

Theory of Magnetism and the Ground-State Energy of a Linear Chain

DAVID I. PAUL

Department of Physics, University of California, Los Angeles, California

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The theory of strong magnetic effects is investigated from the point of view of orthogonal atomic functions for the case of one dimension. Thus, the exchange integral is considered positive and the interaction between the polar and the nonpolar states for all possible arrangements of electron spins is included in our formulation of the problem. The resulting secular equations are solved for both large and small interactions between states for the case of only one electron spin oriented in a direction opposite to all other electron spins, and they are solved for small interactions between states for the more general case of any number of electron spins being in a given direction. It is shown how inclusion of the polar states can yield either a ferromagnetic or an antiferromagnetic ground state depending on the difference in absolute magnitude between the exchange integral and the sum of other integrals representing electron-nuclei interactions.

I. INTRODUCTION

IN this paper we shall investigate the ground-state energy of a one-dimensional array of atoms. Each atom, in its isolated state, is considered to have one outer electron which is in an s state, all other electrons being in closed shells. We shall consider this problem from the point of view of rigorously orthogonal atomic functions. Thus, the exchange integral is positive for all cases, and the interaction between polar states and nonpolar states for all possible arrangements of electron spins is included in our formulation of the problem. The resulting secular equations are solved rigorously (for both large and small interactions between energy states) for the case of only one electron spin oriented in a direction opposite to all other electron spins and are solved for small interactions between polar and nonpolar energy states for the more general case of any number of electron spins being in a given direction. We shall show how the effect of polar states can yield either an antiferromagnetic or a ferromagnetic ground state depending on the difference in absolute magnitude between the exchange integral and the sum of other integrals representing electron-nuclei interactions. Inasmuch as this is for one dimension, we do not imply an ordered antiferromagnetic state nor do we attach any stability to a ferromagnetic ordered state, these being essentially three-dimensional effects.

The problem of extending the theory of magnetism to include the effect of polar states was considered by Slater¹ for the ferromagnetic case. Thus, Slater considered the interaction of a lowest state where all the electrons had their spins oriented in the same direction with the set of states where one electron only is disturbed from this lowest state by reversing its spin direction and either remaining on its original atom or forming a polar state by migrating to a different atom. The solution to the resulting configuration interaction problem is obtained by means of perturbation theory between the nonpolar states and those excited states consisting of the single electron migrating no further

than to a neighboring atom. In this paper, the reversal of the spin of only one electron is considered as a special case of the more general problem. The solution does not involve the use of perturbation theory and is thus valid for large as well as small interactions between the unperturbed nonpolar and polar energy states. Comparison is made between the two results in the region where they are both valid, and Slater's results are equivalent to ours. In the region of large interactions between states, the results obtained bear out the predictions made by Slater on the basis of his results for small perturbations.

The problem of a linear chain or ring where any number of electrons may reverse their spin was solved by Bethe and Hulthén^{2,3} where, however, the interaction of polar states was not considered. To compensate for this, the exchange integral was allowed to take either positive or negative values for the ferromagnetic and nonferromagnetic cases respectively. By extending the theory to include interactions with polar states, we are able, for small interactions between polar and nonpolar states, to obtain results with the use of a positive exchange integral and to show how the ground-state energy varies as a function of the configuration interaction or correlation energy. Before proceeding to the mathematical formulation of the problem, we mention that this type of problem is being attempted by Mattheiss⁴ using the methods originally formulated by Dirac, Van Vleck, and Serber⁵⁻⁷ using group theory. In this paper, we have considered the problem from the point of view of Slater determinants.

II. FORMULATION OF THE PROBLEM

Consider a periodic array of N atoms arranged in a closed linear chain or ring such that, counting in a counterclockwise direction from a given atom which we

² H. Bethe, *Z. Physik* **71**, 205 (1931).

³ L. Hulthén, *Arkiv Mat. Astron. Fysik* **26A**, 1 (1938).

⁴ L. F. Mattheiss, *Quart. Progress Rept. on the Solid State and Molecular Theory Group, M.I.T.*, July 15, 1959.

⁵ P. A. M. Dirac, *Proc. Roy. Soc. (London)* **A123**, 714 (1929).

⁶ J. H. Van Vleck, *Phys. Rev.* **45**, 405 (1934).

⁷ R. Serber, *Phys. Rev.* **45**, 461 (1934).

¹ J. C. Slater, *Phys. Rev.* **52**, 198 (1937).

arbitrarily choose as being at position one, the $N+1$ atom is this same atom. Each atom, in its isolated state is considered to have one outer or valence electron which is in an s state. The total energy of our system is represented by the Hamiltonian

$$H = \sum_{i=1}^N H(i) + \frac{1}{2} \sum'_{i,j=1}^N e^2/r_{ij} \quad (1)$$

where $H(i)$ represents the energy of the i th electron in the field of all the nuclei and bound electrons, e^2/r_{ij} is the Coulomb interaction potential between the i th and j th electrons, e is the absolute value of the electron charge, and r_{ij} is the distance between the i th and j th electrons. The prime on the last summation sign indicates that the case i equals j is excluded.

Our unperturbed ground states are those where each atom has one outer electron whose spin is oriented in either the plus z or minus z direction. We label the one electron eigenfunctions associated with the positions $f=1, 2, \dots, N$ as $\phi_f(x)\alpha_f(\zeta_i)$, $i=1, 2$, where ζ_1 signifies that the spin associated with this electron is oriented in the plus z direction while ζ_2 indicates the minus direction. We postulate that these atomic type ϕ_f functions are so constructed as to be orthogonal and normalized. Further, we label all those electrons with plus spin by the symbols f_1, f_2, \dots, f_r where r is the total number of electrons with plus spin and $f_1 < f_2 < \dots < f_r$ with respect to position in the ring. We then construct, by the usual method of Slater determinants, antisymmetric wave functions of the nonpolar type

$$\Psi(0; f_1 \dots f_r), \quad (2)$$

which are states consisting of electrons with plus spins at each of the positions $f_1 \dots f_r$ and electrons with minus spins at the remaining positions; and antisymmetric wave functions of the polar type

$$\Psi(f_j, -i; f_1 \dots f_r), \quad (3a)$$

and

$$\Psi(f_j, i; f_1 \dots f_r). \quad (3b)$$

Type (3a) designates those polar states formed by the migration of an electron with plus spin from the position f_j to the position f_j-i , where by the Pauli exclusion principle the electron originally at position f_j-1 has a minus spin. Further, as in type (2), there exist electrons with plus spins at each of the positions $f_1 \dots f_r$, where we include the plus spin associated with the polar atom in the r plus spins, while electrons of minus spin are at the remaining positions. Type (3b) is similar except that the electron with plus spin at position f_j has migrated to the position f_j+i . We adopt here the convention of labeling the polar electrons so that the electron with minus spin is labeled first, and one of these electrons bears the label associated with the position containing no electrons. Thus, in type (3a) we have an electron with minus spin at the position f_j-i and we label it f_j-i , and an electron with plus

spin at the position f_j-i but labeled f_j . This convention should lead to no confusion since our notation clearly indicates which positions contain polar atoms and which positions contain ionic atoms—atoms missing an electron.

For the case of only one electron spin oriented in a direction opposite to all other electrons, these are the only polar wave functions. For the case of more than one oppositely oriented electron spin there are of course wave functions consisting of more than one polar atom. However, in contrast to the single reversed spin problem, we restrict our solution of the more complicated many spin problem to the case of small interactions between functions of the form (1) and (2). In this case, the additional wave functions are not needed (see Appendix A).

We now form the functions $\Phi(r)$ composed of the linear combination of all possible functions of the type (2) and (3) with r electrons having their spins oriented in the plus z direction. Thus,

$$\Phi(r) = \sum_{i=-\frac{1}{2}N}^{\frac{1}{2}N} \sum_{f_1 \dots f_r} a(f_j, i; f_1 \dots f_r) \times \Psi(f_j, i; f_1 \dots f_r), \quad (4)$$

where $f_1 \dots f_r$ indicates the sum over all possible configurations having r plus spins and $i=0$ indicates a nonpolar state such as (2). The construction of this type of wave function was done by Schubin and Wonsowsky⁸ who then proceeded along different lines. Inasmuch as the set of functions $\Phi(r)$, $r=0, 1, \dots, \frac{1}{2}N$, are constants of the motion with respect to the Hamiltonian given in Eq. (1), our problem is to determine the eigenvalues or energy levels E_r corresponding to the eigenfunctions $\Phi(r)$ of the operator H , i.e.,

$$H\Phi(r) = E_r\Phi(r), \quad (5)$$

where we note that

$$\langle \Psi(f_j, i; f_1 \dots f_r) | \Psi(f'_j, i'; f'_1 \dots f'_r) \rangle = \delta_{i', i} \delta_{f'_j, f_j} \delta_{f'_1, f_1} \dots \delta_{f'_r, f_r}. \quad (6)$$

III. $r=1$

We first consider the relatively simple case of all electrons having their spins oriented in the minus z direction except for one electron having its spin in the plus z direction. This case was first considered by Bloch⁹ and later extended by Slater¹ to include the interaction of polar states—a final expression being obtained by the use of perturbation theory. We here extend these results by obtaining an exact solution for the one-dimensional problem.

We define the integrals

$$\langle \phi_{p+1}(1) | H(1) | \phi_p(1) \rangle = N, \quad (7)$$

$$\langle \phi_{p+1}(1) \phi_q(2) | e^2/r_{12} | \phi_p(1) \phi_q(2) \rangle = N_q, \quad (8)$$

⁸ S. Schubin and S. Wonsowsky, Proc. Roy. Soc. (London) A145, 159 (1934).

⁹ F. Bloch, Z. Physik 61, 206 (1930).

$$\langle \phi_p(1)\phi_p(2) | e^2/r_{12} | \phi_p(1)\phi_p(2) \rangle = W, \quad (9)$$

$$\langle \phi_p(1)\phi_{p+1}(2) | e^2/r_{12} | \phi_p(1)\phi_{p+1}(2) \rangle = C, \quad (10)$$

and

$$\langle \phi_p(1)\phi_{p+1}(2) | e^2/r_{12} | \phi_p(2)\phi_{p+1}(1) \rangle = J. \quad (11)$$

Since the $H(i)$ represent the energy of the i th electron in the field of all the nuclei and bound electrons, we see that N is related to the interaction between the electrons and the nuclei and thus to the splitting of the energy bands. For $q=p$ or $p+1$, the integral N_q is a two center integral and cannot be neglected. For $q \neq p$ nor $p+1$, this integral is either a three or four center integral and is small. Nevertheless, in the work following, it is found that N and N_q always occur in the form

$$\begin{aligned} M &\equiv N + \sum_{q \neq p} N_q \\ &= \langle \phi_{p+1}(i) | H(i) \\ &\quad + \sum_{q \neq p} \langle \phi_q(2) | e^2/r_{12} | \phi_q(2) \rangle | \phi_p(i) \rangle. \end{aligned} \quad (12)$$

Remembering that the standard Hartree equation is given by

$$[H(i) + \sum_{q \neq p} \langle \phi_q(2) | e^2/r_{12} | \phi_q(2) \rangle] \phi_p = \epsilon_i \phi_p + \sum_{q \neq p} \lambda_{pq} \phi_q, \quad (13)$$

where the λ_{pq} are the additional LaGrangian multipliers caused by the orthogonality conditions on the ϕ_q , we see that if one used the Hartree equation as a solution for the ϕ_p , then the quantity M could be represented by $\lambda_{p,p+1}$, and the finiteness of M reflects the orthogonality conditions imposed on the ϕ_q . The integral W is the Coulomb energy between two electrons located on the same atom and represents part of the unperturbed energy of the polar states. The integral C is the Coulomb energy between two electrons located on different atoms, while the integral J is the usual exchange integral for rigorously orthogonal atomic functions and is always positive.

The three center integral

$$\langle \phi_p(1)\phi_{p+1}(2) | e^2/r_{12} | \phi_{p+1}(1)\phi_{p+2}(2) \rangle$$

has been discussed by Slater¹ who showed that it is small and can be neglected. We also neglect all four center integrals as well as those integrals containing two atomic type functions which are separated by more than one interatomic distance as is customary.

We now multiply Eq. (5) by Eqs. (2) and (3) in turn, and noting that $r=1$, obtain the set of equations

$$\begin{aligned} \sum_f [a(0; f) \langle \Psi(0; f') | H | \Psi(0; f) \rangle + a(f, 1) \langle \Psi(0; f') | H | \Psi(f, 1) \rangle \\ + a(f, -1) \langle \Psi(0; f') | H | \Psi(f, -1) \rangle] - E_1 a(0; f') = 0, \end{aligned} \quad (13a)$$

$$\begin{aligned} \sum_f [a(0; f) \langle \Psi(f' - 1, 1) | H | \Psi(0; f) \rangle + a(f, 1) \langle \Psi(f' - 1, 1) | H | \Psi(f, 1) \rangle \\ + a(f, -1) \langle \Psi(f' - 1, 1) | H | \Psi(f, -1) \rangle + a(f, 2) \langle \Psi(f' - 1, 1) | H | \Psi(f, 2) \rangle] - E_1 a(f' - 1, 1) = 0, \end{aligned} \quad (13b)$$

$$\begin{aligned} \sum_f [a(0; f) \langle \Psi(f', -1) | H | \Psi(0; f) \rangle + a(f, 1) \langle \Psi(f', -1) | H | \Psi(f, 1) \rangle + a(f, -1) \langle \Psi(f', -1) | H | \Psi(f, -1) \rangle \\ + a(f, -2) \langle \Psi(f', -1) | H | \Psi(f, -2) \rangle] - E_1 a(f', -1) = 0, \end{aligned} \quad (13c)$$

$$\begin{aligned} \sum_f [a(f, 1) \langle \Psi(f' - 2, 2) | H | \Psi(f, 1) \rangle + a(f, 2) \langle \Psi(f' - 2, 2) | H | \Psi(f, 2) \rangle \\ + a(f, 3) \langle \Psi(f' - 2, 2) | H | \Psi(f, 3) \rangle] - E_1 a(f' - 2, 2) = 0, \end{aligned} \quad (13d)$$

$$\begin{aligned} \sum_f [a(f, -1) \langle \Psi(f', -2) | H | \Psi(f, -1) \rangle + a(f, -2) \langle \Psi(f', -2) | H | \Psi(f, -2) \rangle \\ + a(f, -3) \langle \Psi(f', -2) | H | \Psi(f, -3) \rangle] - E_1 a(f', -2) = 0, \end{aligned} \quad (13e)$$

$$\begin{aligned} \sum_f [a(f, 2) \langle \Psi(f' - 3, 3) | H | \Psi(f, 2) \rangle + a(f, 3) \langle \Psi(f' - 3, 3) | H | \Psi(f, 3) \rangle \\ + a(f, 4) \langle \Psi(f' - 3, 3) | H | \Psi(f, 4) \rangle] - E_1 a(f' - 3, 3) = 0, \end{aligned} \quad (13f)$$

...

where we have recognized that

$$\langle \Psi(f, i) | H | \Psi(f', -j) \rangle = 0, \quad i \text{ or } j \geq 2, \quad (14)$$

and

$$\langle \Psi(f, \pm i) | H | \Psi(f', \pm i + n) \rangle = 0, \quad |n| \geq 2. \quad (15)$$

Then, if we define ϵ_r as the energy difference between the energy eigenvalue E_r and the energy of the nonpolar state in which all electron spins are parallel,

$$\epsilon_r = E_r - e + NJ, \quad (16)$$

where e is the sum of the one electron and Coulomb interaction energies of the system, Eqs. (13) reduce to (dropping the primes)

$$\begin{aligned} \epsilon_1 a(0; f) + J[a(0; f+1) + a(0; f-1) - 2a(0; f)] \\ - M[a(f, -1) - a(f+1, -1) \\ + a(f-1, 1) - a(f, 1)] = 0, \end{aligned} \quad (17a)$$

$$\begin{aligned} (\epsilon_1 - W + C - 2J)a(f-1, 1) - Ja(f, -1) - M[a(0; f) \\ - a(0; f-1) + a(f-1, 2) - a(f-2, 2)] = 0, \end{aligned} \quad (17b)$$

$$\begin{aligned} (\epsilon_1 - W + C - 2J)a(f, -1) - Ja(f-1, 1) - M[a(0; f) \\ - a(0; f-1) + a(f, -2) - a(f+1, -2)] = 0, \end{aligned} \quad (17c)$$

$$\begin{aligned} (\epsilon_1 - W - 2J)a(f-2, 2) - M[a(f-2, 1) - a(f-1, 1) \\ + a(f-2, 3) - a(f-3, 3)] = 0, \end{aligned} \quad (17d)$$

$$\begin{aligned} (\epsilon_1 - W - 2J)a(f, -2) - M[a(f, -1) - a(f-1, -1) \\ + a(f, -3) - a(f+1, -3)] = 0, \end{aligned} \quad (17e)$$

$$\begin{aligned} (\epsilon_1 - W - 2J)a(f-3, 3) - M[a(f-3, 2) - a(f-2, 2) \\ + a(f-3, 4) - a(f-4, 4)] = 0, \end{aligned} \quad (17f)$$

...

A. Small Interactions

We shall first solve these equations for the coefficients $a(0; f)$, $a(f, 1)$, and $a(f, -1)$ only, assuming all other coefficients are zero. This will yield the results obtained by Slater valid when the interaction energy (resulting in the term M) between the unperturbed ground state wave functions $a(0; f)$ and the excited polar wave functions is small. We shall then expand on this method and obtain a general solution valid for all values of M .

Thus, subtracting Eq. (15c) from (15b), we get the result

$$a(f-1, 1) = a(f, -1). \quad (18)$$

Using this and putting $f = f+1$ in Eq. (17c), we again subtract Eq. (17c) from Eq. (17b), and substituting this result in Eq. (17a) obtain

$$\epsilon_1 a(0; f) + \{J + [2M^2/(\epsilon_1 - W + C - 3J)]\} \times [a(0; f+1) + a(0; f-1) - 2a(0; f)] = 0. \quad (19)$$

But this equation is of the same form as that solved by Bloch⁹ for the case of nonpolar states. The only differences are that in our case J is always positive as it contains only the Coulomb interaction potential as the perturbing energy term, and that we have the extra term $2M^2/(\epsilon_1 - 3J - W + C)$. Thus, we can immediately write the exact solution to this equation,

$$a(0; f) = e^{ikf}, \quad k = 2\pi p/N, \quad p = 0, 1, \dots, N-1, \quad (20)$$

which yields for ϵ_1 , the energy of the system with respect to its energy when all electron spins are lined up, the equation

$$\epsilon_1 = \frac{1}{2}(W - C + 5J - 2J \cos k) \pm \frac{1}{2}[(J + 2J \cos k + W - C)^2 + 16M^2(1 - \cos k)]^{1/2}. \quad (21)$$

We note the following: (1) when the term M (which arises from the interaction of the unperturbed polar and nonpolar states and which is discussed in the second paragraph of Sec. III), is zero, the ground-state energy reduces to $\epsilon_1 = 2J(1 - \cos k)$, the original expression obtained by Bloch. (2) For $M^2 \ll J^2$ we may expand the square root obtaining the solution (see Fig. 1)

$$\epsilon_1 = 2(1 - \cos k) \times \{J - [2M^2/(W - C + J(1 + 2 \cos k))]\}, \quad (22)$$

for the minus sign in Eq. (21). We may compare this equation with the result obtained by Slater¹ using perturbation theory. He obtains the expression [his Eq. (31) for one dimension]

$$\epsilon_1 = 2J(1 - \cos k) - 4W_R^2(1 - \cos k)/I_1, \quad (23)$$

where I_1 is the difference between the energy of the unperturbed polar and nonpolar states. We may connect our term M^2 with his W_R^2 while the factor $J(1 + 2 \cos k) + W - C$ may be written as the difference between the unperturbed polar energy $3J + W - C$ and the unperturbed nonpolar energy $2J(1 - \cos k)$ and

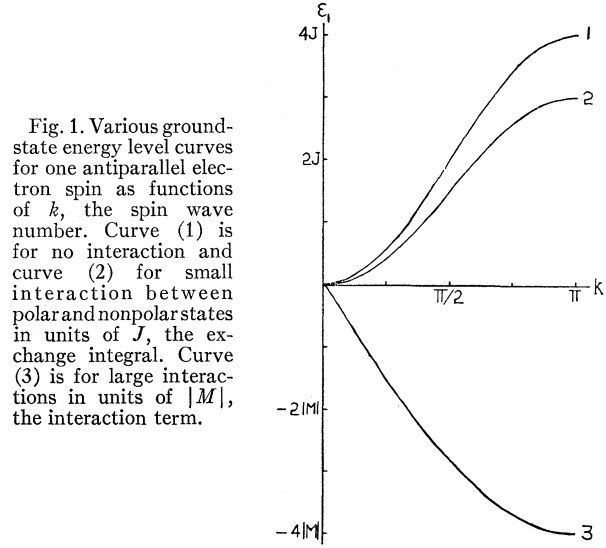


Fig. 1. Various ground-state energy level curves for one antiparallel electron spin as functions of k , the spin wave number. Curve (1) is for no interaction and curve (2) for small interaction between polar and nonpolar states in units of J , the exchange integral. Curve (3) is for large interactions in units of $|M|$, the interaction term.

is thus equivalent to his I_1 . Thus, we have essentially the same form.

B. General Solution

We now obtain a general solution to Eqs. (17) valid for all values of M . We do this by first solving (17a) through (17e) simultaneously but neglecting coefficients of the type $a(f, 3)$ and $a(f, -3)$. Following a procedure very similar to that just used, we obtain the results

$$a(f-1, 1) = a(f, -1), \quad (24)$$

$$a(f-2, 2) = -a(f, -2), \quad (25)$$

and an equation analogous to that of Eq. (19), i.e.,

$$\epsilon_1 a(0; f) + \left[J + \frac{2M^2}{\epsilon_1 - 3J - W + C} - \frac{2M^2(1 - \cos k_2)}{\epsilon_1 - 2J - W} \right] \times [a(0; f+1) + a(0; f-1) - 2a(0; f)] = 0, \quad (26)$$

where we have used the standard notation for continued fractions,

$$\frac{a_1 + b_2}{a_2 + b_3} = a_1 + \frac{b_2}{a_2 + \frac{b_3}{a_3 + \frac{b_4}{a_4 + \dots + \frac{b_n}{a_n}}}} \quad (27)$$

and where k_2 independently takes on the same values as k in Eq. (20), i.e., $k_2 = 2\pi p_2/N$, and $p_2 = 0, 1, \dots, N-1$.

We now solve Eqs. (17a) through (17g) simultaneously, neglecting coefficients of the type $a(f, 4)$ and $a(f, -4)$, and obtain the results of Eqs. (24) and (25)

above, the additional relation $a(f-3, 3)=a(f, -3)$, and the equation

$$\epsilon_1 a(0; f) + \left[J + \frac{2M^2}{\epsilon_1 - 3J - W + C} - \frac{2M^2(1 - \cos k_2)}{\epsilon_1 - 2J - W} - \frac{2M^2(1 - \cos k_3)}{\epsilon_1 - 2J - W} \right] [a(0; f+1) + a(0; f-1) - 2a(0; f)] = 0. \quad (28)$$

Thus, since further equations, (15h), (15i), etc., are of the same form, we may write for the general solution to the system of N equations given in (15),

$$\epsilon_1 - 2(1 - \cos k_1) \left[J + \frac{2M^2}{\epsilon_1 - 3J - W + C} - \frac{2M^2(1 - \cos k_2)}{\epsilon_1 - 2J - W} - \frac{2M^2(1 - \cos k_3)}{\epsilon_1 - 2J - W} - \dots - \frac{2M^2(1 - \cos k_{N/2})}{\epsilon_1 - 2J - W} \right] = 0. \quad (29)$$

For $k_1=0$, the solution to Eq. (29) is $\epsilon_1=0$ as is to be expected. We have already considered the case $M^2 \ll J^2$ in Sec. IIIA. For the case $M^2 \gg J^2$, i.e., the case of strong interactions between the energy states of the unperturbed wave functions, we must sum this continued fraction and solve the resulting equation in ϵ_1 . If $|M| \gg J, W$, and C , we may drop the terms containing these quantities in Eq. (29). If we now assume that all k_i have the same value, (this is an added restriction inasmuch as the k_i take on any one of the N values given in Eq. (20) independently), then the continued fraction is summable with the result, for N not small,

$$\epsilon_1 = -2\sqrt{2}|M|(1 - \cos k)^{\frac{1}{2}}. \quad (30)$$

Further, it is apparent that Eq. (30) yields both an upper bound (i.e., $k=0$) to the root of ϵ_1 corresponding to the ground state as well as the more interesting lowest energy value corresponding to $\cos k = -1$. Thus, there exists the lowest energy state

$$\epsilon_{\min} = -4|M|, \quad (31)$$

and we see that for a large absolute value of M [where the nature of M is discussed in the paragraph following Eq. (11)], the energy of the state $r=1$ is less than that

when all electron spins are oriented in the same direction. Thus, the ferromagnetic state is not the most stable state even though the exchange integral is positive, (see Fig. 1).

For the intermediate case, $W > |M| > J$ and C , the continued fraction is still summable if we again assume that all the k_i have the same value, and we obtain

$$\epsilon_1 = 2(1 - \cos k)[J - (2M^2/W)]. \quad (32)$$

In this equation, the sign of ϵ_1 , which determines whether the energy of the single reversed spin is greater or less than the ferromagnetic state, is determined by the quantity $J - (2M^2/W)$. If W , the difference between the energy of the excited polar states and the unperturbed ground states is sufficiently large, then, even when the electrons are quite close and the Fermi energy or electron-nuclei energy is larger than the exchange energy, the ferromagnetic state is still the most stable state.

As Slater¹ points out in his paper, his formula, Eq. (23), being derived from perturbation theory, is not very accurate for large perturbations, and so cannot be compared with our results (29) through (32). Nevertheless, it should be pointed out that the predictions made by Slater on the basis of his results for small W_R are borne out by the above calculations.

IV. $r \leq \frac{1}{2}N$

We now consider the general case where no limit is placed as to the number of electrons whose spins may be parallel or antiparallel. This was first considered by Bethe and Hulthén^{2,3} for nonpolar states. We here extend the theory to include polar states, keeping J always positive, and finding conditions for the lowest energy state. However, we restrict ourselves to the case of small interactions between the unperturbed wave functions of the ground state given by Eq. (2) and those of the excited polar states of the type in Eqs. (3). Thus, as explained in Appendix A, we only consider the wave functions given by Eqs. (2) and (3) where i is put equal to one. Multiplying Eq. (5) by each of the functions (2) and (3) in turn, our secular equations are

$$\sum_{f_1 \dots f_i \dots f_r} [a(f_j, 1; f_1 \dots f_r) \langle \Psi(0; f_1' \dots f_r') | H | \Psi(f_j, 1; f_1 \dots f_r) \rangle + a(f_j, -1; f_1 \dots f_r) \times \langle \Psi(0; f_1' \dots f_r') | H | \Psi(f_j, -1; f_1 \dots f_r) \rangle + a(0; f_1 \dots f_r) \langle \Psi(0; f_1' \dots f_r') | H | \Psi(0; f_1 \dots f_r) \rangle] - E_r a(0; f_1' \dots f_r') = 0 \quad (33)$$

$$\sum_{f_1 \dots f_i \dots f_r} [a(f_j, 1; f_1 \dots f_r) \langle \Psi(f_j' - 1, 1; f_1' \dots f_r') | H | \Psi(f_j, 1; f_1 \dots f_r) \rangle + a(f_j, -1; f_1 \dots f_r) \langle \Psi(f_j' - 1, 1; f_1' \dots f_r') | H | \Psi(f_j, -1; f_1 \dots f_r) \rangle + a(0; f_1 \dots f_r) \langle \Psi(f_j' - 1, 1; f_1' \dots f_r') | H | \Psi(0; f_1 \dots f_r) \rangle] - E_r a(f_j' - 1, 1; f_1' \dots f_r') = 0, \quad (34a)$$

and

$$\sum_{f_1 \dots f_i \dots f_r} [a(f_j, 1; f_1 \dots f_r) \langle \Psi(f_j', -1; f_1' \dots f_r') | H | \Psi(f_j, 1; f_1 \dots f_r) \rangle + a(f_j, -1; f_1 \dots f_r) \langle \Psi(f_j', -1; f_1' \dots f_r') | H | \Psi(f_j, -1; f_1 \dots f_r) \rangle + a(0; f_1 \dots f_r) \langle \Psi(f_j', -1; f_1' \dots f_r') | H | \Psi(0; f_1 \dots f_r) \rangle] - E_r a(f_j', -1; f_1' \dots f_r') = 0. \quad (34b)$$

We note that Eqs. (33) and (34) are representative equations for functions whose spin distributions, indicated by primes, are identical. We expand the antisymmetric functions Ψ , in terms of the one electron atomic type functions ϕ , and using the definitions given in Eqs. (7) through (12), reduce Eqs. (33) and (34) to

$$\begin{aligned} \epsilon_r a(0; \dots f_j \dots) + J \sum_{j=1}^r \{ [a(0; \dots f_j + 1 \dots) - a(0; \dots f_j \dots)] (1 - \delta_{f_{j+1} f_{j+1}^{f_j+1}}) \\ + [a(0; \dots f_j - 1 \dots) - a(0; \dots f_j \dots)] (1 - \delta_{f_{j-1} f_{j-1}^{f_j-1}}) \} - M \sum_j \{ [a(f_j - 1, 1; \dots f_i \dots) \\ + a(f_j, -1; \dots f_i \dots)] (1 - \delta_{f_{j-1} f_{j-1}^{f_i-1}}) - [a(f_j, 1; \dots f_i \dots) + a(f_j + 1, -1; \dots f_i \dots)] (1 - \delta_{f_{j+1} f_{j+1}^{f_i+1}}) \} = 0, \end{aligned} \quad (35)$$

$$\begin{aligned} (\epsilon_r - W + C - 2J) a(f_j - 1, 1; \dots f_i \dots) - J a(f_j, -1; \dots f_i \dots) + J \sum_{i=1 (i \neq j)}^r \{ [a(f_j - 1, 1; \dots f_i + 1 \dots) \\ - a(f_j - 1, 1; \dots f_i \dots)] (1 - \delta_{f_{i+1} f_{i+1}^{f_i+1}}) (1 - \delta_{f_i f_i^{f_i-2}}) + [a(f_j - 1, 1; \dots f_i - 1 \dots) - a(f_j - 1, 1; \dots f_i \dots)] \\ \times (1 - \delta_{f_{i-1} f_{i-1}^{f_i-1}}) \} - M [a(0; \dots f_j \dots) - a(0; \dots f_j - 1 \dots)] (1 - \delta_{f_{j-1} f_{j-1}^{f_j-1}}) = 0, \end{aligned} \quad (36a)$$

and

$$\begin{aligned} (\epsilon_r - W + C - 2J) a(f_j, -1; \dots f_i \dots) - J a(f_j - 1, 1; \dots f_i \dots) + J \sum_{i \neq j} \{ [a(f_j, -1; \dots f_i + 1 \dots) \\ - a(f_j, -1; \dots f_i \dots)] (1 - \delta_{f_{i+1} f_{i+1}^{f_i+1}}) (1 - \delta_{f_i f_i^{f_i-2}}) + [a(f_j, -1; \dots f_i - 1 \dots) - a(f_j, -1; \dots f_i \dots)] \\ \times (1 - \delta_{f_{i-1} f_{i-1}^{f_i-1}}) \} - M [a(0; \dots f_j \dots) - a(0; \dots f_j - 1 \dots)] (1 - \delta_{f_{j-1} f_{j-1}^{f_j-1}}) = 0, \end{aligned} \quad (36b)$$

where we have made use of the delta function to take into account those configurations having electrons with plus spins adjacent to each other or to the polar atoms. Thus, $\delta_{f_{i+1} f_{i+1}^{f_i+1}}$ is unity if the f_{i+1} plus spin is at position $f_i + 1$ and is zero otherwise. Remembering that the f_k are the same in Eqs. (36a) and (36b), we subtract the second equation from the first to get the relation

$$\begin{aligned} (\epsilon_r - W + C - J) d_-(f_j; \dots f_i \dots) + J \sum_{i \neq j} \{ [d_-(f_j; \dots f_i + 1 \dots) - d_-(f_j; \dots f_i \dots)] (1 - \delta_{f_i f_i^{f_i-2}}) \\ + [d_-(f_j; \dots f_i - 1 \dots) - d_-(f_j; \dots f_i \dots)] (1 - \delta_{f_{i-1} f_{i-1}^{f_i-1}}) \} = 0, \end{aligned} \quad (37)$$

where

$$d_-(f_j; \dots f_i \dots) = a(f_j - 1, 1; \dots f_i \dots) - a(f_j, -1; \dots f_i \dots), \quad (38)$$

is a function which is antisymmetric in the position coordinates of the polar atoms. Recognizing Eq. (37) as the equation for the energy of the excited polar states, we note that the solution is analogous to that given by Bethe and Hulthén for the energy of states with no polar atoms, i.e.,

$$\begin{aligned} \sum_{i \neq j} d_-(f_j; \dots f_i + 1 \dots) &= d_-(f_j; \dots f_i \dots) \sum_{p=1 (p \neq j)}^r e^{ik_p}, \\ \sum_{i \neq j} d_-(f_j; \dots f_i - 1 \dots) &= d_-(f_j; \dots f_i \dots) \sum_{p \neq j} e^{-ik_p}, \end{aligned} \quad (39)$$

and thus

$$[\epsilon_r + C - W - J - 2J \sum_{p \neq j} (1 - \cos k_p')] d_-(f_j; \dots f_i \dots) = 0, \quad (40)$$

where the k_p' are determined by the boundary conditions, (see Appendix B). We use the solution $d_-(f_j; \dots f_i \dots) = 0$, or

$$a(f_j - 1, 1; \dots f_i \dots) = a(f_j, -1; \dots f_i \dots). \quad (41)$$

Noting that, except for the case where $f_j + 1 = f_{j+1}$, Eq. (36b) is also valid for configurations where f_j is put at $f_j + 1$ and all other plus spins are made to retain their original positions, we make this substitution and subtract the resulting equation from Eq. (36a). If we further observe that the terms

$$\begin{aligned} (\epsilon_r - W + C - 3J) d(f_j; \dots f_i \dots) + J \sum_{i \neq j} \{ [d(f_j; \dots f_i + 1 \dots) - d(f_j; \dots f_i \dots)] (1 - \delta_{f_{i+1} f_{i+1}^{f_i+1}}) (1 - \delta_{f_i f_i^{f_i-2}}) \\ + [d(f_j; \dots f_i - 1 \dots) - d(f_j; \dots f_i \dots)] (1 - \delta_{f_{i-1} f_{i-1}^{f_i-1}}) \} \end{aligned} \quad (42)$$

and their counterpart for f_j placed equal to $f_j + 1$, where

$$d(f_j; \dots f_i \dots) = a(f_j, -1; \dots f_i \dots) + a(f_j - 1, 1; \dots f_i \dots),$$

may be represented as (see Appendix B),

$$[\epsilon_r - W + C - 3J - 2J \sum_{p \neq j} (1 - \cos k_p')] d(f_j; \dots f_i \dots)$$

and

$$[\epsilon_r - W + C - 3J - 2J \sum_{p \neq j} (1 - \cos k_p')] (1 - \delta_{f_{j+1} f_{j+1}^{f_j+1}}) d(f_j + 1; \dots f_i \dots)$$

respectively, then, we obtain after summing over all j , the equation

$$\begin{aligned} & [\epsilon_r - W + C - 3J - 2J \sum_{p \neq j} (1 - \cos k_p')] \sum_j [d(f_j; \dots f_i \dots) - (1 - \delta_{f_{j+1} f_i+1}) d(f_j + 1; \dots f_i \dots)] \\ & + 2M \sum_j \{ [a(0; \dots f_j + 1 \dots) - a(0; \dots f_j \dots)] (1 - \delta_{f_{j+1} f_i+1}) \\ & + [a(0; \dots f_j - 1 \dots) - a(0; \dots f_j \dots)] (1 - \delta_{f_{j-1} f_i-1}) \} = 0. \end{aligned} \quad (43)$$

Finally, using Eq. (41), we substitute Eq. (43) into Eq. (35) and get

$$\epsilon_r a(0; \dots f_j \dots) + \{ J + [2M^2 / (\epsilon_r - W + C - 3J - 2J \sum_{p \neq j} (1 - \cos k_p'))] \} \sum_j \{ [a(0; \dots f_j + 1 \dots) - a(0; \dots f_j \dots)] (1 - \delta_{f_{j+1} f_i+1}) + [a(0; \dots f_j - 1 \dots) - a(0; \dots f_j \dots)] (1 - \delta_{f_{j-1} f_i-1}) \} = 0. \quad (44)$$

But this equation is of the same form as that solved by Bethe and Hulthén for the case of nonpolar wave functions. The only difference is that J is always positive and there is the extra term

$$2M^2 / [\epsilon_r - W + C - 3J - 2J \sum_{p \neq j} (1 - \cos k_p')] \quad (45)$$

which, compared with the extra term in Eq. (19) for only one spin reversed, contains the additional sum over p part. From Bethe and Hulthén's work, we can write down the exact solution as

$$\begin{aligned} \epsilon_r(k_j) = & \frac{3}{2}J + \frac{1}{2}(W - C) + J \sum_{p=1}^r (1 - \cos k_p') + J \sum_{q=1}^r (1 - \cos k_q) \pm \{ [\frac{3}{2}J + J \sum_{p=1}^r (1 - \cos k_p') \\ & - J \sum_{q=1}^r (1 - \cos k_q) + \frac{1}{2}(W - C)]^2 + 4M^2 \sum_{q=1}^r (1 - \cos k_q) \}^{\frac{1}{2}}. \end{aligned} \quad (46)$$

We note the following: (1) when M is zero (i.e., no interaction between the unperturbed wave functions), the energy ϵ_r reduces to the original expression

$$\epsilon_r = 2J \sum_q (1 - \cos k_q)$$

obtained by Bethe and Hulthén. (2) For $M^2 \ll J^2$, (weak interaction between the unperturbed wave functions), we may expand the square root in Eq. (46) obtaining the solution

$$\epsilon_r = 2J \sum_q (1 - \cos k_q) \times \{ 1 - [2M^2 / (J^2(1 + 2 \cos k) + JW - JC)] \} \quad (47)$$

where we have neglected the small difference between k_q and k_p' , (see Appendix B), and written k for k_j .

It would be desirable at this point to consider the case of strong interactions, $M^2 \gg J^2$, as in Sec. IIIB. However, as pointed out in the Appendix, when the interaction terms represented by M are large, the solution for $r \geq 2$ becomes questionable. Thus, we merely indicate the general trend by noting that for $M^2 \gg J^2$ and W , the energy expression given by Eq. (46) becomes

$$\epsilon_r \sim -2|M| [\sum_q (1 - \cos k_q)]^{\frac{1}{2}} \quad (48)$$

and we see that the energy continues to decrease as r increases, reaching its lowest value at $r = \frac{1}{2}N$. For $W > M > J$,

$$\epsilon_r \sim 2 \sum_q (1 - \cos k_q) [J - (2M^2/W - C)], \quad (49)$$

we again get a criterion for stability between the relative magnitudes of the ratios $J/|M|$ and $|M|/W$ as we did in Sec. IIIB for just one reversed spin.

We conclude with the general statement that consideration of the polar states allows the use of orthogonal

functions, (implicitly assumed in most ferromagnetic and antiferromagnetic calculations), and thus a positive exchange integral while still yielding conditions for a ferromagnetic or antiferromagnetic state, bearing out Slater's statements concerning this matter.

APPENDIX A

A more general unperturbed antisymmetric wave function than that given in Eq. (4) is

$$\begin{aligned} \Phi(r) = & \sum_{m=0}^{N/2} \sum_{i_1 \dots i_m} \sum_{p_1 \dots p_m} \sum_{f_1 \dots f_r} \\ & \times a(p_1 \dots p_m, i_1 \dots i_m; f_1 \dots f_r) \\ & \times \Psi(p_1 \dots p_m, i_1 \dots i_m; f_1 \dots f_r), \end{aligned} \quad (A1)$$

where m is the number of polar atoms and the symbols p_j and i_j designate the migration of an electron with plus spin from the position p_j to the position $p_j + i_j$. For $r > 1$, this expression gives wave functions not considered in our paper. However, wave functions having two or more polar atoms of the type given in Eq. (A1) have no direct interaction with nonpolar wave functions, i.e.,

$$\langle \Psi(p_1 \dots p_m, i_1 \dots i_m; f_1 \dots f_r) | H | \Psi(0; f_1' \dots f_r') \rangle = 0, \quad m \geq 2. \quad (A2)$$

Also, there is no direct interaction between the nonpolar wave functions and those wave functions consisting of one polar atom whose extra electron has migrated further than one interatomic distance, i.e.,

$$\langle \Psi(p_j, i_j; f_1 \dots f_r) | H | \Psi(0; f_1' \dots f_r') \rangle = 0, \quad |i_j| \geq 2, \quad (A3)$$

where we are using the conditions discussed in the paragraph following Eq. (11). Similarly, wave functions of three or more polar atoms, of one polar atom whose electron has migrated more than two interatomic units, and of two polar atoms with both electrons having migrated further than nearest neighbors have no direct interaction with the wave functions considered in Eq. (4) for $i \leq 1$. It is true of course that wave

functions consisting of one polar atom whose extra electron has migrated from an atom further than one interatomic distance and of two polar atoms whose extra electrons come from neighboring atoms do have interaction terms of the type M with our one polar atom wave functions given in Eq. (3) for $i=1$, and this modification, in turn, may influence the ground-state energy. In fact, the secular equation is of the form

$$\begin{vmatrix} H_1-E, & H_{10}, & 0, & 0, & 0, & \dots \\ H_{01}, & H_1-E, & H_{12}, & 0, & 0, & \\ 0, & H_{21}, & H_2-E, & H_{23}, & 0, & \\ 0, & 0, & H_{32}, & H_3-E, & H_{34}, & \\ \vdots & & & & & \ddots \\ \vdots & & & & & \\ \vdots & & & & & H_r-E \end{vmatrix} = 0, \quad (\text{A4})$$

where

$$H_m = \langle \Phi_m(r) | H | \Phi_m(r) \rangle, \quad (\text{A5})$$

$$H_{m,n} = \langle \Phi_m(r) | H | \Phi_n(r) \rangle, \quad (\text{A6})$$

and

$$\begin{aligned} \Phi_m(r) = & \sum_{i_1 \dots i_m} \sum_{p_1 \dots p_m} \sum_{f_1 \dots f_r} \\ & \times a(p_1 \dots p_m, i_1 \dots i_m; f_1 \dots f_r) \\ & \times \Psi(p_1 \dots p_m, i_1 \dots i_m; f_1 \dots f_r). \end{aligned} \quad (\text{A7})$$

Neglecting all but the first two elements in rows one and two (as well as terms contained in these elements such as $i_1 \geq 2$) is equivalent to assuming the interaction terms between the unperturbed states are small. It would of course be desirable to obtain a general solution for both large r and large interaction terms. Work is proceeding along these lines.

APPENDIX B

Equation (37) is identical in form with Eq. (III,15) of Hulthén³ except for the added restrictions with respect to the two atomic positions for the polar and ionic atoms. Essentially, one could consider Eq. (37) as the problem of a linear chain with fixed end points occurring at f_j+1 for one end and f_j-2 at the other end. Further, that there are $r-1$ electrons with plus

spin and a total of $N-2$ electrons. A solution to this problem may be obtained by a typical application of Born-Von Kármán boundary conditions, i.e., we add a hypothetical atom having an electron with a minus spin on each end and impose the requirement that the hypothetical electron of minus spin at position f_j have the same phase as the electron at f_j-2 . If N is a large number and the interaction is short range (both factors true in this case), the additional atoms cannot affect the nature of the frequency distribution and at the same time they take proper account of the number degrees of freedom. Thus, the solution is the same as that obtained by Bethe and Hulthén, except that Eq. (III,21) of Hulthén, i.e.,

$$Nk_j + 2\pi\lambda_j + \sum_l \phi_{jl}, \quad \lambda_j = 0, 1, 2, \dots, N-1,$$

where the ϕ_j represent the phases in the solution is replaced by

$$Nk_j' + 2\pi\lambda_j + \sum_l \phi_{jl}', \quad \lambda_j = 0, 1, 2, \dots, N-3. \quad (\text{B1})$$

Since, in this paper, we are not concerned with $\lambda_j > \frac{1}{2}N$, we may assume, as the only significant difference in the solution of Eq. (37) from the usual Bethe-Hulthén solution, the fact that we have only $r-1$ spin waves. In Eq. (47) we even neglect the small difference between k_j and k_j' .