

Magnetism and the Ground-State Energy of a Linear Chain. II. Configuration Interaction Effects

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We continue the investigation, begun in the previous paper of this series, on the ground-state energy of a one-dimensional chain of atoms from the point of view of orthogonal atomic functions. Thus, the exchange integral is positive and the configuration interaction between polar and nonpolar states is included. Our results are extended to include the condition of a large amount of overlap among the unperturbed nonorthogonal atomic functions

resulting in a strong interaction between the orthogonalized nonpolar and polar energy states for the case of two electrons having their spins oriented opposite to all other electron spins. These results indicate that for this case the energy of the unmagnetized state is lower than that obtained when all the electron spins are parallel and that the system is nonferromagnetic.

I. INTRODUCTION

IN this paper, we have extended the investigations of the ground-state energy of a one-dimensional array of atoms begun previously by the author¹ (hereafter referred to as DP I). This extension gives us further information about the correlation energy of such a ground state and also allows us to make some comments with respect to the validity of the Dirac spin Hamiltonian when the atomic functions are non-orthogonal.

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 treat this problem from the point of view of rigorously orthogonal atomic wave functions. Thus, the exchange integral is always positive, and the interaction between polar and nonpolar states must be included. In this paper we have succeeded in obtaining results for the case of two electrons having their spins oriented in a direction opposite to all other electron spins. These results are valid for the first time in the region of large interactions between polar and nonpolar states. Slater² has pointed out that in order to orthogonalize the atomic wave functions it is necessary to form a linear combination of these non-orthogonal atomic functions with the polar state atomic wave functions. Thus, if the amount of overlap of the nonorthogonal atomic wave functions is large or the interatomic distance between atoms is small for the substance, then the region of strong interactions between orthogonalized nonpolar and polar states is a very important one—in particular, since almost all calculations assume orthogonalized wave functions. In DP I, the secular equations for the case of only one electron spin oriented in a direction opposite to all other electron spins was solved rigorously for both large and small interactions. *Note added in proof.*—In DP I, the summation of the continued fraction in Eq. (29) is exact for large M inasmuch as the k_i are always equal—private communication with L. Mattheiss. Although this was of interest, especially for the ferromagnetic

case, the solution for two electron spins reversed in direction takes into account the effect of spin-spin interaction.

The problem of extending the theory of magnetism to include the effect of polar states was first considered by Slater² for the ferromagnetic case. Thus, Slater compared the energy of a lowest state where all the electrons had their spins oriented in the same direction with the energy of 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 nearest neighbor atom. The solution of the resulting configuration interaction problem for one electron spin reversed 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 DP I, the reversal of only one electron spin is solved rigorously—without the use of perturbation theory and including those polar states formed by the electron migrating to any other atom—and is thus valid for large as well as small interactions between the orthogonalized nonpolar and polar energy states. The problem of a linear chain or ring where any number of electrons may reverse their spin was solved by Bethe³ and Hulthén⁴ 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. In DP I, we extended the theory to include interactions with polar states. For small interactions between polar and nonpolar states, we were able to obtain results valid for any number of reversed electron spins and to show how the ground-state energy varies as a function of the configuration interaction or correlation energy. It was found that the usual exchange integral in the Dirac-Van Vleck spin operator is replaced by the difference between the exchange integral and the ratio of the square of the interaction energy divided by the polar

¹ D. I. Paul, Phys. Rev. **118**, 92 (1960).

² J. C. Slater, Phys. Rev. **52**, 198 (1937).

³ H. Bethe, Ann. Physik **71**, 205 (1931).

⁴ L. Hulthén, Arkiv. Mat. Astron. Fysik **26a**, 1 (1938).

energy, and the sign of the coefficient is determined by the difference in magnitude of these two quantities.

The results obtained in this paper are for the case of two electrons having their spin reversed, and are valid for large interactions. These results indicate that for this case the energy of the unmagnetized state is lower than that obtained when all the electron spins are parallel and that the system is nonferromagnetic.

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 counter-clockwise direction from a given atom which we 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

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

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, subject to the restriction that there exist a total of two electrons with their spin in the plus z direction—all other electrons having their spins in the 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 selected positions in the linear ring by the symbols, f_1, f_2, f_3, \dots where $f_1 < f_2 < f_3 < \dots$.

We then construct by the usual method of Slater determinants, antisymmetric wave functions of the nonpolar type

$$\Psi(f_1 f_2), \quad (2)$$

which are states consisting of two electrons with plus spins at the positions f_1 and f_2 , and electrons with minus spins at the remaining positions. Since f_2 is always greater than f_1 , this notation is in accordance with the quantum mechanical statement of the indistinguishability of two states differing only by the interchange of their electrons. We also construct antisymmetric wave

functions of the polar types

$$\Psi(f_1 f_2 f_3), \quad (3)$$

and

$$\Psi(f_1 f_2, f_3 f_4). \quad (4)$$

The first position in type (3) designates the location of a plus spin located on a nonpolar atom while the second position designates the location of a polar atom formed by the migration of an electron with plus spin from the location given by the third position. Since the interchange of a polar position with a position containing either one or no electrons is a distinguishable state, any permutation of the three symbols is permissible. The wave function given in Eq. (4) designates the states consisting of two polar atoms, located at f_1 and f_2 , and formed by the migration of two electrons—one from the third position designated in this example by f_3 and the other from the fourth position designated by f_4 . In accordance with the above mentioned quantum mechanical principle, we impose the requirements that the location of the first position must always be less than the location of the second position and similarly that the location of the third position must always be less than the location of the fourth position in our linear ring of atoms. Thus, the wave function

$$\Psi(f_1 f_4, f_2 f_3), \quad (4a)$$

is a permissible wave function while the function

$$\Psi(f_2 f_1, f_3 f_4), \quad (5)$$

is not allowed as it has already been enumerated by Eq. (4). Finally, to avoid ambiguity, we adopt here the convention of labeling the polar electrons so that the electron with minus spin is always labeled first with respect to position in the ring and one of the two polar electrons in the first polar atom bears, the label associated with the first position containing no electrons. Thus, in Eq. (4) we have an electron with plus spin at each of the positions f_1 and f_2 , but they are labeled f_3 and f_4 , respectively, while in Eq. (4a) we have an electron with plus spin at the position f_1 but labeled f_2 and an electron with minus spin at the position f_4 but labeled f_3 . This convention should lead to no confusion since our notation clearly indicates which positions contain polar atoms and which positions contain atoms missing an electron.

For the case we are considering—that of two electrons oriented in a direction opposite to all other electrons—these are the only possible wave functions for the atomic s state. For more than two oppositely oriented electron spins the different types of wave functions increases and the problem becomes more complicated.

We now form the function $\Phi(2)$ composed of the linear combination of all possible functions of the types

(2), (3), and (4). Thus,

$$\Phi(2) = \sum_{f_1 f_2} a(f_1 f_2) \Psi(f_1 f_2) + \sum_{f_1 f_2 f_3} a(f_1 f_2 f_3) \Psi(f_1 f_2 f_3) \\ + \sum_{f_1 f_2 f_3 f_4} a(f_1 f_2 f_3 f_4) \Psi(f_1 f_2 f_3 f_4), \quad (6)$$

where the summations are over all possible allowed values and permutations of the f 's and

$$H\Phi(2) = E_2 \Phi(2). \quad (7)$$

III. THE SECULAR EQUATIONS

We recall the integrals defined and discussed in DP I, i.e.,

$$\langle \phi_p(1) \phi_p(2) | e^2/r_{12} | \phi_p(1) \phi_p(2) \rangle = W, \quad (8)$$

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

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

and

$$\langle \phi_{p+1}(1) | H(1) + \sum_{q \neq p} \langle \phi_q(2) | e^2/r_{12} | \phi_q(2) \rangle | \phi_p(1) \rangle = M. \quad (11)$$

The integrals W and C represent, respectively, major and minor contributions to the formation of a polar atom; J is the usual exchange integral and is always positive; and M is our interaction integral or off diagonal matrix element between the polar and nonpolar states and is a direct reflection of the orthogonality conditions imposed on the atomic functions (See DP I). Essentially, the imposing of orthogonality requirements on the atomic functions is satisfied by a linear combination of these nonorthogonal atomic functions with the polar state atomic wave functions. This raises the unperturbed ground-state energy level such that the new ground-state level corresponding to the orthogonal atomic functions $\phi_f(x)$ may now interact strongly with the excited polar states which in turn may interact strongly with each other, and M may be quite large. As is customary, we neglect all three and four center integrals as well as those integrals containing two atomic type functions which are separated by more than one interatomic distance.

We now multiply Eq. (7) by Eqs. (2), (3), and (4) in turn and obtain the set of equations defining the coefficients given by the a 's in terms of matrix elements of the Ψ 's. Then, with the aid of Eqs. (8) through (11), we may evaluate these matrix elements and obtain the complete set of secular equations defining the coefficients for the case of two electrons with reversed spin. We have done this but list the equations for only the first few configurations in this paper. Thus, defining ϵ_2

as the energy difference between the energy eigenvalue E_2 and the energy of the nonpolar state in which all electron spins are parallel, i.e.,

$$\epsilon_2 = E_2 - e + NJ, \quad (12)$$

where e is the sum of the one-electron and Coulomb interaction energies of the system, we get the secular equations

$$\epsilon_2 a(f_1 f_2) + J \{ a(f_1 - 1 f_2) + a(f_1 f_2 + 1) - 2a(f_1 f_2) \\ + [a(f_1 + 1 f_2) + a(f_1 f_2 - 1) - 2a(f_1 f_2)] (1 - \delta_{f_1 + 1 f_2}) \} \\ - M \{ a(f_2 f_1 f_1 - 1) + a(f_2 f_1 - 1 f_1) - a(f_1 f_2 f_2 + 1) \\ - a(f_1 f_2 + 1 f_2) + [a(f_1 f_2 f_2 - 1) + a(f_1 f_2 - 1 f_2) \\ - a(f_2 f_1 f_1 + 1) - a(f_2 f_1 + 1 f_1)] (1 - \delta_{f_1 + 1 f_2}) \} = 0, \quad (13a)$$

$$(\epsilon_2 - W + C - 2J) a(f_1 f_2 f_2 + 1) \\ + J \{ [a(f_1 + 1 f_2 f_2 + 1) - a(f_1 f_2 f_2 + 1)] (1 - \delta_{f_1 + 1 f_2}) \\ + a(f_1 - 1 f_2 f_2 + 1) - a(f_1 f_2 f_2 + 1) - a(f_1 f_2 + 1 f_2) \} \\ - M \{ a(f_1 f_2 + 1) - a(f_1 f_2) - a(f_1 f_2 f_2 + 2) \\ + a(f_1 f_2 - 1 f_2 + 1) (1 - \delta_{f_1 + 1 f_2}) + a(f_2 f_2 - 1 f_2 + 1) \delta_{f_1 + 1 f_2} \\ + a(f_1 - 1 f_2, f_1 f_2 + 1) + a(f_1 f_2, f_1 - 1 f_2 + 1) \\ - [a(f_1 f_2, f_1 + 1 f_2 + 1) + a(f_1 + 1 f_2, f_1 f_2 + 1)] \\ \times (1 - \delta_{f_1 + 1 f_2}) \} = 0, \quad (13b)$$

$$(\epsilon_2 - W + C - 2J) a(f_2 f_1 - 1 f_1) + J \{ a(f_2 + 1 f_1 - 1 f_1) \\ - a(f_2 f_1 - 1 f_1) + [a(f_2 - 1 f_1 - 1 f_1) \\ - a(f_2 f_1 - 1 f_1)] (1 - \delta_{f_1 + 1 f_2}) - a(f_2 f_1 f_1 - 1) \} \\ - M \{ a(f_1 f_2) - a(f_1 - 1 f_2) + a(f_2 f_1 - 2 f_1) \\ - a(f_2 f_1 - 1 f_1 + 1) (1 - \delta_{f_1 + 1 f_2}) - a(f_1 f_1 - 1 f_1 + 1) \delta_{f_1 + 1 f_2} \\ + [a(f_1 - 1 f_2 - 1, f_1 f_2) + a(f_1 - 1 f_2, f_1 f_2 - 1)] \\ \times (1 - \delta_{f_1 + 1 f_2}) - a(f_1 - 1 f_2, f_1 f_2 + 1) \\ - a(f_1 - 1 f_2 + 1, f_1 f_2) \} = 0, \quad (13c)$$

and for $i \geq 2$,

$$(\epsilon_2 - W - 2J) a(f_1 f_2 f_2 + i) \\ + J \{ [a(f_1 + 1 f_2 f_2 + i) - a(f_1 f_2 f_2 + i)] (1 - \delta_{f_1 + 1 f_2}) \\ + a(f_1 - 1 f_2 f_2 + i) - a(f_1 f_2 f_2 + i) \} \\ - M \{ a(f_1 f_2 + 1 f_2 + i) - a(f_1 f_2 f_2 + i + 1) \\ - a(f_1 f_2 f_2 + i - 1) + a(f_1 f_2 - 1 f_2 + i) (1 - \delta_{f_1 + 1 f_2}) \\ + a(f_2 f_2 - 1 f_2 + i) \delta_{f_1 + 1 f_2} + a(f_1 - 1 f_2, f_1 f_2 + i) \\ + a(f_1 f_2 f_1 - 1 f_2 + i) - [a(f_1 f_2, f_1 + 1 f_2 + i) \\ + a(f_1 + 1 f_2, f_1 f_2 + i)] (1 - \delta_{f_1 + 1 f_2}) \} = 0, \quad (13d)$$

$$(\epsilon_2 - W - 2J) a(f_2 f_1 - i f_1) \\ + J \{ a(f_2 + 1 f_1 - i f_1) - a(f_2 f_1 - i f_1) \\ + [a(f_2 - 1 f_1 - i f_1) - a(f_2 f_1 - i f_1)] (1 - \delta_{f_1 + 1 f_2}) \} \\ - M \{ a(f_2 f_1 - i + 1 f_1) + a(f_2 f_1 - i - 1 f_1) \\ - a(f_2 f_1 - i f_1 - 1) - a(f_2 f_1 - i f_1 + 1) (1 - \delta_{f_1 + 1 f_2}) \\ - a(f_1 f_1 - i f_1 + 1) \delta_{f_1 + 1 f_2} + [a(f_1 - i f_2 - 1, f_1 f_2) \\ + a(f_1 - i f_2, f_1 f_2 - 1)] (1 - \delta_{f_1 + 1 f_2}) - a(f_1 - i f_2, f_1 f_2 + 1) \\ - a(f_1 - i f_2 + 1, f_1 f_2) \} = 0. \quad (13e)$$

For $f_2 < f_1 + i$, we have

$$\begin{aligned}
 &(\epsilon_2 - W - 2J)a(f_2 f_1 f_1 + i) \\
 &+ J\{[a(f_2 + 1 f_1 f_1 + i) - a(f_2 f_1 f_1 + i)] \\
 &\times (1 - \delta_{f_1 + i - 1 f_2}) + [a(f_2 - 1 f_1 f_1 + i) - a(f_2 f_1 f_1 + i)] \\
 &\times (1 - \delta_{f_1 + 1 f_2})\} - M\{a(f_2 f_1 - 1 f_1 + i) \\
 &- a(f_2 f_1 f_1 + i + 1) + a(f_2 f_1 + 1 f_1 + i)(1 - \delta_{f_1 + 1 f_2}) \\
 &+ a(f_1 f_1 + 1 f_1 + i)\delta_{f_1 + 1 f_2} - a(f_1 + i f_1 f_1 + i - 1)\delta_{f_1 + i - 1 f_2} \\
 &- a(f_2 f_1 f_1 + i - 1)(1 - \delta_{f_1 + i - 1 f_2}) \\
 &+ [a(f_1 f_2, f_2 - 1 f_1 + i) - a(f_1 f_2 - 1, f_2 f_1 + i)] \\
 &\times (1 - \delta_{f_1 + 1 f_2}) + [a(f_1 f_2, f_2 + 1 f_1 + i) \\
 &- a(f_1 f_2 + 1, f_2 f_1 + i)](1 - \delta_{f_1 + i - 1 f_2})\} = 0. \quad (13f)
 \end{aligned}$$

Further,

$$\begin{aligned}
 &(\epsilon_2 - 2W + 2C - 4J)a(f_1 f_2, f_1 + 1 f_2 + 1) \\
 &+ J[a(f_1 f_1 + 1, f_1 + 2 f_1 + 3)\delta_{f_1 + 2 f_2} \\
 &- a(f_1 f_2 + 1, f_1 + 1 f_2) - a(f_1 + 1 f_2 f_1 f_2 + 1)] \\
 &- M\{a(f_1 f_2 - 1, f_1 + 1 f_2 + 1) - a(f_1 f_2, f_1 + 1 f_2 + 2) \\
 &+ a(f_1 - 1 f_2, f_1 + 1 f_2 + 1) - a(f_1 f_2, f_1 + 2 f_2 + 1) \\
 &+ a(f_2 + 1 f_1 f_1 + 1) - a(f_2 f_1 f_1 + 1) + a(f_1 + 1 f_2 f_2 + 1) \\
 &- a(f_1 f_2 f_2 + 1) + [a(f_1 + 2 f_1 f_1 + 3) - a(f_1 + 1 f_1 f_1 + 3)] \\
 &\times \delta_{f_1 + 2 f_2}\} = 0, \quad (13g)
 \end{aligned}$$

$$\begin{aligned}
 &(\epsilon_2 - 2W + 2C - 4J)a(f_1 f_2 + 1, f_1 + 1 f_2) \\
 &+ (J - C)a(f_1 f_2 + 1, f_1 + 1 f_2)\delta_{f_1 + 2 f_2} \\
 &- J[a(f_1 f_2, f_1 + 1 f_2 + 1) + a(f_1 + 1 f_2 + 1, f_1 f_2)] \\
 &- M[a(f_1 f_2 + 2, f_1 + 1 f_2) - a(f_1 f_2 + 1 f_1 + 1 f_2 - 1) \\
 &+ a(f_1 - 1 f_2 + 1, f_1 + 1 f_2) - a(f_1 f_2 + 1, f_1 + 2 f_2) \\
 &+ a(f_2 + 1 f_1 f_1 + 1) - a(f_2 f_1 f_1 + 1) + a(f_1 + 1 f_2 + 1 f_2) \\
 &- a(f_1 f_2 + 1 f_2)] = 0, \quad (13h)
 \end{aligned}$$

:

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 and configurations having two polar atoms adjacent. Thus, $\delta_{f_1 + 1 f_2}$ is unity if the f_2 position is located at the position $f_1 + 1$ and is zero otherwise. Additional equations are given by the relationships

$$\begin{aligned}
 a(f_1 f_2 + i f_2) &= (-)^{i+1} a(f_1 f_2 f_2 + i), \\
 a(f_2 f_1 + i f_1) &= (-)^{i+1} a(f_2 f_1 f_1 + i), \\
 a(f_1 + i f_2 + j, f_1 f_2) &= (-)^{i+j} a(f_1 f_2, f_1 + i f_2 + j).
 \end{aligned} \quad (14)$$

We shall, in this paper, consider the solution to these equations for M large corresponding to the strong interaction case. However, in order to unify the subject it is necessary to make some statements about the case of small interactions, i.e., W large compared to M , which was done in DP I for any number of electron spins reversed. As pointed out in that paper and emphasized here, for W large it is only necessary (as in standard perturbation theory) to consider the coefficients of the low-energy configurations, (i.e., $a(f_1 f_2)$, $a(f_1 f_2 f_2 + 1)$, $a(f_1 f_2 + 1 f_2)$, $a(f_2 f_1 f_1 - 1)$, and $a(f_2 f_1 - 1 f_1)$ for the case

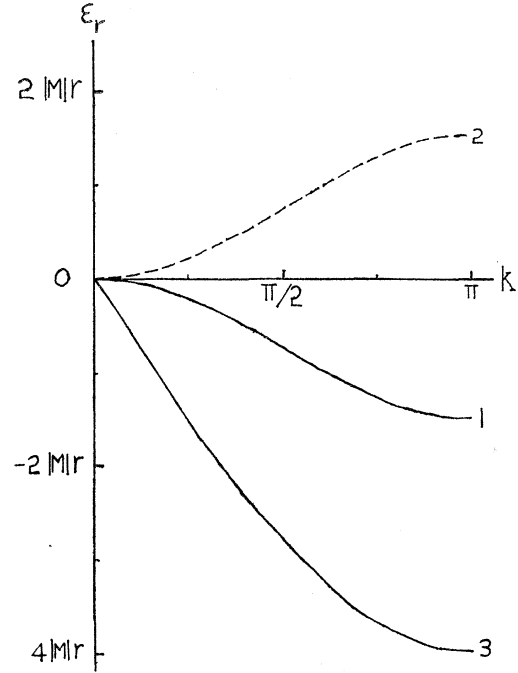


FIG. 1. Ground-state energy levels for r reversed electron spins as functions of k , the spin wave number. Curve (1) illustrates the nonferromagnetic case for small interactions M between orthogonalized polar and nonpolar states while curve (3) is for large interactions. Curve (2) is the ferromagnetic case for small interactions—the broken line signifying omission of the complex k values which are statistically small in number.

of two electron spins reversed). Thus, all other coefficients were put equal to zero, and the computations involved only equations of the form (13a) through (13c). We obtained the result valid for any number, r , of electrons with positive spin,

$$\epsilon_r = 2 \left[J - \frac{2M^2}{W - C} \right] \sum_{i=1}^r (1 - \cos k_i). \quad (15)$$

It is important to note that the inclusion of the set of next higher energy configurations given by the migration of one of the electrons with a positive spin a distance of two atoms from its original position or the migration of each of the two electrons with positive spin to their nearest neighboring atoms, i.e., inclusion of coefficients of the type $a(f_1 f_2 f_2 + 2)$ and $a(f_1 f_2, f_1 + 1 f_2 + 1)$, will change the value for ϵ_2 by the addition of a multiplicative factor of the form $1 + O(M^2/W^2)$ and similarly for ϵ_r . Thus, for W large compared to M , Eq. (15) is an accurate result, and the sign of the coefficient will determine the ground-state behavior of the system, (ferromagnetic for $J > 2M^2/(W - C)$ and nonferromagnetic for $J < 2M^2/(W - C)$). This is illustrated in Fig. 1, curves (1) and (2). Thus, for the case of weak interactions between the orthogonalized nonpolar and polar states, our result [equivalent to that obtained by Slater² for the case of only one

electron spin oriented in a direction opposite to all others but in DP I—our Eq. (15)—extended to r oppositely oriented spins] yields a criterion for determining the sign and magnitude of the coefficient and thus of the magnetic behavior of the substance.

Inasmuch as Eq. (15) was obtained in DP I from an equation of the same form as that used by Bethe,³ the wave number k for this one dimensional case may take on complex as well as real values, corresponding to spin clusters. The real values will be the lowest energy states for nonferromagnetic materials while the complex values (statistically small in number) will be the lowest energy states (in one dimension) for the ferromagnetic case.

We now continue our discussion of the strong interaction case but shall find the above comments useful in Sec. V.

IV. STRONG INTERACTIONS

In this section we consider the interaction integral M between the orthogonalized polar and nonpolar states to be much greater than W or J (see Sec. III). We first examine the case where only one of the electrons with plus spin can migrate to another atom which is taken to be its nearest neighbor. Then Eqs. (13a) through (13c) yield the result

$$\epsilon_2 a(f_1 f_2) + (M^2/\epsilon_2) \{ a(f_1 f_2 + 1) + a(f_1 - 1 f_2) - 2a(f_1 f_2) + [a(f_1 + 1 f_2) + a(f_1 f_2 - 1) - 2a(f_1 f_2)] \times (1 - \delta_{f_1+1} f_2) \} = 0. \quad (16)$$

This type of equation is analogous to that which has been solved rigorously by Bethe³ and Hulthén⁴ except that instead of the exchange integral J we have the quantity M^2/ϵ_2 . Thus, we may immediately write down the solution as

$$a(f_1 f_2) = c_1 e^{i(k_1 f_1 + k_2 f_2)} + c_2 e^{i(k_2 f_1 + k_1 f_2)}, \quad (17)$$

and obtain as our value for the ground-state energy

$$\epsilon_2 = -2|M| \left[\sum_{i=1}^2 (1 - \cos k_i) \right]^{\frac{1}{2}}, \quad (18)$$

where the k_i values are those given by Bethe and Hulthén.

Let us now extend our solution of the set of equations (13) to include the case where one of the electrons with plus spin can migrate as far as its second nearest neighbor or both electrons with plus spin can migrate to their respective nearest neighbors. Thus, we consider coefficients of the form $a(f_1 f_2)$, $a(f_1 f_2 f_2 + 1)$, $a(f_1 f_2 f_2 + 2)$ and $a(f_1 f_2, f_1 + 1 f_2 + 1)$ and various allowed permutations thereof—setting all other coefficients equal to zero. Using Eqs. (13a) through (13h) we get

$$\epsilon_2 a(f_1 f_2) + \{ 2M^2/[\epsilon_2 - (2M^2/\epsilon_2)(1 - \cos k) - (8M^2/\epsilon_2) \times (1 - \cos k)] \} \{ a(f_1 - 1 f_2) + a(f_1 f_2 + 1) - 2a(f_1 f_2) + [a(f_1 + 1 f_2) + a(f_1 f_2 - 1) - 2a(f_1 f_2)] \times (1 - \delta_{f_1+1} f_2) \} = 0, \quad (19)$$

where we have recognized that terms such as

$$2a(f_1 f_2 f_2 + 1) - a(f_1 f_2 + 1 f_2 + 2) - a(f_1 f_2 - 1 f_2),$$

and

$$2a(f_1 f_2 f_2 + 1) - a(f_1 + 1 f_2 f_2 + 1) - a(f_1 - 1 f_2 f_2 + 1)$$

can be represented as $2(1 - \cos k)a(f_1 f_2 f_2 + 1)$ and $2(1 - \cos k)a(f_1 f_2 f_2 + 1)$, respectively—assuming, in the spirit of the solution of Eq. (16), solutions of the form

$$\begin{aligned} a(f_1 f_2 + 1 f_2 + 2) &= e^{ik} a(f_1 f_2 f_2 + 1), \\ a(f_1 + 1 f_2 f_2 + 1) &= e^{ik} a(f_1 f_2 f_2 + 1). \end{aligned} \quad (20)$$

In obtaining Eq. (19) it was also necessary to impose the conditions

$$\begin{aligned} [a(f_1 f_1 f_1 + 1) - a(f_1 + 1 f_1 f_1 + 1) - a(f_1 + 2 f_1 f_1 + 1) \\ + a(f_1 - 1 f_1 f_1 + 1) + 4a(f_1 + 1 f_1 - 1 f_1) - 4a(f_1 f_1 - 1 f_1) \\ - 4a(f_1 f_1 + 1 f_1 + 2) + 4a(f_1 + 1 f_1 + 1 f_1 + 2)] \delta_{f_1+1} f_2 = 0, \end{aligned}$$

and

$$\begin{aligned} [a(f_1 + 2 f_1 + 1 f_1 + 2) - a(f_1 f_1 f_1 + 1) + 4a(f_1 + 1 f_1 f_1 + 1) \\ - 4a(f_1 + 1 f_1 + 1 f_1 + 2) + 3a(f_1 f_1 + 1 f_1 + 2) \\ - 3a(f_1 + 2 f_1 f_1 + 1)] \delta_{f_1+2} f_2 = 0. \end{aligned} \quad (21)$$

These conditions are equivalent to the spin-spin interaction terms usually dropped in spin wave calculations. Bethe,³ considering only the nonpolar wave function coefficients in Eq. (13a), arrived similarly at the spin-spin interaction condition

$$a(f_1 f_1) + a(f_1 + 1 f_1 + 1) - 2a(f_1 f_1 + 1) = 0$$

from which he obtained the allowed complex values of k or spin clusters for the one dimensional case and which we also get for our solution in Eq. (18). As we note, the higher energy polar coefficients $a(f_1 f_2 f_2 + 1)$ yield conditions which are considerably more complex. Their solution is incompatible with Eq. (20), and essentially we are neglecting the spin-spin interaction between polar atoms. The justification for neglect of the polar spin-spin interaction for the case of only two electrons having their spins reversed cannot necessarily be extended to the case where a large number of electrons have their spins reversed. Therefore, these results—to the extent that we have neglected the spin-spin interaction between polar states—are limited to a number of reversed electron spins, r , small compared to N .

The solution of Eq. (19) is

$$\epsilon_2 = -|M| [8(1 - \cos k) + 2(1 - \cos k) + 4 \sum_{i=1}^2 (1 - \cos k_i)]^{\frac{1}{2}}. \quad (22)$$

We note that Bethe³ has shown that the term $2 \sum_i (1 - \cos k_i)$ takes on the value $\sin^2 \text{Re}(k_i)$ for k_i complex and that this solution has a smaller value than the allowed real wave numbers. However, since we want to determine the lowest energy state using the

coefficient $-|M|$, we choose the real k_i . Further, placing

$$k = k_i, \quad (23)$$

Eq. (22) may be condensed to read

$$\epsilon_2 = -3|M| \left[\sum_{i=1}^2 (1 - \cos k_i) \right]^{\frac{1}{2}}. \quad (24)$$

Equation (24) is of the same form as Eq. (18) but has a lower energy level by a factor of 1.5.

We can continue this process of including higher energy configuration coefficients. The next set would include coefficients of the form $a(f_1 f_2 f_3 + 3)$ and $a(f_1 f_2, f_1 + 1 f_2 + 2)$. We write down the result here as

$$\epsilon_2 \approx -4.8|M|(1 - \cos k)^{\frac{1}{2}}. \quad (25)$$

Similarly, if we include the next set of higher energy configuration coefficients of the form $a(f_1 f_2 f_3 + 4)$, $a(f_1 f_2, f_1 + 1 f_2 + 3)$, and $a(f_1 f_2, f_1 + 2 f_2 + 2)$, our results are further modified to read

$$\epsilon_2 \approx -5.1|M|(1 - \cos k)^{\frac{1}{2}}. \quad (26)$$

We note that while Eq. (24) modifies Eq. (18) by a factor of 1.5, Eq. (25) changes Eq. (24) by a factor of only 1.14, and Eq. (26) in turn modifies Eq. (25) by only 1.07 or a change of seven percent. Thus, the modifications appear to drop off very rapidly, and we may suspect that the inclusion of higher energy coefficients beyond those considered will cause only a small additional change to the result given by Eq. (26), reducing finally to an expression equal to twice that given in DP I for one electron with reversed spin, i.e.,

$$\epsilon_2 = -4\sqrt{2}|M|(1 - \cos k)^{\frac{1}{2}}.$$

V. SUMMARY AND DISCUSSION

We may summarize as follows: the usual Dirac spin operator Hamiltonian

$$J \sum_{i,j} \mathbf{S}_i \cdot \mathbf{S}_j \quad (27)$$

contains, among other approximations, the assumption that compensation for the lack of orthogonality of the wave functions can be performed by varying the sign and magnitude of the exchange integral depending on the nature of the substance. Computations using this operator yield, for the ferromagnetic approximation of nearly all electron spins aligned, the dispersion relation

$$\epsilon_r = 2J \sum_{i=1}^r (1 - \cos k_i), \quad (28)$$

where small spin-spin interaction effects are neglected. Bethe,³ using a method different from Eq. (27) showed that in one dimension this equation was also correct for large r and that the spin-spin interaction effects manifested themselves through complex values of k_i .

Our investigation, which eliminates the orthogonality approximation (J is always positive and we include the polar states) yields dispersion relations which depend on the magnitude of an interaction integral M between the polar and nonpolar energy states. We note from Slater's² work that the strength of this interaction M is dependent on the amount of polar wave function added to the unperturbed nonorthogonal atomic functions to form the orthogonal set of atomic functions $\phi_r(x)$. In fact, it was shown in DP I that the interaction integral M is a direct consequence of the lack of orthogonality of these atomic functions. Essentially, the orthogonalization of the unperturbed atomic functions raises the unperturbed ground state energy level such that the new ground state level corresponding to the orthogonal atomic functions $\phi_r(x)$ may now interact strongly with the excited polar states which in turn may interact strongly with each other. Thus, the amount of interaction between the energy states or the magnitude of the off-diagonal matrix elements M is a direct function of the amount of overlap of the nonorthogonal atomic wave functions or the interatomic distance in the solid.

For weak interactions between polar and nonpolar states, i.e., $M < W$, we have obtained the following one-dimensional dispersion relation:

$$\epsilon_r = 2\{J - [2M^2/(W - C)]\} \sum_i (1 - \cos k_i) + O(M^2/W^2). \quad (29)$$

For M^2/W very much less than J , this equation is the same as Eq. (28) got by Bethe. For the case of some overlapping of the atomic functions but essentially weak interactions, Eq. (29) shows that the effect of considering the orthogonality relations from a rigorous point of view is to modify the coefficient of Eq. (28) by the additional term M^2/W . If this term is less than the exchange integral J , the coefficient is positive, and we have the ferromagnetic case. If, however, M^2/W is greater than J , then r becomes large, and the substance is nonferromagnetic.

For strong interactions between polar and nonpolar states, i.e., $M > W$ and J , assuming ϵ_r for $r > 2$ has the same form as that given in Sec. IV, we may write

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

for r much less than N .

This is illustrated in Fig. 1, curve (3).