and average values of the operator $A_z = S_{1z} - S_{2z}$:

$$E_1 = \frac{I}{4} + \frac{\mu_B}{2}(H_{1z} + H_{2z}), \quad \Psi_1 = \Psi_\uparrow^T, \quad (A_z)_{11} = 0; \tag{43}$$

$$E_2 = \frac{I}{4} - \frac{\mu_B}{2}(H_{1z} + H_{2z}), \quad \Psi_2 = \Psi_\downarrow^T, \quad (A_z)_{22} = 0; \tag{44}$$

$$E_3 = -\frac{I}{4} + \frac{1}{2}[I^2 + \mu_B^2(H_{1z} - H_{2z})^2]^{1/2},$$

$$\Psi_3 = \frac{1}{F}\{[I + \sqrt{I^2 + \mu_B^2(H_{1z} - H_{2z})^2}]\Psi^T + \mu_B(H_{1z} - H_{2z})\Psi^S\}, \tag{45}$$

$$(A_z)_{33} = \mu_B(H_{1z} - H_{2z})[I^2 + \mu_B^2(H_{1z} - H_{2z})^2]^{-1/2};$$

$$E_4 = -\frac{I}{4} - \frac{1}{2}[I^2 + \mu_B^2(H_{1z} - H_{2z})^2]^{1/2},$$

$$\Psi_4 = \frac{1}{F}\{[I + \sqrt{I^2 + \mu_B^2(H_{1z} - H_{2z})^2}]\Psi^S - \mu_B(H_{1z} - H_{2z})\Psi^T\}, \tag{46}$$

$$(A_z)_{44} = -(A_z)_{33};$$

$$F = \{[I + \sqrt{I^2 + \mu_B^2(H_{1z} - H_{2z})^2}]^2 + \mu_B^2(H_{1z} - H_{2z})^2\}^{1/2},$$

where $\Psi_\uparrow^T$, $\Psi_\downarrow^T$, and Ψ^T are triplet states with S_Z equal to +1, −1, and 0 respectively, and Ψ^S is a singlet state.

Let us assume that H_{1Z} and H_{2Z} can vary freely in the range between −H and +H, where $H > 0$. Then the minimum value of the levels E_1 and E_2 is

$$E_\parallel = \frac{I}{4} - |\mu_B|H, \tag{47}$$

which corresponds to the state $\Psi_\downarrow^T$ when $\mu_B > 0$ and to the state $\Psi_\uparrow^T$ when $\mu_B < 0$. The index ∥ denotes that the energy (47) is reached at $H_{1Z} = H_{2Z} = \pm H$, i.e., when the fields H_1 and H_2 have the same direction (both are either parallel or antiparallel to the z axis).

The minimum value of the levels E_3 and E_4 is

$$E_{\uparrow\downarrow} = -\frac{I}{4} - \frac{1}{2}(I^2 + 4\mu_B^2H^2)^{1/2}, \tag{48}$$

where the index ↑↓ denotes that (48) is reached in the case when H_1 and H_2 are directed oppositely ($H_{1Z} = -H_{2Z} = \pm H$).

From (47) and (48) we get

$$E_{\uparrow\downarrow} - E_\parallel = \tfrac{1}{2}[2|\mu_B|H - I - \sqrt{(2|\mu_B|H \mp |I|)^2 \pm 4|\mu_B||I|H}]. \tag{49}$$

The right side of (49) is negative when $I > 0$ and positive when $I < 0$. Consequently in the case when $I < 0$, when the exchange without allowance for the fields H_1 and H_2 contributes to the "ferromagnetic" orientation of the spins, the same exchange contributes to parallel orientation of fields H_1 and H_2 of equal magnitude. In the case when $I > 0$, and the exchange without allowance for the field H_1 and H_2 contributes to the realization of the singlet state, the same exchange contributes to antiparallel orientation of the equal fields H_1 and H_2. Thus, when $I > 0$ the minimum energy corresponds to the Hamiltonian

$$\mathcal{H} = I(S_1S_2) \pm \mu_B HA_z, \tag{50}$$

which is obtained from (42) by making the substitution $H_{1Z} = -H_{2Z} = \pm H$, and the maximum value $\langle A_Z \rangle$, which equals, according to (46),

$$\langle A_z \rangle = \mp \frac{2\mu_B H}{(I^2 + 4\mu_B^2H^2)^{1/2}}. \tag{51}$$

A comparison of expressions (51) and (48) shows that degeneracy takes place in this case, since $\pm\mu_B$ corresponds to the same energy. This degeneracy is connected with the assumption that the sources of the field of given intensity H can freely change their orientation relative to the z axis. In the case of fixed field sources, and consequently fixed values of H_{1Z} and H_{2Z}, there is, of course, no degeneracy. This is seen from (45) and (46), for different signs of $\langle A_Z \rangle$ correspond to different energies.

The foregoing shows that the presence of local magnetic fields can lead to satisfaction of the condition (12), i.e., $\langle A_Z \rangle \neq 0$, and consequently to the possibility of antiferromagnetism.

It is possible to propose various models that ensure the appearance of local magnetic fields. Besides the spin-orbit interaction, interest attaches in this respect to the separation in[18] of the roles played by different d-electrons in the establishment of the magnetic order. If, for example, we assume, following[18], that the ferromagnetic coupling is due to e-electrons (or, depending on the lattice, conversely, p-electrons), then the role of the magnetizing (non-exchange) factor can be assigned to p-electrons (or, conversely, to e-electrons) of the d-shell. These models, however, will not be considered here, since the main purpose of the article is to establish a connection between the antiferromagnetism and the indeterminacy of the multiplicity, independently of the concrete details of the model.[2)]

The existence of such a connection follows not only from an analysis of the above-considered Hamiltonians that are usually employed in the quantum-mechanical study of antiferromagnetism, but also (as shown by the necessary condition (12) derived by us) from the general notion of antiferromagnetic ordering as an aggregate of two sublattices magnetized in parallel but with zero total magnetization. In particular, regardless of the origin of the classical antiferromagnetic state (2), it can be shown that in this state the indeterminacy of the multiplicity is equal to the maximum value of the spin of the system. All this makes it possible to state that the appearance of two sublattices with antiparallel magnetization and with zero total magnetization is closely connected with the multiplicity indeterminacy, which thus turns out to be essential for realization of antiferromagnetism.

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[2)] The question of the origin of operators of the type pA in Hamiltonians of antiferromagnets is an independent problem, which calls for a more detailed analysis of the properties of real crystals. The problem in a somewhat different form holds also in the case of ferromagnetism. For example, the question of how the magnetization vector is oriented in each given domain (parallel or antiparallel to any one of the easiest-magnetization axis) calls for detailed information on the distribution of the internal magnetic stray fields, etc. Only an exact knowledge of these obviously sensitive properties allows us to say anything concerning the lifting of the degeneracy with respect to direction, i.e., with respect to a definite orientation of the magnetization vector at each point of the ferromagnet.

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