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An Idealized Model for the Band Theory of Ferromagnetism

by

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I. INTRODUCTION

The first successful theory of ferromagnetism was the molecular field theory proposed by Weiss in 1907¹⁾. But the magnetic dipole interactions he had in mind proved to be too small to account for the observed transition temperatures. It was not until the arrival of quantum theory that Heisenberg²⁾ showed that the interactions were quantum mechanical in origin and were a direct consequence of the restrictions placed on the wave functions by the Pauli principle. These interactions are called exchange interactions. The corresponding energies are actually the difference of electrostatic energies of wave functions with different symmetric properties.

It is nowadays believed that the electrons principally responsible for ferromagnetism are those in unfilled inner shells (3d electrons in transition elements and 4f electrons in rare earth elements), or more specifically (in transition elements at least) the spin angular momenta of these electrons, because the orbital angular momenta are completely quenched as indicated by the measured value of the g-factors. Therefore, in a theory of ferromagnetism, we will have to study the behavior of these electrons and we can identify the magnetization of a system as the total

spin S of these electrons.

In treating quantum mechanically any system of more than two interacting particles, no exact solution to the wave equation of the system can be obtained, and some method of approximation must be applied. Thus, in dealing with the electrons in a molecule, two different ways of approximation have been tried: the Heitler-London method and the molecular orbital method. Similarly, in the theory of ferromagnetism, there have been two different approaches: the Heisenberg theory and the band theory. The Heisenberg theory, initiated by Heisenberg²⁾ in 1928, considers the electrons as localized in each atom, just as the Heitler-London method does; while the band theory, initiated by Bloch³⁾ in 1929, considers the electrons as moving through the whole crystal, just as the molecular orbital method considers the electrons as moving through the whole molecule. In their primitive forms, both theories are far from adequate. And it is not unusual that to improve one theory, some ideas of the opposite theory are used. Thus, in the later developments of both theories, the distinction between them becomes less clear-cut. As a matter of fact, Thompson⁴⁾ has combined these two theories into a unified theory of ferromagnetism. It is also believed that, if

carried out far enough, both theories will lead to the same result. However, some preference should be given to the one that starts closer to the final form. Several experiments, such as neutron diffraction⁵⁾, Hall effect measurement⁶⁾, etc. give indications in favor of the band theory.

The general idea of the band theory can be described briefly as follows: The band energy favors nonmagnetic states, because the lowest band energy is obtained when the lowest energy levels in a band are each occupied by two electrons with antiparallel spins. The exchange energy, which exists only between states of parallel spins and is always positive between orthogonal states⁷⁾ (see also Appendix I) but always appears with negative sign in the expressions for total energies, favors magnetic states, because the lowest possible total exchange energy is obtained when as many as possible electrons have parallel spins. So the problem of the existence of ferromagnetism is a problem of the relative importance of band energy and exchange energy. And the reason why we have ferromagnetism in such elements as iron, cobalt and nickel is that for these elements the energy bands of the 3d electrons are so narrow that the effect of band energy is less important than that of exchange energy. So the condition for the

existence of ferromagnetism is simply an energy band narrow enough.

Following Bloch, other people, such as Stoner⁸⁾, Slater⁹⁾, Mott¹⁰⁾, Wohlfarth¹¹⁾, etc., have made great contributions to the band theory of ferromagnetism. In their original forms, the works of these authors were all based on single determinantal functions as the wave functions for a system of electrons. But the single determinantal functions are just eigenfunctions of $\hat{S}_z$, the z-component of the total spin of the system. They are not necessarily eigenfunctions of $\hat{S}$, the total spin of the system. And we believe that, in discussing the problem of ferromagnetism, we should be concerned with $\hat{S}$, not $\hat{S}_z$. Actually, it has already been pointed out by Herring¹²⁾ in his recent book that "the absence of spin waves in the simplest theories of itinerant-electron ferromagnetism was only another illustration of the inadequacy of models using only determinantal wave functions," and that "a ferromagnetic determinantal wave function is taken into a non-determinantal form by a rigid rotation that alters the direction of the magnetic moment." From the above discussion, we believe that the single determinantal function is not the right one to be used in dealing with the problem

of ferromagnetism, but only a set of determinantal functions linearly combined to make an eigenfunction of $\hat{S}$.

The Hamiltonian of a system of N (for convenience, N will be assumed to be an even number) electrons moving in a crystal can be written as

$$\hat{H} = \sum_{i=1}^N \left[-\frac{\hbar^2}{2m} \nabla_i^2 + U(r_i) \right] + \sum_{i>j} V(r_i, r_j) = \hat{H}_0 + \hat{H}_I \quad (1)$$

where $U(r_i)$ is an averaged potential, periodic with the period of the lattice, and $V(r_i, r_j)$ is the remaining shielded interelectron interaction, which will be assumed to be

$$V(r_i, r_j) = \frac{e^2 \exp\{-\alpha|r_i - r_j|\}}{|r_i - r_j|} \quad (2)$$

Now suppose the wave equation including only the one-electron part of the Hamiltonian H_0 has been solved self-consistently to give a set of eigenvalues $\epsilon_1, \epsilon_2, \dots, \epsilon_C$; they will form an energy band and will be called band energies. The corresponding one-electron eigenfunctions are $u_1, u_2, \dots, u_C$; they are the so-called Bloch states and will be assumed to be orthonormalized. We will assume $C \geq N$, for otherwise we can consider "holes" instead of electrons.

Once the Bloch states are known, then, using the representation theory of permutation groups, it is possible

to construct systematically wave functions of the system which will satisfy the Pauli principle and also be eigenfunctions of both $\hat{S}$ and $\hat{S}_z$ ¹³⁾. It is also possible to derive the general expressions for the multiplicity, or degeneracy, of the states¹⁴⁾ and for the matrix elements of the Hamiltonian if we assumed that the direct inter-electron interactions and the exchange interactions between any pair of Bloch states are all equal. As an application of all these results, a highly idealized model for the band theory of ferromagnetism is presented in this thesis.

In this model, the following simplifying assumptions will be made:

1. The energy band is rectangular with band width $C\epsilon$. There are C/d (assuming C and N to be multiples of d) energy levels with energies differing successively by $d\epsilon$, and in each level, there are d different states with crystal momenta of the same magnitude but different directions. Therefore, we have $\epsilon_1 = \epsilon_2 = \dots = \epsilon_d = d\epsilon$, $\epsilon_{d+1} = \epsilon_{d+2} = \dots = \epsilon_{2d} = 2d\epsilon, \dots, \epsilon_{C-d+1} = \epsilon_{C-d+2} = \dots = \epsilon_C = C\epsilon$. This is intended to represent the 3d shell. The 4s electrons are neglected.

2. The direct interaction between all states, and the exchange interaction between all states with the same

spin, is equal to the same constant V .

3. The interaction is such as to conserve crystal momentum. We made the first assumption because it is simple. We made the second assumption because, as calculated by Slater⁹⁾, the exchange integral between two Bloch states in the 3d band is almost entirely obtained when the two electrons are located in the same lattice. We made the third assumption because it will more or less justify our calculation of the partition function based on the diagonal elements of the Hamiltonian, otherwise the problem will become too complicated to handle. That it is important in most treatments of electrons in metals has already been pointed out by Houston¹⁵⁾.

II. GENERAL PRINCIPLE

The Hamiltonian in Eq. (1) is invariant under all permutations of the spatial coordinates and of the spin coordinates of the N electrons. (The Hamiltonian does not contain the spin at all.) This is the basic reason that the permutation group theory can play such an important role in our problem. Let us denote the permutation operators by P^O , P^S or P ; the P^O 's are to operate on the orbital coordinates, the P^S 's are to operate on spin coordinates and the P 's are permutation operators in the most general sense. There are $N!$ P^O 's, $N!$ P^S 's and $N!$ P 's. They form isomorphic permutation groups of degree N denoted by $G^O(N)$, $G^S(N)$ and $G(N)$ respectively, i.e. $G^O(N) \cong G^S(N) \cong G(N)$.

In the representation theory of permutation groups, it is known that there is a one-to-one correspondence between the irreducible representations of $G(N)$ and the partitions of N . Therefore an irreducible representation can be identified by its corresponding partition and written as $D_{(\lambda_1, \lambda_2, \dots, \lambda_k)}$, or simply $D_{(\lambda)}$, where $(\lambda_1, \lambda_2, \dots, \lambda_k)$ is a partition of N with the properties:

$\lambda_1 + \lambda_2 + \dots + \lambda_k = N$ and $\lambda_1 \geq \lambda_2 \geq \dots \geq \lambda_k$. A partition can be represented by a Young's tableau. The partition represented by the transposed tableau of (λ) will be called the

associated partition of (λ) and written as $(\tilde{\lambda})$, and $D_{(\tilde{\lambda})}$ will be called the associated representation of $D_{(\lambda)}$. $D_{(\lambda)}$ and $D_{(\tilde{\lambda})}$ are of the same dimensions with the relation

$$D_{(\lambda)}(P) = (-1)^P D_{(\tilde{\lambda})}(P) \quad (3)$$

where $(-1)^P$ is either "+" or "-" depending on P is even or odd, and $D_{(\lambda)}(P)$ is the matrix in $D_{(\lambda)}$ corresponding to P .

Since $\hat{H}$ does not contain the spins at all, a stationary pure state can be an eigenstate of $\hat{S}$ and $\hat{S}_z$. And since both $\hat{S}$ and $\hat{S}_z$ are invariant under P^S , the eigenfunctions of both $\hat{S}$ and $\hat{S}_z$ corresponding to fixed eigenvalue S and S_z will form a basis for an irreducible representation of $G^S(N)$, and hence of $G(N)$. To obtain such eigenfunctions, let us consider a product function of the one-electron spin functions of N electrons of the form:

$$e = \alpha(\sigma_1) \alpha(\sigma_2) \cdots \alpha(\sigma_{\frac{N}{2}+S_z}) \beta(\sigma_{\frac{N}{2}+S_z+1}) \cdots \beta(\sigma_N) \quad (4)$$

By applying all the P^S 's to e , we can get a set of different orthogonal product functions $(e_1, e_2, \dots, e_q)$ where

$q = \frac{N!}{(\frac{N}{2}+S_z)!(\frac{N}{2}-S_z)!}$. This set of product functions will form a basis for a reducible representation of $G^S(N)$ of dimension

q . Let us denote this reducible representation by

$\Delta_{(\frac{N}{2}+S_z, \frac{N}{2}-S_z)}$ to indicate that the basis consists of

product functions of $(\frac{N}{2} + S_z)$ α 's and $(\frac{N}{2} - S_z)$ β 's. From a certain theorem¹⁴⁾ of the representation theory of permutation groups, we know that $\Delta_{(\frac{N}{2}+S_z, \frac{N}{2}-S_z)}$ can be reduced into the following irreducible representations:

$$\begin{cases} \Delta_{(\frac{N}{2}+S_z, \frac{N}{2}-S_z)} = D_{(N,0)} \oplus D_{(N-1,1)} \oplus \cdots \oplus D_{(\frac{N}{2}+S_z, \frac{N}{2}-S_z)} & \text{if } S_z \geq 0 \\ \Delta_{(\frac{N}{2}+S_z, \frac{N}{2}-S_z)} = D_{(N,0)} \oplus D_{(N-1,1)} \oplus \cdots \oplus D_{(\frac{N}{2}-S_z, \frac{N}{2}+S_z)} & \text{if } S_z < 0 \end{cases} \quad (5)$$

In other words, the set of functions $(e_1, e_2, \dots, e_q)$ are all eigenfunctions of $\hat{S}_z$ with eigenvalue S_z , and we can form such linear combinations of the e 's as to be eigenfunctions of $\hat{S}$ with eigenvalue $S = |S_z|, |S_z| + 1, \dots, \frac{N}{2}$. It is known¹³⁾ that the number of different linear combinations which are eigenfunctions of $\hat{S}$ with eigenvalue S is

$$h = \binom{N}{\frac{N}{2}-S} - \binom{N}{\frac{N}{2}-S-1} \quad (6)$$

This set of h functions will be a complete set of eigenfunctions of both $\hat{S}$ and $\hat{S}_z$ with eigenvalue S and S_z , and, as mentioned previously, will form a basis for a certain irreducible representation of dimension h . Let us denote this irreducible representation by Γ_S to indicate that this irreducible representation can have a basis consisting of eigenfunctions of $\hat{S}$ with eigenvalue S . It can be shown that the irreducible representation Γ_S is identically the

irreducible representation $D(\frac{N}{2}+S, \frac{N}{2}-S)$.

Let us denote the set of h functions by $g_1(S, S_z), g_2(S, S_z), \dots, g_h(S, S_z)$. Since they form a complete set, any wave function which is an eigenfunction of both $\hat{S}$ and $\hat{S}_z$ with eigenvalue S and S_z can be written as a linear combination of the g 's, and, since a wave function is a function of both orbital coordinates and spin coordinates, the coefficients of this linear combination will be functions of the orbital coordinates of the N electrons. So we can write the total wave function as

$$\Psi(S, S_z) = \frac{1}{\sqrt{h}} \sum_{\ell=1}^h \phi_{\ell}(r_1, r_2, \dots, r_N) g_{\ell}(S, S_z, \sigma_1, \sigma_2, \dots, \sigma_N) \quad (7)$$

But, in order to satisfy the Pauli exclusion principle, any physically acceptable wave function must be antisymmetric under the exchange of any pair of coordinates (spatial and spin go together), i.e.

$$P^o P^s \Psi = (-1)^P \Psi \quad (8)$$

Now let us see what the Pauli principle tells us about the ϕ 's. We must have

$$P^o P^s \Psi = \frac{1}{\sqrt{h}} \sum_{\ell=1}^h P^o \phi_{\ell} P^s g_{\ell} = (-1)^P \frac{1}{\sqrt{h}} \sum_{\ell=1}^h \phi_{\ell} g_{\ell} \quad (9)$$

or

$$\sum_{\ell=1}^h P^{\circ} \phi_{\ell} \left[\sum_{k=1}^h \Gamma_S(P)_{\ell k} g_k \right] = (-1)^P \sum_{\ell=1}^h \phi_{\ell} g_{\ell} \quad (10)$$

We can always choose our g_k 's to be an orthonormal set in which case $\Gamma_S(P)$ is orthogonal. Let us multiply both sides of Eq. (10) by g_m and sum over all spin coordinates to get

$$\sum_{\ell=1}^h \Gamma_S(P)_{\ell m} P^{\circ} \phi_{\ell} = (-1)^P \phi_m \quad (11)$$

Now multiply both sides by $\Gamma_S(P^{-1})_{mk}$ and sum over m , we obtain

$$P^{\circ} \phi_k = (-1)^P \sum_m \Gamma_S(P^{-1})_{mk} \phi_m = (-1)^P \sum_m \Gamma_S(P)_{km} \phi_m \quad (12)$$

Thus we see that the ϕ 's should form a basis for the irreducible representation associated with Γ_S . Let us denote this irreducible representation by $\tilde{\Gamma}_S$. Γ_S is identically $D(\frac{N}{2}+S, \frac{N}{2}-S)$. The associated irreducible representation is $D(\frac{N}{2}-S, \frac{N}{2}+S)$, since $(2^{\frac{N}{2}-S}, 1^{2S})$ is the associated partition of $(\frac{N}{2}+S, \frac{N}{2}-S)$. So $\tilde{\Gamma}_S$ is identically $D(\frac{N}{2}-S, \frac{N}{2}+S)$. Therefore, due to the restriction of the Pauli principle, the only physically acceptable spatial wave functions are those which form bases of irreducible representations of $G_{\frac{N}{2}-S}^r(N)$ corresponding to partition of N of the form $(2^{\frac{N}{2}-S}, 1^{2S})$. It will become clear later that this implies

that no orbital can be occupied by more than two electrons.

To obtain such bases, let us consider the following product function of the Bloch states:

$$f = u_{\mu_1}(r_1) u_{\mu_1}(r_2) \cdots u_{\mu_Q}(r_{2Q-1}) u_{\mu_Q}(r_{2Q}) u_{i_1}(r_{2Q+1}) \cdots u_{i_R}(r_N) \quad (13)$$

By applying all the P^r 's to f , we can get a set of different orthogonal product functions $(f_1, f_2, \dots, f_k)$ where $k = N!/2^Q$. This set of product functions will form a basis for a reducible representation of $G^O(N)$ of dimension k .

In the set of product functions $(f_1, f_2, \dots, f_k)$, $u_{\mu_1}, u_{\mu_2}, \dots, u_{\mu_Q}$ are doubly occupied and $u_{i_1}, \dots, u_{i_R}$ are singly occupied. We say that $(f_1, f_2, \dots, f_k)$ arise from a single configuration. A configuration is specified if we specify which orbitals are doubly occupied and which orbitals are singly occupied. Configurations with the same number of doubly occupied orbitals and the same number of singly occupied orbitals will be considered as belonging to the same "mode." The number of doubly occupied orbitals will be denoted by Q , and that of singly occupied orbitals by R . Thus, a mode can be specified by two numbers, Q and R , or just one number R , since $Q = (N-R)/2$; so a mode can be identified by R . But it is more convenient to define another number $r = R/2$, and let a mode be identified by r

written as $M(r)$. The ℓ^{th} configuration of $M(r)$ will be denoted by $C(r, \ell)$. The sets of product functions arising from configurations belonging to the same mode $M(r)$ will form bases of the same reducible representation of $G^O(N)$ denoted by $\Lambda(r)$. And from the above mentioned theorem¹⁴⁾, we know that $\Lambda(r)$ contains $\tilde{\Gamma}_S$ as often as $\left\{ \binom{2r}{r-S} - \binom{2r}{r-S-1} \right\}$ times, if $S \leq r$.

By now, we are already in a position to enumerate all the physically acceptable states in an energy band with C available orbitals to be occupied by N electrons. The total number of possible modes is $N/2 + 1$ corresponding to $r = 0, 1, 2, \dots, N/2$. The total number of configurations belonging to the mode $M(r)$ is

$$m(r) = \frac{C!}{(C-Q)! Q!} \cdot \frac{(C-Q)!}{(C-Q-R)! R!} = \frac{C!}{(C-\frac{N}{2}-r)! (\frac{N}{2}-r)! (2r)!} \quad (14)$$

The total number of possible bases for $\tilde{\Gamma}_S$ contained in each configuration belonging to $M(r)$ is $\left\{ \binom{2r}{r-S} - \binom{2r}{r-S-1} \right\}$, if $S \leq r$. There are always $(2S+1)$ possible bases for Γ_S corresponding to $S_z = -S, -S+1, \dots, 0, \dots, S-1, S$. Any basis of $\tilde{\Gamma}_S$ can be combined with any basis of Γ_S to form a physically acceptable state. Therefore, the total number of possible states with eigenvalue S is

$$\begin{aligned}
 T(S) &= \sum_{r=S}^{N/2} \frac{C!}{(C-\frac{N}{2}-r)!(\frac{N}{2}-r)!(2r)!} \left\{ \binom{2r}{r-S} - \binom{2r}{r-S-1} \right\} (2S+1) \\
 &= \frac{(2S+1)^2}{(C+1)} \binom{C+1}{\frac{N}{2}+S+1} \binom{C+1}{\frac{N}{2}-S}
 \end{aligned} \tag{15}$$

and the total number of all possible states of the system is

$$T = \sum_{S=0}^{N/2} T(S) = \frac{(2C)!}{(2C-N)! N!} \tag{16}$$

The derivation of the above formulas will be given in Appendix II. Eq. (16) is, as it should be, also the total number of possible different determinantal states.

III. DERIVATION OF THE MATRIX ELEMENTS OF THE HAMILTONIAN

A. General Formalism

As given in the previous section, the wave functions of our system are of the form

$$\psi(S, S_z) = \frac{1}{\sqrt{h}} \sum_{i=1}^h \phi_i(r_1, \dots, r_N) g_i(S, S_z, \sigma_1, \dots, \sigma_N) \quad (17)$$

and the matrix elements are of the form

$$\begin{aligned} & \langle \psi'(S', S'_z) | \hat{H} | \psi(S, S_z) \rangle \\ &= \frac{1}{\sqrt{h h'}} \sum_{\sigma_1} \dots \sum_{\sigma_N} \int dr_1 \dots \int dr_N \left[\sum_{i'=1}^{h'} \phi_{i'}^*(r_1, \dots, r_N) g_{i'}(S', S'_z, \sigma_1, \dots, \sigma_N) \right] \\ & \quad \hat{H} \left[\sum_{i=1}^h \phi_i(r_1, \dots, r_N) g_i(S, S_z, \sigma_1, \dots, \sigma_N) \right] \end{aligned} \quad (18)$$

Since $\hat{H}$ is independent of the spins, we can first sum over them, and because of the orthonormal property of the g 's, we have

$$\sum_{\sigma_1} \dots \sum_{\sigma_N} g_{i'}(S', S'_z, \sigma_1, \dots, \sigma_N) g_i(S, S_z, \sigma_1, \dots, \sigma_N) = \delta_{SS'} \delta_{S_z S'_z} \delta_{ii'} \quad (19)$$

So we conclude that the matrix elements are non-vanishing only between those states of the same S and S_z . And Eq.

(18) is reduced to

$$\begin{aligned} & \langle \psi'(S, S_z) | \hat{H} | \psi(S, S_z) \rangle \\ &= \frac{1}{h} \sum_{i=1}^h \int dr_1 \dots \int dr_N \phi_i^*(r_1, \dots, r_N) \phi_i(r_1, \dots, r_N) \end{aligned} \quad (20)$$

where ϕ_i and ϕ'_i must be the i^{th} partner in two bases for the same irreducible representation $\tilde{\Gamma}_S$.

The ϕ 's can be obtained most easily by using the projection operators defined as follows:

$$\zeta_{ij}^S = \sum_P \tilde{\Gamma}_S(P)_{ij}^* P^o \quad (21)$$

where $\tilde{\Gamma}_S(P)_{ij}^*$ is the complex conjugate of the ij element of the matrix representing P in the irreducible representation $\tilde{\Gamma}_S$, and the summation is over all the permutations P in $G(N)$. When ζ_{ij}^S operates on a function like f in Eq. (13), it will give the i^{th} partner in the basis corresponding to the j^{th} column of $\tilde{\Gamma}_S$. Adopting a more informative notation, we have

$$\phi_{ij} = \sqrt{\frac{h}{2^q N!}} \sum_P \tilde{\Gamma}_S(P)_{ij}^* P^o f^{rl} \quad (22)$$

where $\sqrt{\frac{h}{2^q N!}}$ is the normalization factor, h is the dimension of $\tilde{\Gamma}_S$, and f^{rl} is the product function of $C(r, l)$.

Now the set of functions $\phi_{1j}, \phi_{2j}, \dots, \phi_{hj}$ will form a basis for $\tilde{\Gamma}_S$, and j can be $1, 2, \dots$, or h , so we have h such sets.

But some of them will vanish, and some of them may not be linearly independent. So it is convenient to choose the representation matrices of $\tilde{\Gamma}_S$ in such a scheme that some of the sets vanish identically and the remaining ones are

linearly independent.

The product function $f^{r\ell}$ is invariant under $(1,2)$, $(3,4), \dots, (2Q-1, 2Q)$, or any product of them; where $(1,2)$ represents the exchange of r_1 and r_2 , etc., and $Q = \frac{N}{2} - r$. These permutations together with the identity will form a subgroup H_Q of $G^O(N)$ of order 2^Q , and H_Q will also be a subgroup of the subgroup $H_{Q'}$, if $Q \leq Q'$. We can see that H_Q is an Abelian group, and $P_Q^2 = I$, where P_Q represents any element of H_Q ; therefore all the irreducible representations of H_Q are one dimensional, and the matrices are either (1) or (-1) . Now, let us take the matrices of $\tilde{\Gamma}_S$ in such a way that the matrices for elements of the largest subgroup of this kind, i.e. $H_{Q=N/2}$, appear in reduced (diagonal) form:

$$\tilde{\Gamma}_S(P_{Q=N/2})_{ij} = \pm \delta_{ij} \quad (23)$$

Further we number the rows and columns of these matrices in such a way that the first h_0 diagonal elements are "+1" for all $2^{N/2}$ matrices $\tilde{\Gamma}_S(P_{Q=N/2})$; the next $(h_1 - h_0)$ diagonal elements are "+1" for all $2^{N/2-1}$ matrices $\tilde{\Gamma}_S(P_{Q=N/2-1})$, and "-1" for at least one of the matrices of the rest in the subgroup $H_{Q=N/2}$; the next $(h_2 - h_1)$ diagonal elements are "+1" for all $2^{N/2-2}$ matrices

$\tilde{\Gamma}_S^{(P_{Q=N/2-2})}$, and "-1" for at least one of the matrices of the rest of $H_{Q=N/2}$, etc. Then, it can be shown¹⁶⁾ that corresponding to a product function $f^{r\ell}$, the first h_r sets of the basis functions are linearly independent and the rest of them vanish identically. It can also be shown that the number of non-vanishing sets is

$$h_r = \binom{2r}{r-S} - \binom{2r}{r-S-1} \quad (24)$$

Now we can specify that the states $\psi(s, s_z)$ and $\psi'(s, s_z)$ of Eq. (20) come from the basis corresponding to the j and j' th column of $\tilde{\Gamma}_S$ out of $f^{r\ell}$ and $f^{r'\ell'}$, and will be denoted by ψ_j and $\psi_{j'}$ respectively. Then we can write

$$\begin{aligned} \langle \psi_{j'} | \hat{H} | \psi_j \rangle &= \frac{1}{h} \sum_{i=1}^h \langle \phi_{ij'} | \hat{H} | \phi_{ij} \rangle \\ &= \frac{1}{2^{(Q+Q')/2} N!} \sum_{i=1}^h \langle \zeta_{ij'}^S f^{r'\ell'} | \hat{H} | \zeta_{ij}^S f^{r\ell} \rangle \\ &= \frac{1}{2^{(Q+Q')/2} N!} \sum_{i=1}^h \langle f^{r'\ell'} | \zeta_{ij'}^{S\dagger} \hat{H} | \zeta_{ij}^S f^{r\ell} \rangle \\ &= \frac{1}{2^{(Q+Q')/2} N!} \sum_{i=1}^h \langle f^{r'\ell'} | \hat{H} | \zeta_{ij'}^{S\dagger} \zeta_{ij}^S f^{r\ell} \rangle \\ &= \frac{1}{2^{(Q+Q')/2} N!} \sum_{i=1}^h \langle f^{r'\ell'} | \hat{H} | \zeta_{j'i}^S \zeta_{ij}^S f^{r\ell} \rangle \\ &= \frac{1}{2^{(Q+Q')/2} N!} \cdot \frac{N!}{h} \sum_{i=1}^h \langle f^{r'\ell'} | \hat{H} | \zeta_{jj}^S f^{r\ell} \rangle \end{aligned} \quad (24)$$

$$\begin{aligned}
&= \frac{1}{2^{(Q+Q')/2}} \langle f^{r'l'} | \hat{H} | \zeta_{jj}^S f^{rl} \rangle \\
&= \frac{1}{2^{(Q+Q')/2}} \sum_P \tilde{\Gamma}_S(P)_{jj}^* \langle f^{r'l'} | \hat{H} | P^o f^{rl} \rangle
\end{aligned}$$

In the above derivation, we have used the following facts:
 $\hat{H}$ and P^o are commutative; $\tilde{\Gamma}_S$ is a unitary representation;
 and¹³⁾

$$\zeta_{ij}^S \zeta_{kl}^{S'} = \frac{N!}{h} \delta_{SS'} \delta_{kj} \zeta_{il}^S \quad (25)$$

It should be noticed that $\langle \psi_{j'} | \hat{H} | \psi_j \rangle$ is non-vanishing only for $j = 1, 2, \dots, h_r$ and $j' = 1, 2, \dots, h_{r'}$ (without losing generality, we will assume that $r \leq r'$, therefore $h_r \leq h_{r'}$). This means that only the first h_r -by- h_r part of the representation matrices of $\tilde{\Gamma}_S$ is significant. But in the following discussion, when $r \neq r'$, we will try to use only those matrices which are in the reduced form with the first h_r -by- h_r part as a reduced unit, thus only the h_r -by- h_r part is non-vanishing. This part is invariant with respect to permutations of the subgroup H_Q , because this part of the matrices of P_Q is a unit matrix. Let us call it "invariant part" and denote it by $[\tilde{\Gamma}_S]^{h_r}$.

Let us denote another subgroup consisting of all permutations among the last R coordinates $r_{2Q+1}, r_{2Q+2}, \dots, r_N$ by H_R , and any element of H_R by P_R . It is obvious that H_R is isomorphic to the permutation group of degree R , i.e. $G(R)$. And it can be shown¹⁷⁾ that in our choice of the matrices, the $\tilde{\Gamma}_S^{h_r}(P_R)$'s are already in reduced form and that $[\tilde{\Gamma}_S^{h_r}(P_R)]^{h_r}$ is an h_r -dimensional irreducible representation of $G(R)$. The following can also be shown¹⁶⁾:

$$1. \quad \tilde{\Gamma}_S(2s-1, t) + \tilde{\Gamma}_S(2s, t) \quad \text{is of reduced form, and} \\ [\tilde{\Gamma}_S(2s-1, t) + \tilde{\Gamma}_S(2s, t)]^{h_r} = -I \quad (26)$$

$$[\tilde{\Gamma}_S(2s-1, t)]^{h_r} = [\tilde{\Gamma}_S(2s, t)]^{h_r} = -\frac{1}{2}I \quad (27)$$

where $s \leq Q$, $2s-1 \neq t \neq 2s$ and I is h_r -dimensional unit matrix.

$$2. \quad [\tilde{\Gamma}_S((2s-1, t)(2s, t'))]^{h_r} = \frac{1}{2}I + \frac{1}{2}[\tilde{\Gamma}_S(t, t')]^{h_r} \quad (28)$$

$$3. \quad [\tilde{\Gamma}_S(T(2s-1, t))]^{h_r} = [\tilde{\Gamma}_S(T(2s, t))]^{h_r} = -\frac{1}{2}[\tilde{\Gamma}_S(T)]^{h_r} \quad (29)$$

where T is any permutation not containing $2s-1$ and $2s$.

$$4. \quad [\tilde{\Gamma}_S(T(2s-1, t)(2s, t'))]^{h_r} = \frac{1}{2}[\tilde{\Gamma}_S(T)]^{h_r} + \frac{1}{2}[\tilde{\Gamma}_S(T(t', t))]^{h_r} \quad (30)$$

Since $f^{r\ell}$ is invariant under P_Q , we have

$$P_c P_Q f^{r\ell} = P_c f^{r\ell} \quad (31)$$

So it is convenient to classify $G^0(N)$ into $c = N!/2^Q$ left cosets with respect to the subgroup H_Q . Then, we have

$$P_1^0 f^{r\ell} = P_2^0 f^{r\ell} \quad (32)$$

if P_1^0 and P_2^0 are in the same coset. Therefore Eq. (24)' can be written as

$$\begin{aligned} \langle \psi_j' | \hat{H} | \psi_j \rangle &= \frac{1}{2^{(Q+Q')/2}} \sum_{P_Q} \sum_{P_c} \tilde{\Gamma}_S(P_c P_Q)_{jj}^* \langle f^{r\ell'} | \hat{H} | P_c P_Q f^{r\ell} \rangle \\ &= 2^{(Q-Q')/2} \sum_{P_c} \tilde{\Gamma}_S(P_c)_{jj}^* \langle f^{r\ell'} | \hat{H} | P_c f^{r\ell} \rangle \end{aligned} \quad (33)$$

where in the summation over P_c we take only one element out of each coset, and in the last step we have used the property

$$[\tilde{\Gamma}_S(P_c P_Q)]^{h_r} = [\tilde{\Gamma}_S(P_c)]^{h_r} \quad (34)$$

B. Diagonal Elements

Let us consider the case when $f^{r'\ell'} = f^{r\ell}$, i.e. the situation within a single configuration. Eq. (33) becomes

$$\langle \psi_j' | \hat{H} | \psi_j \rangle = \sum_{P_c} \tilde{\Gamma}_S(P_c)_{jj}^* \langle f^{r\ell} | \hat{H} | P_c f^{r\ell} \rangle \quad (35)$$

Since the Hamiltonian consists of terms depending on coordinates of one and two electrons, $\langle f^{rl} | H | P_c f^{rl} \rangle$ vanishes except when in f^{rl} and $P_c f^{rl}$ not more than two electrons are in different orbitals, i.e. we must have $P_c = E$, the identity, or $P_c = (t, t')$, where (t, t') is not one of $(1, 2), (3, 4), \dots, (2Q-1, 2Q)$. Using Eq. (27), the calculation of Eq. (35) can be carried out to give the following result:

$$\begin{aligned}
 \langle \psi_j | \hat{H} | \psi_j \rangle = & \left\{ \sum_{m=1}^Q 2\epsilon_{u_m} + \sum_{n=1}^R \epsilon_{i_n} + \sum_{m>m'}^Q [4J_{u_m u_{m'}} - 2K_{u_m u_{m'}}] \right. \\
 & + \sum_{m=1}^Q J_{u_m u_m} + \sum_{m=1}^Q \sum_{n=1}^R [2J_{u_m i_n} - K_{u_m i_n}] + \sum_{n>n'}^R J_{i_n i_{n'}} \Big\} \delta_{j,j} \\
 & + \sum_{n>n'}^R \tilde{\Gamma}_S^*(2Q+n, 2Q+n')_{jj} K_{i_n i_{n'}}
 \end{aligned} \tag{36}$$

where

$$\epsilon_i = \int u_i^*(r) \left[-\frac{\hbar^2}{2m} \nabla^2 + U(r) \right] u_i(r) dV \tag{37}$$

is the one-electron, or band, energy;

$$J_{ij} = \int u_i^*(r_1) u_j^*(r_2) V(r_1, r_2) u_i(r_1) u_j(r_2) dV_1 dV_2 \tag{38}$$

is the direct interelectron interaction; and

$$K_{ij} = \int u_i^*(r_1) u_j^*(r_2) V(r_1, r_2) u_j(r_1) u_i(r_2) dV_1 dV_2 \tag{39}$$

is the exchange interelectron interaction. In our model

we assume that the direct and exchange interaction between any pair of Bloch orbitals are all equal to a constant V . But before equalizing the direct and exchange interaction, it is instructive to keep some distinction between them. So let us temporarily put all the direct interactions to a constant J and all the exchange interactions to a constant K . Then, Eq. (36) is reduced to

$$\begin{aligned}
 \langle \psi_j | \hat{H} | \psi_j \rangle &= \left\{ B(r, l) + \frac{Q(Q-1)}{2} [4J - 2K] + QJ + QR[2J - K] + \frac{R(R-1)}{2} J \right\} \delta_{jj} \\
 &\quad + K \sum_{n > n'}^R \tilde{\Gamma}_S(2Q+n, 2Q+n')_{jj}^* \\
 &= \left\{ B(r, l) + \frac{N(N-1)}{2} J - \left[\frac{N(N-1)}{2} - r(r-1) \right] K \right\} \delta_{jj} \\
 &\quad + K \sum_{n > n'}^R \tilde{\Gamma}_S(2Q+n, 2Q+n')_{jj}^*
 \end{aligned} \tag{40}$$

where we have defined

$$B(r, l) = \sum_{m=1}^Q 2\epsilon_{\mu_m} + \sum_{n=1}^R \epsilon_{\lambda_n} \tag{41}$$

to be the total band energy of the ℓ^{th} configuration in $M(r)$. From the last form of Eq. (40), we can see that the total direct interaction energy is a constant $\frac{N(N-1)}{2} J$.

Now let us consider the last term in Eq. (40). The summation runs over all exchange permutations of the last R coordinates. These exchange permutations will form a complete class of the subgroup H_R . Since $[\tilde{\Gamma}_S(P_R)]^{h_r}$ is an h_r -dimensional irreducible representation of H_R , by

Schur's lemma, we have

$$\sum_{n>n'}^R \tilde{\Gamma}_S(2Q+n, 2Q+n')_{jj}^* = \frac{R(R-1)}{2} \cdot \frac{\chi_r}{h_r} \delta_{jj} \quad (42)$$

where¹⁸⁾

$$\chi_r = -\binom{2r-2}{r-S} + \binom{2r-2}{r-S-1} - \binom{2r-2}{r-S-2} + \binom{2r-2}{r-S-3} \quad (43)$$

is the character of the exchange class in $[\tilde{\Gamma}_S(P_R)]^{h_r}$.

Putting the expression in Eqs. (24) and (43) into Eq. (42), we have

$$\sum_{n>n'}^R \tilde{\Gamma}_S(2Q+n, 2Q+n')_{jj}^* = -[r^2 - 2r + S^2 + S] \delta_{jj} \quad (44)$$

Putting Eq. (44) into Eq. (40) and putting $J = K = V$ we have

$$\langle \psi_j | \hat{H} | \psi_j \rangle = \left\{ B(r, l) + \left[\frac{N^2}{4} + r - S(S+1) \right] V \right\} \delta_{jj} \quad (45)$$

From Eq. (45), we can see that, in our model, the h_r states coming from a single configuration belonging to the mode $M(r)$ with eigenvalue S are eigenstates of the Hamiltonian with the same energy, provided that we consider only the situation within a single configuration. Anyway, the diagonal elements of the Hamiltonian are

$$\langle \psi_j | \hat{H} | \psi_j \rangle = B(r, l) + \left[\frac{N^2}{4} + r - S(S+1) \right] V \quad (46)$$

C. Configuration Interactions

Let us rewrite Eq. (33) as follows

$$\begin{aligned} \langle \psi_j' | \hat{H} | \psi_j \rangle = & 2^{(Q-Q')/2} \sum_{P_c} \tilde{T}_S(P_c)_{jj}^* \left[\langle f^{r' \ell'} | \hat{H}_0 | P_c f^{r \ell} \rangle \right. \\ & \left. + \langle f^{r' \ell'} | \hat{H}_I | P_c f^{r \ell} \rangle \right] \end{aligned} \quad (47)$$

and consider the case when $C(r, \ell) \neq C(r', \ell')$. Then

$\langle f^{r' \ell'} | \hat{H}_0 | P_c f^{r \ell} \rangle$ vanishes identically. So Eq. (47) is reduced to

$$\langle \psi_j' | \hat{H} | \psi_j \rangle = 2^{(Q-Q')/2} \sum_{P_c} \tilde{T}_S(P_c)_{jj}^* \langle f^{r' \ell'} | \hat{H}_I | P_c f^{r \ell} \rangle \quad (48)$$

But $\langle f^{r' \ell'} | \hat{H}_I | P_c f^{r \ell} \rangle$ will not vanish only when $C(r', \ell')$ and $C(r, \ell)$ differs by not more than two orbitals. And due to the assumption of the conservation of crystal momentum, it is obvious that if $C(r', \ell')$ and $C(r, \ell)$ are not the same, they must differ by at least two orbitals, and the sums of crystal momenta of the two pairs of different orbitals must be equal. This is a very severe restriction, and will reduce the effect of interconfiguration interaction to a negligible quantity in comparison with the diagonal elements of the Hamiltonian. Thus, it will justify our later calculations of magnetization based on taking the diagonal elements of the Hamiltonian as eigenenergies.

In discussing the configuration interaction between two configurations $C(r', \ell')$ and $C(r, \ell)$, it is convenient

to arrange the product functions $f^{r'l'}$ and f^{rl} in such a way that:

1. f^{rl} and $f^{r'l'}$ are of the form as given in Eq. (13) with doubly occupied orbitals appear first and singly occupied orbitals follow.

2. In f^{rl} , the two orbitals which are different from the corresponding ones in $f^{r'l'}$ appear as close as possible to the boundary between doubly occupied and singly occupied orbitals.

3. $f^{r'l'}$ takes such form that as many as possible orbitals can be "forgotten." The forgotten orbitals must be identical in $f^{r'l'}$ and f^{rl} and must be different from any of the "kept" ones. Only the kept ones will be significant in our problem.

In writing out f^{rl} and $f^{r'l'}$, we will retain only the significant ones. For instance, a case when

$$f^{rl} = u_{u_1}(r_1) u_{u_1}(r_2) \cdots u_{u_{Q-1}}(r_{2Q-3}) u_{u_{Q-1}}(r_{2Q-2}) u_a(r_{2Q-1}) u_a(r_{2Q})$$

$$u_b(r_{2Q+1}) u_c(r_{2Q+2}) u_{i_3}(r_{2Q+3}) \cdots u_{i_R}(r_N)$$

and $f^{r'l'} = u_{u_1}(r_1) u_{u_1}(r_2) \cdots u_{u_{Q-1}}(r_{2Q-3}) u_{u_{Q-1}}(r_{2Q-2}) u_c(r_{2Q-1})$

$$u_c(r_{2Q}) u_d(r_{2Q+1}) u_a(r_{2Q+2}) u_{i_3}(r_{2Q+3}) \cdots u_{i_R}(r_N)$$

will be denoted simply by

$$\langle C(2Q-1)C(2Q)d(2Q+1)a(2Q+2)/a(2Q-1)a(2Q)b(2Q+1)c(2Q+2) \rangle.$$

We will have the following different cases to consider:

$$a. \quad r'-r = 0$$

$$1. \langle C(2Q+1)C(2Q+2)/a(2Q+1)b(2Q+2) \rangle$$

$\langle f^{re'} | H_I | P_c f^{re} \rangle$ will not vanish only when $P_c = E$ or $P_c = (2Q+1, 2Q+2)$. $(2Q+1, 2Q+2)$ is an element of the subgroup H_{Q+1} . So, in our choice of the representation matrices, $\tilde{\Gamma}_S(2Q+1, 2Q+2)$ is diagonalized. The first h_{r-1} diagonal elements are "+1," the rest of them are either "+1" or "-1." We can number the rows and columns in such order that in $[\tilde{\Gamma}_S(2Q+1, 2Q+2)]^{h_r}$ the "+1"'s appear first, the "-1"'s follow. Then, since $(2Q+1, 2Q+2)$ is also an element in the subgroup H_R with irreducible representation $[\tilde{\Gamma}_S(P_R)]^{h_r}$, the trace of $[\tilde{\Gamma}_S(2Q+1, 2Q+2)]^{h_r}$ is given in Eq. (43), and the number of "+1"'s is

$$j_r^+ = \frac{1}{2} \{ h_r + \chi_r \} \quad (49)$$

$$= \frac{1}{2} \left\{ \binom{2r}{r-5} - \binom{2r}{r-5-1} - \binom{2r-2}{r-5} + \binom{2r-2}{r-5-1} - \binom{2r-2}{r-5-2} + \binom{2r-2}{r-5-3} \right\}$$

So we have

$$\begin{cases} \langle \psi_j' | \hat{H} | \psi_j \rangle = 2V \delta_{jj} & \text{for } j \leq j_r^+ \\ \langle \psi_j' | \hat{H} | \psi_j \rangle = 0 & \text{for } j > j_r^+ \end{cases} \quad (50)$$

$$2. \langle b(2Q-1)b(2Q)c(2Q+1) | a(2Q-1)a(2Q)b(2Q+1) \rangle$$

$$\langle f^{re'} | \hat{H}_I | P_c f^{re} \rangle \text{ will not vanish only when}$$

$P_c = (2Q-1, 2Q+1)$ or $P_c = (2Q, 2Q+1)$. (It should be noted that $(2Q-1, 2Q+1)$ $(2Q-1, 2Q)$ and $(2Q, 2Q+1)$ $(2Q-1, 2Q)$ are in the same cosets as $(2Q-1, 2Q+1)$ and $(2Q, 2Q+1)$ respectively.) By Eq. (27), we have

$$\langle \psi_j' | \hat{H} | \psi_j \rangle = -V \delta_{jj} \quad \text{for } j \leq h_r \quad (51)$$

$$3. \langle c(2Q-1)c(2Q)d(2Q+1)a(2Q+2) | a(2Q-1)a(2Q)b(2Q+1)c(2Q+2) \rangle$$

$$\langle f^{re'} | \hat{H}_I | P_c f^{re} \rangle \text{ will not vanish only when}$$

$P_c = (2Q-1, 2Q+2)$, $P_c = (2Q, 2Q+2)$, $P_c = (2Q-1, 2Q+2) (2Q, 2Q+1)$ or $P_c = (2Q, 2Q+2) (2Q-1, 2Q+1)$. By Eq. (27) and (30) and the discussion in case 1, we have

$$\begin{cases} \langle \psi_j' | \hat{H} | \psi_j \rangle = V \delta_{jj} & \text{for } j \leq j_r^+ \\ \langle \psi_j' | \hat{H} | \psi_j \rangle = -V \delta_{jj} & \text{for } j > j_r^+ \end{cases} \quad (52)$$

$$4. \langle c(2Q-3)c(2Q-2)d(2Q-1)d(2Q)a(2Q+1)b(2Q+2) | a(2Q-3)a(2Q-2)b(2Q+1)b(2Q)c(2Q+1)d(2Q+2) \rangle$$

$$\langle f^{re'} | \hat{H}_I | P_c f^{re} \rangle \text{ will not vanish only when}$$

$$P_c = (2Q-3, 2Q+1)(2Q-1, 2Q+2),$$

$$P_c = (2Q-3, 2Q+1)(2Q, 2Q+2),$$

$$P_c = (2Q-2, 2Q+1)(2Q-1, 2Q+2),$$

$$P_c = (2Q-2, 2Q+1)(2Q, 2Q+2),$$

$$P_c = (2Q-3, 2Q+1)(2Q-1, 2Q+2)(2Q-2, 2Q), \quad P_c = (2Q-3, 2Q+1)(2Q, 2Q+2)(2Q-2, 2Q-1),$$

$$P_c = (2Q-2, 2Q+1)(2Q-1, 2Q+2)(2Q-3, 2Q), \quad P_c = (2Q-2, 2Q+1)(2Q, 2Q+2)(2Q-3, 2Q-1).$$

and we have

$$\begin{cases} \langle \psi'_j | \hat{H} | \psi_j \rangle = 3V \delta_{jj} & \text{for } j \leq j_r^+ \\ \langle \psi'_j | \hat{H} | \psi_j \rangle = -V \delta_{jj} & \text{for } j > j_r^+ \end{cases} \quad (53)$$

$$\text{b. } r' - r = 1$$

$$5. \langle b(2Q-1)c(2Q) | a(2Q-1)a(2Q) \rangle$$

$$\langle f^{r'l'} | \hat{H}_I | P_c f^{rl} \rangle \text{ will not vanish only when } P_c = E.$$

So we have

$$\langle \psi'_j | \hat{H} | \psi_j \rangle = \sqrt{2} V \delta_{jj} \quad (54)$$

$$6. \langle c(2Q-1)d(2Q)a(2Q+1) | a(2Q-1)a(2Q)b(2Q+1) \rangle$$

$$\langle f^{r'l'} | \hat{H}_I | P_c f^{rl} \rangle \text{ will not vanish only when}$$

$$P_c = (2Q-1, 2Q+1) \text{ or } P_c = (2Q, 2Q+1). \text{ So we have}$$

$$\langle \psi'_j | \hat{H} | \psi_j \rangle = \sqrt{2} V [\tilde{\Gamma}_S(2Q-1, 2Q+1) + \tilde{\Gamma}_S(2Q, 2Q+1)]_{jj}^* \quad (55)$$

But $[\tilde{\Gamma}_S(2Q-1, 2Q+1) + \tilde{\Gamma}_S(2Q, 2Q+1)]$ is of reduced form, therefore by Eq. (26) we have

$$\langle \psi'_j | \hat{H} | \psi_j \rangle = -\sqrt{2} V \delta_{jj} \quad \text{for } j \leq h_r \quad (56)$$

$$7. \langle c(2Q-3)c(2Q-2)a(2Q-1)b(2Q) | a(2Q-3)a(2Q-2)b(2Q-1)b(2Q) \rangle$$

$$\langle f^{r_2'} | \hat{H}_I | P_c f^{r_2} \rangle \text{ will not vanish only when}$$

$P_c = (2Q-3, 2Q-1)$ or $P_c = (2Q-2, 2Q-1)$. So we have

$$\langle \psi'_j | \hat{H} | \psi_j \rangle = -\sqrt{2} V \delta_{jj} \quad \text{for } j \leq h_r \quad (57)$$

$$8. \langle c(2Q-3)c(2Q-2)a(2Q-1)b(2Q)d(2Q+1) | a(2Q-3)a(2Q-2)b(2Q-1)b(2Q)c(2Q+1) \rangle$$

$$\langle f^{r_2'} | \hat{H}_I | P_c f^{r_2} \rangle \text{ will not vanish only when}$$

$$P_c = (2Q-3, 2Q+1)(2Q-3, 2Q-1), \quad P_c = (2Q-2, 2Q+1)(2Q-3, 2Q-1),$$

$$P_c = (2Q-3, 2Q+1)(2Q-2, 2Q-1), \quad P_c = (2Q-2, 2Q+1)(2Q-2, 2Q-1).$$

So we have

$$\begin{aligned} \langle \psi'_j | \hat{H} | \psi_j \rangle &= \sqrt{2} V [\tilde{\Gamma}_S(12Q-3, 2Q+1)(2Q-3, 2Q-1) + \tilde{\Gamma}_S(12Q-2, 2Q+1)(2Q-3, 2Q-1) \\ &\quad + \tilde{\Gamma}_S(12Q-3, 2Q+1)(2Q-2, 2Q-1) + \tilde{\Gamma}_S(12Q-2, 2Q+1)(2Q-2, 2Q-1)]_{jj}^* \\ &= \sqrt{2} V \left\{ \tilde{\Gamma}_S(2Q-3, 2Q+1) + \tilde{\Gamma}_S(2Q-2, 2Q+1) \right\} \tilde{\Gamma}_S(2Q-3, 2Q-1) \\ &\quad + \left\{ \tilde{\Gamma}_S(2Q-3, 2Q+1) + \tilde{\Gamma}_S(2Q-2, 2Q+1) \right\} \tilde{\Gamma}_S(2Q-2, 2Q-1) \Big]_{jj}^* \end{aligned}$$

$$\begin{aligned}
&= \sqrt{2} V \left[- \left\{ \tilde{f}_S(2Q-3, 2Q-1) + \tilde{f}_S(2Q-2, 2Q-1) \right\} \right]_{jj}^* \\
&= \sqrt{2} V \delta_{jj} \quad \text{for } j \leq h_r \quad (58)
\end{aligned}$$

$$c. \quad r' - r = 2$$

$$9. \langle a(2Q-3)b(2Q-2)c(2Q-1)d(2Q) | a(2Q-3)a(2Q-2)b(2Q-1)b(2Q) \rangle$$

$$\langle f^{re'} | \hat{H}_I | P_c f^{re} \rangle \text{ will not vanish only when}$$

$$P_c = (2Q-2, 2Q-1) \text{ or } P_c = (2Q-2, 2Q). \text{ So we have}$$

$$\langle \psi_j' | \hat{H} | \psi_j \rangle = -2V \delta_{jj} \quad \text{for } j \leq h_r \quad (59)$$

IV. ILLUSTRATIONS

The eventual purpose of this thesis is to study the condition for the existence of ferromagnetism and the temperature dependence of the magnetization in a system of many electrons. To carry out the calculations of such a large system, approximations must be introduced. Consequently, some significant features may become obscured. Besides, the adequacy of the approximations introduced may well be doubted. Therefore, before going to the calculations of a large system, it is instructive to consider some simple systems whose calculations we can carry out more exactly.

A. Four Particle System

Let us first consider a system of four electrons, and suppose there are four available orbitals u_1, u_2, u_3, u_4 with band energy $2\epsilon, 2\epsilon, 4\epsilon, 4\epsilon$, and crystal momentum $k_1, -k_1, k_2, -k_2$ respectively. All the possible configurations $C(r, \ell)$, their total band energies $B(r, \ell)$ and their total crystal momenta $K(r, \ell)$ can be listed as follows:

r	ℓ	$C(r, \ell)$	$B(r, \ell)$	$K(r, \ell)$
0	1	$(u_1 u_1 u_2 u_2)$	8ϵ	0
	2	$(u_1 u_1 u_3 u_3)$	12ϵ	$2k_1 + 2k_2$
	3	$(u_1 u_1 u_4 u_4)$	12ϵ	$2k_1 - 2k_2$
	4	$(u_2 u_2 u_3 u_3)$	12ϵ	$-2k_1 + 2k_2$
	5	$(u_2 u_2 u_4 u_4)$	12ϵ	$-2k_1 - 2k_2$
	6	$(u_3 u_3 u_4 u_4)$	16ϵ	0

1	1	$(u_1 u_1 u_2 u_3)$	10ϵ	$k_1 + k_2$
	2	$(u_1 u_1 u_2 u_4)$	10ϵ	$k_1 - k_2$
	3	$(u_2 u_2 u_1 u_3)$	10ϵ	$-k_1 + k_2$
	4	$(u_2 u_2 u_1 u_4)$	10ϵ	$-k_1 - k_2$
	5	$(u_1 u_1 u_3 u_4)$	12ϵ	$2k_1$
	6	$(u_2 u_2 u_3 u_4)$	12ϵ	$-2k_1$
	7	$(u_3 u_3 u_1 u_2)$	12ϵ	$2k_2$
	8	$(u_4 u_4 u_1 u_2)$	12ϵ	$-2k_2$
	9	$(u_3 u_3 u_1 u_4)$	14ϵ	$k_1 + k_2$
	10	$(u_3 u_3 u_2 u_4)$	14ϵ	$-k_1 + k_2$
	11	$(u_4 u_4 u_1 u_3)$	14ϵ	$k_1 - k_2$
	12	$(u_4 u_4 u_2 u_3)$	14ϵ	$-k_1 - k_2$
<hr/>				
2	1	$(u_1 u_2 u_3 u_4)$	12ϵ	0

To obtain the eigenenergies, we need only to solve the secular equations consisting of states with the same total momenta. In the following we will list the configurations corresponding to all possible values of S and K , and using the formula for the matrix elements of the Hamiltonian derived in the previous section, we can also write down the corresponding secular equations:

$$S=0$$

$$K=0 \quad \begin{vmatrix} C(0,1), C(0,6), C(2,1) \\ x-8\epsilon-4V & 0 & 2V & 0 \\ 0 & x-16\epsilon-4V & 2V & 0 \\ 2V & 2V & x-12\epsilon-6V & 0 \\ 0 & 0 & 0 & x-12\epsilon-6V \end{vmatrix} = 0$$

$$\left. \begin{array}{ll} K=2k_1+2k_2 & C(0,2) \\ K=2k_1-2k_2 & C(0,3) \\ K=-2k_1+2k_2 & C(0,4) \\ K=-2k_1-2k_2 & C(0,5) \end{array} \right\} x=12\epsilon+4V$$

$$\begin{array}{ll}
 K = k_1 + k_2 & C(1,1), C(1,9) \\
 K = k_1 - k_2 & C(1,2), C(1,11) \\
 K = -k_1 + k_2 & C(1,3), C(1,10) \\
 K = -k_1 - k_2 & C(1,4), C(1,12)
 \end{array} \left. \vphantom{\begin{array}{l} K = k_1 + k_2 \\ K = k_1 - k_2 \\ K = -k_1 + k_2 \\ K = -k_1 - k_2 \end{array}} \right\} \begin{vmatrix} x - 10\epsilon - 5V & -V \\ -V & x - 14\epsilon - 5V \end{vmatrix} = 0$$

$$\begin{array}{ll}
 K = 2k_1 & C(1,5) \\
 K = -2k_1 & C(1,6) \\
 K = 2k_2 & C(1,7) \\
 K = -2k_2 & C(1,8)
 \end{array} \left. \vphantom{\begin{array}{l} K = 2k_1 \\ K = -2k_1 \\ K = 2k_2 \\ K = -2k_2 \end{array}} \right\} x = 12\epsilon + 5V$$

$$S=1$$

$$K=0 \quad C(2,1) \quad x = 12\epsilon + 4V$$

$$\begin{array}{ll}
 K = k_1 + k_2 & C(1,1), C(1,9) \\
 K = k_1 - k_2 & C(1,2), C(1,11) \\
 K = -k_1 + k_2 & C(1,3), C(1,10) \\
 K = -k_1 - k_2 & C(1,4), C(1,12)
 \end{array} \left. \vphantom{\begin{array}{l} K = k_1 + k_2 \\ K = k_1 - k_2 \\ K = -k_1 + k_2 \\ K = -k_1 - k_2 \end{array}} \right\} \begin{vmatrix} x - 10\epsilon - 3V & -V \\ -V & x - 14\epsilon - 3V \end{vmatrix} = 0$$

$$\begin{array}{ll}
 K = 2k_1 & C(1,5) \\
 K = -2k_1 & C(1,6) \\
 K = 2k_2 & C(1,7) \\
 K = -2k_2 & C(1,8)
 \end{array} \left. \vphantom{\begin{array}{l} K = 2k_1 \\ K = -2k_1 \\ K = 2k_2 \\ K = -2k_2 \end{array}} \right\} x = 12\epsilon + 3V$$

$$S=2$$

$$K=0 \quad C(2,1) \quad x = 12\epsilon$$

All the secular equations listed above can be easily solved. All the eigenenergies (in terms of ϵ) as functions of the ratio V/ϵ are shown graphically in Fig. 1. The number appearing on each curve is the degeneracy of that eigenstate. From Fig. 1, we can see that there is a critical point at $(V/\epsilon)_c = 1.2248$; when V/ϵ is less than $(V/\epsilon)_c$, the ground state is a state with $S = 0$, i.e. the system is non-ferromagnetic; when V/ϵ is greater than $(V/\epsilon)_c$, the ground state is a state with $S = 2$, i.e. the system is ferromagnetic. The dashed line is the energy without configuration interaction. By comparing the dashed line with the solid line, we can see the effect of configuration interaction, i.e. the condition for the existence of ferromagnetism changes from $V/\epsilon > 1$ to $V/\epsilon > 1.2248$. Based on the eigenenergies and the corresponding degeneracies, we can calculate the temperature dependence of the magnetization as shown in Fig. 2, where the number on each curve is the ratio V/ϵ .

B. Eight Particle System

Now let us consider a system of eight electrons, and suppose there are eight available orbitals $u_1, u_2, u_3, u_4, u_5, u_6, u_7, u_8$, with band energy $2\epsilon, 2\epsilon, 4\epsilon, 4\epsilon, 6\epsilon, 6\epsilon, 8\epsilon, 8\epsilon$, and crystal momentum $k_1, -k_1, k_2, -k_2, k_3, -k_3, k_4, -k_4$ respectively.

FIGURE 1

FIGURE 2

FIGURE 3

FIGURE 4

To treat such a system in all detail is already a very big job. But what we are most interested in is the ground state energy. So let us just consider the case when $S = 0$ and $K = 0$. The solution of the secular equation in this case can reasonably be expected to give the ground state energy, if the ground state is not the one with $S = 4$. In this case, there are altogether 19 possible configurations, which will be listed in the following together with the corresponding diagonal matrix elements $E_d(r, \ell)$ and the number of possible states h_r :

r	ℓ	$c(r, \ell)$	$E_d(r, \ell)$	h_r
0	1	$(u_1 u_1 u_2 u_2 u_3 u_3 u_4 u_4)$	$24\epsilon + 16V$	1
	2	$(u_1 u_1 u_2 u_2 u_5 u_5 u_6 u_6)$	$32\epsilon + 16V$	1
	3	$(u_1 u_1 u_2 u_2 u_7 u_7 u_8 u_8)$	$40\epsilon + 16V$	1
	4	$(u_3 u_3 u_4 u_4 u_5 u_5 u_6 u_6)$	$40\epsilon + 16V$	1
	5	$(u_3 u_3 u_4 u_4 u_7 u_7 u_8 u_8)$	$48\epsilon + 16V$	1
	6	$(u_5 u_5 u_6 u_6 u_7 u_7 u_8 u_8)$	$56\epsilon + 16V$	1
2	1	$(u_1 u_1 u_2 u_2 u_3 u_4 u_5 u_6)$	$28\epsilon + 18V$	2
	2	$(u_1 u_1 u_2 u_2 u_3 u_4 u_7 u_8)$	$32\epsilon + 18V$	2
	3	$(u_3 u_3 u_4 u_4 u_1 u_2 u_5 u_6)$	$32\epsilon + 18V$	2
	4	$(u_1 u_1 u_2 u_2 u_5 u_6 u_7 u_8)$	$36\epsilon + 18V$	2
	5	$(u_3 u_3 u_4 u_4 u_1 u_2 u_7 u_8)$	$36\epsilon + 18V$	2
	6	$(u_5 u_5 u_6 u_6 u_1 u_2 u_3 u_4)$	$36\epsilon + 18V$	2
	7	$(u_3 u_3 u_4 u_4 u_5 u_6 u_7 u_8)$	$44\epsilon + 18V$	2
	8	$(u_5 u_5 u_6 u_6 u_1 u_2 u_7 u_8)$	$44\epsilon + 18V$	2
	9	$(u_7 u_7 u_8 u_8 u_1 u_2 u_3 u_4)$	$44\epsilon + 18V$	2

10		$(u_5 u_5 u_6 u_6 u_3 u_4 u_7 u_8)$	$48\epsilon + 18V$	2
11		$(u_7 u_7 u_8 u_8 u_1 u_2 u_5 u_6)$	$48\epsilon + 18V$	2
12		$(u_7 u_7 u_8 u_8 u_3 u_4 u_5 u_6)$	$52\epsilon + 18V$	2
<hr/>				
4	1	$(u_1 u_2 u_3 u_4 u_5 u_6 u_7 u_8)$	$40\epsilon + 20V$	14
<hr/>				

The total number of possible states is $6 + 2 \times 12 + 14 = 44$, so the dimension of our secular equation is also 44. But this secular equation can be reduced, and the dimension of the reduced secular equation containing the ground state is just 19, the number of possible configurations in this case. This 19-by-19 secular equation has been solved by using IBM-7040 computer. The result together with the energy of the state with $S=4$ is shown in Fig. 3, where the number on some of the curves indicates the number of eigenvalues that are almost coincident. From Fig. 3, we can see that the condition for ferromagnetism is $(V/\epsilon)_c > 1.1$. The temperature dependence of the magnetization of eight particle system calculated by taking the diagonal elements as eigenvalues is shown in Fig. 4.

C. Discussion

By comparing the results of the calculations of four particle system and eight particle system, we can find the following indications:

1. The effect of the configuration interaction changes the condition for ferromagnetism of the four particle system by about 22% and that of eight particle system by about 10%. This suggests that the effect of configuration interaction becomes less important as the number of particles increases. Hence our later calculations will be made by neglecting the configuration interaction.

2. The corresponding normalized curves of magnetization in the two systems are quite similar except the one with $V/\epsilon = 1.2$. The significant difference in this case shows the effect of configuration interaction.

3. The high temperature limit of the magnetization of the eight particle system is lower than that of the four particle system and the variation of the magnetization curves of the former is sharper than that of the latter. These suggest that as the number of particles increases the Curie temperature transition will become sharper.

In both of these small systems, we do have ferromagnetic states at low temperature, if V is large enough when compared with ϵ ; but we do not have critical transition temperatures where the systems change suddenly from magnetic states to non-magnetic states, i.e. the Curie temperatures. This can be understood by the following

reasons: At extremely low temperature, the ground state is overwhelmingly important, so the magnetism of a system is determined by the energies of the states; while at extremely high temperature, it is determined by the numbers of states because all states are equally important. Or if we consider the free energy of a system, it is obvious that at lower temperature, the internal energy term gives the more important contribution; while at high temperature, the entropy term gives the more important contribution. The Curie temperature can be understood as the transition point of relative importance between the energies of states and the multiplicities of states. We can have an overwhelmingly large number of states with very small S only when we have a large number of particles in a system. So the existence of a sharp Curie temperature is essentially a phenomenon of a large system.

V. CALCULATION OF MAGNETIZATION

A. High Temperature Limit

In the high temperature limit, every state is of equal importance, and the magnetization of the system can be calculated by the following formula

$$\langle S \rangle_{\infty} = \frac{\sum_{S=0}^{N/2} S T(S)}{\sum_{S=0}^{N/2} T(S)} \quad (60)$$

where $T(S)$ is the total number of possible states with eigenvalue S as given by Eq. (15). The calculation of Eq. (60) can be carried out rigorously without making any approximations or assumptions to give the following result:

$$\langle S \rangle_{\infty} = \frac{(N - \frac{N^2}{2C} + \frac{1}{2}) \left[\frac{C!}{(C - \frac{N}{2})! (\frac{N}{2})!} \right]^2}{\frac{(2C)!}{(2C-N)! N!}} - \frac{1}{2} \quad (61)$$

The derivation of the above equation will be given in Appendix II. Using the Stirling's formula for the factorial functions, Eq. (61) can be simplified to be

$$\langle S \rangle_{\infty} \approx (2N - \frac{N^2}{C} + 1) \sqrt{\frac{C}{\pi(2C-N)N}} - \frac{1}{2} \approx \sqrt{\frac{(2C-N)N}{\pi C}} \quad (62)$$

To normalize the magnetization, we have

$$\frac{\langle S \rangle}{N/2} \approx 2 \sqrt{\frac{2C-N}{\pi C N}} \quad (63)$$

From Eq. (63) we can see that the normalized magnetization at the high temperature limit is of the order of $1/\sqrt{N}$, which is vanishingly small. It is understandable as due to the overwhelmingly large number of states with small S . Thus we have rigorously proved that at the high temperature limit, no system of the form considered can have spontaneous magnetization.

B. Low Temperature Limit

One of the most important problems of ferromagnetism is the condition for the existence of ferromagnetism at absolute zero temperature, i.e. the condition for the ground state to be a magnetic state. If we take the diagonal elements of the Hamiltonian as the eigenenergies (i.e. to neglect the effect of configuration interaction), then from Eq. (46) we have

$$E(S, r, l) = B(r, l) + \left[\frac{N^2}{4} + r - S(S+1) \right] V \quad (64)$$

So the only unknown term is the total band energy $B(r, l)$.

If we arrange the configurations in such order that

$B(r, l) \leq B(r, l+1)$, then we need only to consider $B(r, l)$,

since we are now interested only in the possible candidates

for the ground state. Under the first assumption about the band structure of our model, $B(r,1)$ as a function of r has a certain periodic feature with period d . So it is convenient to express r as

$$r = qd + t \quad (65)$$

where q and t are natural numbers and $t < d$. Then we have

$$B(r,1) = \left[\frac{N}{2} \left(\frac{N}{2} + d \right) + q^2 d^2 + td(2q+1) \right] \epsilon \quad (66)$$

Putting Eq. (66) into Eq. (64) we have

$$E(S,r,1) = \left[\frac{N}{2} \left(\frac{N}{2} + d \right) + q^2 d^2 + td(2q+1) \right] \epsilon + \left[\frac{N^2}{4} + qd + t - S(S+1) \right] V \quad (67)$$

By observing Eq. (67), we can see that, for a given S , the lowest possible energy is the one corresponding to the lowest possible value of r , i.e. $r = S$. So, to find the ground state, we can put $r = S$. Replacing the S in Eq. (67) by the expression in Eq. (65), we have

$$\begin{aligned} E(S,S,1) = & \left[\frac{N}{2} \left(\frac{N}{2} + d \right) \epsilon + \frac{N^2}{4} V \right] + [q^2 d^2 + 2qtd](\epsilon - V) \\ & + t(d\epsilon - tV) \end{aligned} \quad (68)$$

The first term on the right hand side of the above equation is constant. So, if $\epsilon - V \neq 0$, the second term is most important. Then, by considering the second term, we can draw the conclusion: If $\epsilon > V$, the ground state will be the

the one when $[q^2 d^2 + 2qtd]$ assumes the smallest possible value, i.e. the one with $S = 0$, hence we have a nonmagnetic state; if $\epsilon < V$, the ground state will be the one when $[q^2 d^2 + 2qtd]$ assumes the largest possible value, i.e. the one with $S = N/2$, hence we have a magnetic state. If $\epsilon - V = 0$, the second term vanishes, and by studying the third term, we find that we have ground states whenever S is a multiple of d .

However, the effect of configuration interaction will lower the eigenenergies of the nonmagnetic ground states more than those of magnetic ground states. Therefore, all we can say is that $V = \epsilon$ is the lower bound of V for the existence of ferromagnetism. But the illustrations in the previous section indicate that this is a close lower bound.

C. Curie Temperature

Another important problem of ferromagnetism is the existence of the Curie temperature T_c . In the following we are going to see how it occurs.

At temperatures higher than the absolute zero temperature, we have to consider states with energies higher than the ground state energy, the so-called excitation states. To treat such cases, we must first of all construct the partition function of our system. And again, to

simplify our situation, we will take the diagonal elements of the Hamiltonian as eigenenergies. This approximation that we are making here is not so bad as when we made it in determining the ground state, because our final result will not be so sensitive to the exact values of the eigenenergies. Now the partition function can be written as

$$Z = \sum_{S=0}^{N/2} \sum_{r=S}^{N/2} \sum_{l=1}^{m(r)} (2S+1) \left\{ \binom{2r}{r-S} - \binom{2r}{r-S-1} \right\} \times \exp \left\{ -\frac{1}{\kappa T} \left[B(r, l) + \left(\frac{N^2}{4} + r - S^2 - S \right) V \right] \right\} \quad (69)$$

where

$$(2S+1) \left\{ \binom{2r}{r-S} - \binom{2r}{r-S-1} \right\} = (2S+1)^2 \frac{(2r)!}{(r+S+1)!(r-S)!}$$

is the degeneracy of the corresponding state in our present simplified situation, and the summation over l runs over all configurations in the mode.

Let us first consider the summation over l , since only the term $B(r, l)$ depends on l , we can write

$$\begin{aligned} \sum_{l=1}^{m(r)} e^{-\frac{B(r, l)}{\kappa T}} &= e^{-\frac{B(r, 1)}{\kappa T}} \left[a_0(r) + a_1(r) e^{-\frac{d\epsilon}{\kappa T}} + \dots + a_n(r) e^{-\frac{nd\epsilon}{\kappa T}} \right] \\ &= e^{-\frac{B(r, 1)}{\kappa T}} H(r, T) \end{aligned} \quad (70)$$

where we have defined

$$H(r, T) = a_0(r) + a_1(r) e^{-\frac{d\epsilon}{\kappa T}} + \dots + a_n(r) e^{-\frac{nd\epsilon}{\kappa T}} + \dots \quad (71)$$

and $a_n(r)$ is the number of configurations in $M(r)$ with total band energy $nd\epsilon$ above the ground configuration energy in $M(r)$. It is difficult to determine exactly the $a_n(r)$'s. However, after studying the situation, we find that the overall distribution of the $a_n(r)$'s for a given value of r is very close to a Gaussian distribution with a very sharp peak at

$$\bar{n}_p = \left[\frac{NC}{2} - \frac{N^2}{4} - g^2 d - td(2g+1) \right] / d \quad (72)$$

and a standard deviation

$$\sigma = \left[\frac{1}{6} C \left(CN - \frac{N^2}{2} - \frac{Cr}{4} \right) \right]^{1/2} \quad (73)$$

This seems to suggest that a Gaussian distribution might be a good approximation, but unfortunately this is not true when the temperature is lower than the Curie temperature because then those configurations with total energies lies low are much more important than the others and in this region a Gaussian distribution fails to approximate the real situation. And a study of the situation of low lying configurations shows that the $a_n(r)$'s as functions of r are periodic with period d . The first few of them are given as follows:

$$a_0(r) = \binom{d}{t} \binom{d}{t} \quad (74)$$

$$a_1(r) = 2 \binom{d}{1} \binom{d}{t} \left\{ \binom{d}{t+1} + \binom{d}{t-1} \right\} \quad (75)$$

$$a_2(r) = \left\{ \binom{d}{1} \binom{d}{t+1} + \binom{d}{1} \binom{d}{t-1} \right\} + 2 \binom{d}{t} \left\{ \binom{d}{1} \binom{d}{t+1} + \binom{d}{1} \binom{d}{t-1} \right\} \\ + \binom{d}{2} \binom{d}{t+2} + \binom{d}{2} \binom{d}{t-2} + \binom{d}{1} \binom{d}{1} \binom{d}{t} \} \quad (76)$$

But in our mind the period d is of the order of $\sqrt{N}$ which is vanishingly small when compared with the whole range of S (i.e. $N/2$); so as far as the average value of S is concerned, the variation of the $a_n(r)$'s within a period is not significant. Therefore, to simplify our calculation, we can "smear out" the distribution of the $a_n(r)$'s over a period. Then the $a_n(r)$'s for small n are independent of r , e.g.

$$\langle a_0 \rangle = \left[\sum_{t=0}^{d-1} \binom{d}{t} \binom{d}{t} \right] / d = \left[\binom{2d}{d} - 1 \right] / d \quad (77)$$

The above discussion gives us the following limit values for $H(r, T)$:

$$\begin{cases} H(r, T) = \langle a_0 \rangle & \text{for } T=0 \\ H(r, T) = \frac{c!}{(c - \frac{N}{2} - r)! (\frac{N}{2} - r)! (2r)!} e^{-n_p d \epsilon / kT} & \text{for } T=\infty \end{cases} \quad (78)$$

So let us assume that $H(r, T)$ can be approximated by the following expression

$$H(r,T) \approx \frac{C!}{(C-\frac{N}{2}-r)!(\frac{N}{2}-r)!(2r)!} \exp\left\{-1/\left[\frac{1}{\log \alpha} + \frac{1}{n_p d \epsilon / \kappa T}\right]\right\} \quad (79)$$

where we have defined

$$\alpha = \langle a_0 \rangle \cdot \frac{C!}{(C-\frac{N}{2}-r)!(\frac{N}{2}-r)!(2r)!} \quad (80)$$

We have adopted the expression in Eq. (79) because it gives the correct values at both limits. And considering the order of magnitude, the $B(r,1)$ and n_p as given exactly in Eqs. (66) and (72) can well be approximated by

$$B(r,1) \approx \left[\frac{N^2}{4} + \frac{Nd}{2} + q^2 d^2 + 2t q d + t^2 \right] \epsilon = \left[\frac{N^2}{4} + \frac{Nd}{2} + r^2 \right] \epsilon \quad (81)$$

$$n_p \approx \left[\frac{NC}{2} - \frac{N^2}{4} - q^2 d^2 - 2t q d - t^2 \right] / d = \left[\frac{NC}{2} - \frac{N^2}{4} - r^2 \right] / d \quad (82)$$

Then Eq. (70) becomes

$$\sum_{l=1}^{m(r)} e^{-\frac{B(r,l)}{\kappa T}} \approx \frac{C!}{(C-\frac{N}{2}-r)!(\frac{N}{2}-r)!(2r)!} \exp\left\{-\frac{\epsilon}{\kappa T} \left[\frac{N^2}{4} + \frac{Nd}{2} + r^2 \right] \right. \\ \left. -1/\left[\frac{1}{\log \alpha} + \frac{\kappa T}{\left(\frac{NC}{2} - \frac{N^2}{4} - r^2 \right) \epsilon} \right] \right\} \quad (83)$$

Putting this into Eq. (69) and taking those factors which are independent of the summation variables out of the summation signs, we have

$$\begin{aligned}
Z &\approx A \sum_{S=0}^{N/2} \sum_{r=S}^{N/2} \frac{(2S+1)^2 C!}{(C-\frac{N}{2}-r)!(\frac{N}{2}-r)!(r+S+1)!(r-S)!} \exp\left\{-\frac{1}{\kappa T} [S(S+1)V - (r^2\epsilon + rV)]\right. \\
&\quad \left. - 1 / \left[\frac{1}{\log \alpha} + \frac{\kappa T}{(\frac{NC}{2} - \frac{N^2}{4} - r^2)\epsilon} \right] \right\} \\
&= A \sum_{S=0}^{N/2} \sum_{r=S}^{N/2} W(S, r)
\end{aligned} \tag{84}$$

where we have defined

$$A = \exp\left\{-\frac{1}{\kappa T} \left[\frac{N}{2} \left(\frac{N}{2} + d \right) \epsilon + \frac{N^2}{2} V \right] \right\} \tag{85}$$

$$\begin{aligned}
W(S, r) &= \frac{(2S+1)^2 C!}{(C-\frac{N}{2}-r)!(\frac{N}{2}-r)!(r+S+1)!(r-S)!} \exp\left\{ \frac{1}{\kappa T} [S(S+1)V \right. \\
&\quad \left. - (r^2\epsilon + rV)] - 1 / \left[\frac{1}{\log \alpha} + \frac{\kappa T}{(\frac{NC}{2} - \frac{N^2}{4} - r^2)\epsilon} \right] \right\}
\end{aligned} \tag{86}$$

In order to study the behavior of the function $W(S, r)$, it is convenient to use the Stirling's formula for the factorial functions, to multiply both numerator and denominator by $(\epsilon/\kappa T)^{2C+4}$ and to define

$$\begin{aligned}
\epsilon' &= \frac{\epsilon}{\kappa T}, \quad \rho = \frac{V}{\epsilon}, \quad X_a = (C - \frac{N}{2})\epsilon', \quad X_b = \frac{N}{2}\epsilon', \quad X = S\epsilon', \quad Y = r\epsilon', \\
G(X, Y) &= \epsilon' \log W(X, Y)
\end{aligned} \tag{87}$$

and noting that ϵ' and $d\epsilon'$ are very small when compared with any of the X 's and Y , we have

$$\begin{aligned}
G(X,Y) \approx & (X_a+X_b) \log(X_a+X_b) - (X_a-Y) \log(X_a-Y) - (X_b-Y) \log(X_b-Y) \\
& - (Y+X) \log(Y+X) - (Y-X) \log(Y-X) + \rho X^2 - Y^2 \quad (88) \\
& - T_1 T_2 / (T_1 + T_2)
\end{aligned}$$

where

$$T_1 = (X_a+X_b) \log(X_a+X_b) - (X_a-Y) \log(X_a-Y) - (X_b-Y) \log(X_b-Y) - 2Y \log 2Y \quad (89)$$

$$T_2 = X_a X_b - Y^2 \quad (90)$$

Then, suppose that (X_o, Y_o) is the maximum point of $G(X, Y)$ in the X - Y plane, the Taylor series expansion of $G(X, Y)$ around (X_o, Y_o) can be written as

$$\begin{aligned}
G(X, Y) = G(X_o, Y_o) + \frac{1}{2!} \left[\frac{\partial^2 G(X_o, Y_o)}{\partial X_o^2} (X-X_o)^2 + 2 \frac{\partial^2 G(X_o, Y_o)}{\partial X_o \partial Y_o} (X-X_o)(Y-Y_o) \right. \\
\left. + \frac{\partial^2 G(X_o, Y_o)}{\partial Y_o^2} (Y-Y_o)^2 \right] + \dots \quad (91)
\end{aligned}$$

$$\begin{aligned}
\therefore W(X, Y) \approx e^{G(X_o, Y_o)/\epsilon'} \exp \left\{ \frac{1}{2\epsilon'} \left[\frac{\partial^2 G(X_o, Y_o)}{\partial X_o^2} (X-X_o)^2 \right. \right. \\
\left. \left. + 2 \frac{\partial^2 G(X_o, Y_o)}{\partial X_o \partial Y_o} (X-X_o)(Y-Y_o) + \frac{\partial^2 G(X_o, Y_o)}{\partial Y_o^2} (Y-Y_o)^2 \right] \right\} \quad (92)
\end{aligned}$$

Since the second derivatives of $G(X, Y)$ at (X_o, Y_o) are negative, from Eq. (92) we can see that $W(X, Y)$ is of the form of a Gaussian distribution in two dimensions with standard deviation

$$\sigma \sim \sqrt{\epsilon'} = \sqrt{2X_b/N} \sim 1/\sqrt{N} \quad (93)$$

which is vanishingly small. This means that $W(X,Y)$ has a very sharp peak at (X_o, Y_o) ; therefore, we have

$$\langle S \rangle = \langle \frac{X}{\epsilon'} \rangle \approx \frac{X_o}{\epsilon'} \quad (94)$$

Now (X_o, Y_o) can be determined by the following simultaneous equations:

$$\begin{cases} \frac{\partial G(X_o, Y_o)}{\partial X_o} \approx 2\rho X_o - \log(Y_o + X_o) + \log(Y_o - X_o) = 0 \end{cases} \quad (95)$$

$$\begin{cases} \frac{\partial G(X_o, Y_o)}{\partial Y_o} \approx \log(X_a - Y_o) + \log(X_b - Y_o) - \log(Y_o + X_o) - \log(Y_o - X_o) - 2Y_o \\ - [T_2'^2 \log \frac{(X_a - Y_o)(X_b - Y_o)}{(2Y_o)^2} - T_1'^2 2Y_o] / (T_1' + T_2')^2 = 0 \end{cases} \quad (96)$$

where $T_1' = T_1(Y = Y_o)$ and $T_2' = T_2(Y = Y_o)$. Eq. (95) can be solved easily to give

$$Y_o = X_o \coth \rho X_o \quad (97)$$

Putting Eq. (97) into Eq. (96), we obtain an equation which determines the X_o . This equation can be solved numerically. For different T , X_a and X_b are different, hence X_o is different. Thus we can find the temperature

dependence of the magnetization. Let us define the normalized magnetization as

$$\xi = \frac{\langle S \rangle}{N/2} \approx \frac{X_o}{X_b} \quad (98)$$

and

$$\eta = \frac{X_b}{X_a} = \frac{N}{2C-N} \quad (99)$$

The results of the calculations of ξ as a function of T/T_c with $\rho = 1.6$ and $\eta = 0.2, 0.8, 1.0$ are given in Fig. 5. It has been observed that the magnetization curves are not very sensitive to ρ (>1.3) and η . The experimental results of the magnetizations of iron, cobalt and nickel are also shown in Fig. 5. This indicates that the theoretical results of the present idealized model agree with the experimental results surprisingly well. The Curie temperature as function of ρ corresponding to different values of η has also been calculated. The result is given in Fig. 6.

FIGURE 5

FIGURE 6

APPENDIX I

Positive Nature of Exchange Integrals

When the one-electron wave functions are orthogonal (this is true in the present thesis since the Bloch functions are used), the exchange integrals are reduced to the following form

$$K_{ij} = \int u_i^*(r_1) u_j^*(r_2) V(r_1, r_2) u_j(r_1) u_i(r_2) du_1 du_2 \quad (\text{AI-1})$$

That this is necessarily positive whenever $V(r_1, r_2)$ is positive definite has been pointed out by Slater⁷⁾. But as far as we know, Slater has given a rigorous proof only for the case when $V(r_1, r_2) = \frac{e^2}{|r_1 - r_2|}$ and the boundary condition is typical with atoms or molecules.¹⁹⁾ In the present appendix, we are going to extend Slater's proof to a case applicable to the present thesis, i.e. when $V(r_1, r_2) = \frac{e^2 \exp\{-\alpha|r_1 - r_2|\}}{|r_1 - r_2|}$ and the boundary condition is periodic, typical in the customary treatment of solids.

If we write $u_i^*(r_1) u_j(r_1) = F(r_1)$, the exchange integral may be rewritten in the form

$$K_{ij} = \int F(r_1) F^*(r_2) V(r_1, r_2) du_1 du_2 \quad (\text{AI-2})$$

We may now define a potential, as

$$\phi(r_1) = \int F^*(r_2) V(r_1, r_2) du_2 \quad (\text{AI-3})$$

By Green's theorem, we have

$$\begin{aligned} & \int [\phi(r_2) \nabla^2 V(r, r_2) - V(r, r_2) \nabla^2 \phi(r_2)] dV_2 \\ &= \int [\phi(r_2) \nabla_2 V(r, r_2) - V(r, r_2) \nabla \phi(r_2)] \cdot dS_2 \end{aligned} \quad (\text{AI-4})$$

Now if the integration is taken over a periodic unit in a crystal, i.e. a rectangular block, the integrand on the right hand side of Eq. (AI-4) will be of the same magnitude but opposite directions at corresponding points on opposite surface of the rectangular block, so the surface integral vanishes. We also have

$$\nabla^2 V(r, r_2) = -4\pi \delta(r - r_2) + \alpha^2 V(r, r_2) \quad (\text{AI-5})$$

Therefore Eq. (AI-4) becomes

$$\phi(r) = \frac{1}{4\pi} \int [\alpha^2 \phi(r_2) - \nabla^2 \phi(r_2)] V(r, r_2) dV_2 \quad (\text{AI-6})$$

Comparing Eq. (AI-6) with Eq. (AI-3), we have

$$F^*(r_2) = \frac{1}{4\pi} [\alpha^2 \phi(r_2) - \nabla^2 \phi(r_2)] \quad (\text{AI-7})$$

from which

$$F(r) = \frac{1}{4\pi} [\alpha^2 \phi^*(r) - \nabla^2 \phi^*(r)] \quad (\text{AI-8})$$

We may now use these results to write the exchange integral in the form

$$K_{ij} = \frac{\alpha^2}{4\pi} \int \phi^*(r) \phi(r) dv_i - \frac{1}{4\pi} \int \phi(r) \nabla^2 \phi^*(r) dv_i \quad (\text{AI-9})$$

We now use the vector identity

$$\nabla \cdot (\phi \nabla \phi^*) = \phi \nabla^2 \phi^* + \nabla \phi \cdot \nabla \phi^* \quad (\text{AI-10})$$

which holds for any pair of functions ϕ , ϕ^* . We integrate this equation over the rectangular block. The divergence on the left hand side, by the divergence theorem, integrates to a surface integral over the volume enclosing the rectangular block, and in our case this surface integral vanishes. Hence we are left with the result that

$$\int \phi \nabla^2 \phi^* dv = - \int \nabla \phi \cdot \nabla \phi^* dv \quad (\text{AI-11})$$

That is, we have

$$K_{ij} = \frac{1}{4\pi} \int [|\alpha \phi(r)|^2 + |\nabla \phi(r)|^2] dv_i \quad (\text{AI-12})$$

This is necessarily positive, which was to be proved.

APPENDIX II

Derivation of $T(S)$, T and $\langle S \rangle_\infty$

From Eq. 15 we have

$$\begin{aligned}
T(S) &= (2S+1) \sum_{r=S}^{N/2} \frac{C!}{(C-\frac{N}{2}-r)!(\frac{N}{2}-r)!(2r)!} \left\{ \binom{2r}{r-S} - \binom{2r}{r-S-1} \right\} \\
&= (2S+1) \sum_{r=S}^{N/2} \frac{C!}{(C-\frac{N}{2}-r)!(\frac{N}{2}-r)!(2r)!} \cdot \frac{(2S+1) \cdot (2r)!}{(r+S+1)!(r-S)!} \quad (\text{AII-1}) \\
&= \frac{(2S+1)}{C+1} \binom{C+1}{\frac{N}{2}+S+1} \sum_{r=S}^{N/2} \binom{C-\frac{N}{2}-S}{r-S} \binom{\frac{N}{2}+S+1}{\frac{N}{2}-r}
\end{aligned}$$

And we know that

$$\begin{aligned}
(1+x)^{C-\frac{N}{2}-S} &= \binom{C-\frac{N}{2}-S}{0} + \binom{C-\frac{N}{2}-S}{1} x + \dots + \binom{C-\frac{N}{2}-S}{\frac{N}{2}-S-1} x^{\frac{N}{2}-S-1} \\
&\quad + \binom{C-\frac{N}{2}-S}{\frac{N}{2}-S} x^{\frac{N}{2}-S} + \dots + \binom{C-\frac{N}{2}-S}{C-\frac{N}{2}-S} x^{C-\frac{N}{2}-S} \quad (\text{AII-2})
\end{aligned}$$

$$\begin{aligned}
(1+x)^{\frac{N}{2}+S+1} &= \binom{\frac{N}{2}+S+1}{0} + \binom{\frac{N}{2}+S+1}{1} x + \dots + \binom{\frac{N}{2}+S+1}{\frac{N}{2}-S-1} x^{\frac{N}{2}-S-1} \\
&\quad + \binom{\frac{N}{2}+S+1}{\frac{N}{2}-S} x^{\frac{N}{2}-S} + \dots + \binom{\frac{N}{2}+S+1}{\frac{N}{2}+S+1} x^{\frac{N}{2}+S+1} \quad (\text{AII-3})
\end{aligned}$$

So the coefficient of $x^{\frac{N}{2}-S}$ in the expansion of

$$(1+x)^{C-\frac{N}{2}-S} \cdot (1+x)^{\frac{N}{2}+S+1} = (1+x)^{C+1} \quad \text{will be}$$

$$\begin{aligned}
& \binom{C-\frac{N}{2}-S}{0} \binom{\frac{N}{2}+S+1}{\frac{N}{2}-S} + \binom{C-\frac{N}{2}-S}{1} \binom{\frac{N}{2}+S+1}{\frac{N}{2}-S-1} + \dots + \binom{C-\frac{N}{2}-S}{\frac{N}{2}-S} \binom{\frac{N}{2}+S+1}{0} \\
&= \sum_{r=S}^{N/2} \binom{C-\frac{N}{2}-S}{r-S} \binom{\frac{N}{2}+S+1}{\frac{N}{2}-r} = \binom{C+1}{\frac{N}{2}-S}
\end{aligned} \tag{AII-4}$$

Putting Eq. (AII-4) into Eq. (AII-1) we have

$$T(S) = \frac{(2S+1)^2}{C+1} \binom{C+1}{\frac{N}{2}+S+1} \binom{C+1}{\frac{N}{2}-S} \tag{AII-5}$$

$$\begin{aligned}
& \therefore \sum_{S=0}^{N/2} \sum_{r=S}^{N/2} \frac{C!}{(C-\frac{N}{2}-r)! (\frac{N}{2}-r)! (2r)!} \left\{ \binom{2r}{r-S} - \binom{2r}{r-S-1} \right\} \\
&= \sum_{S=0}^{N/2} \frac{T(S)}{2S+1} = \sum_{S=0}^{N/2} \frac{2S+1}{C+1} \binom{C+1}{\frac{N}{2}+S+1} \binom{C+1}{\frac{N}{2}-S}
\end{aligned} \tag{AII-6}$$

and

$$\begin{aligned}
& \sum_{r=0}^{N/2} \sum_{S=0}^r \frac{C!}{(C-\frac{N}{2}-r)! (\frac{N}{2}-r)! (2r)!} \left\{ \binom{2r}{r-S} - \binom{2r}{r-S-1} \right\} \\
&= \sum_{r=0}^{N/2} \frac{C!}{(C-\frac{N}{2}-r)! (\frac{N}{2}-r)! (2r)!} \left\{ \left[\binom{2r}{r} - \binom{2r}{r-1} \right] + \left[\binom{2r}{r-1} - \binom{2r}{r-2} \right] \right. \\
&\quad \left. + \dots + \left[\binom{2r}{1} - \binom{2r}{0} \right] + \left[\binom{2r}{0} - 0 \right] \right\} \\
&= \sum_{r=0}^{N/2} \frac{C!}{(C-\frac{N}{2}-r)! (\frac{N}{2}-r)! (2r)!} \binom{2r}{r} = \binom{C}{\frac{N}{2}} \sum_{r=0}^{N/2} \binom{C-\frac{N}{2}}{r} \binom{\frac{N}{2}}{\frac{N}{2}-r} \\
&= \binom{C}{\frac{N}{2}} \binom{C}{\frac{N}{2}}
\end{aligned} \tag{AII-7}$$

But Eqs. (AII-6) and (AII-7) are exactly the same except that the summations are taken in different order. So we have

$$\binom{C}{\frac{N}{2}} \binom{C}{\frac{N}{2}} = \sum_{S=0}^{N/2} \frac{2S+1}{C+1} \binom{C+1}{\frac{N}{2}+S+1} \binom{C+1}{\frac{N}{2}-S} \quad (\text{AII-8})$$

Putting $2S+1 = (N+2S+2) - (N+1)$, Eq. (AII-8) becomes

$$\begin{aligned} \binom{C}{\frac{N}{2}} \binom{C}{\frac{N}{2}} &= 2 \sum_{S=0}^{N/2} \binom{C}{\frac{N}{2}+S} \binom{C+1}{\frac{N}{2}-S} - \frac{N+1}{C+1} \sum_{S=0}^{N/2} \binom{C+1}{\frac{N}{2}+S+1} \binom{C+1}{\frac{N}{2}-S} \\ &= 2 \sum_{S=0}^{N/2} \binom{C}{\frac{N}{2}+S} \binom{C+1}{\frac{N}{2}-S} - \frac{N+1}{C+1} \cdot \frac{1}{2} \binom{2C+2}{N+1} \end{aligned} \quad (\text{AII-9})$$

$$\therefore \sum_{S=0}^{N/2} \binom{C}{\frac{N}{2}+S} \binom{C+1}{\frac{N}{2}-S} = \frac{1}{2} \binom{2C+1}{N} + \frac{1}{2} \binom{C}{\frac{N}{2}} \binom{C}{\frac{N}{2}} \quad (\text{AII-10})$$

Putting $2S+1 = (2C-N+2S+2) - (2C-N+1)$, Eq. (AII-8) becomes

$$\begin{aligned} \binom{C}{\frac{N}{2}} \binom{C}{\frac{N}{2}} &= 2 \sum_{S=0}^{N/2} \binom{C+1}{\frac{N}{2}+S+1} \binom{C}{\frac{N}{2}-S} - \frac{2C-N+1}{C+1} \sum_{S=0}^{N/2} \binom{C+1}{\frac{N}{2}+S+1} \binom{C+1}{\frac{N}{2}-S} \\ &= 2 \sum_{S=0}^{N/2} \binom{C+1}{\frac{N}{2}+S+1} \binom{C}{\frac{N}{2}-S} - \frac{2C-N+1}{C+1} \cdot \frac{1}{2} \binom{2C+2}{N+1} \end{aligned} \quad (\text{AII-11})$$

$$\therefore \sum_{S=0}^{N/2} \binom{C+1}{\frac{N}{2}+S+1} \binom{C}{\frac{N}{2}-S} = \frac{1}{2} \binom{2C+1}{N+1} + \frac{1}{2} \binom{C}{\frac{N}{2}} \binom{C}{\frac{N}{2}} \quad (\text{AII-12})$$

Now we are ready to calculate

$$\begin{aligned}
T &= \sum_{S=0}^{N/2} T(S) = \sum_{S=0}^{N/2} \frac{(2S+1)^2}{C+1} \binom{C+1}{\frac{N}{2}+S+1} \binom{C+1}{\frac{N}{2}-S} \\
&= \sum_{S=0}^{N/2} \left\{ \frac{2S+1}{C+1} \binom{C+1}{\frac{N}{2}+S+1} \right\} \left\{ (2S+1) \binom{C+1}{\frac{N}{2}-S} \right\} \\
&= \sum_{S=0}^{N/2} \left\{ \frac{(N+2S+2)-(N+1)}{C+1} \binom{C+1}{\frac{N}{2}+S+1} \right\} \left\{ [(2C-N+2S+2)-(2C-N+1)] \binom{C+1}{\frac{N}{2}-S} \right\} \\
&= \sum_{S=0}^{N/2} \left\{ 2 \binom{C}{\frac{N}{2}+S} - \frac{(N+1)}{C+1} \binom{C+1}{\frac{N}{2}+S+1} \right\} \left\{ 2(C+1) \binom{C}{\frac{N}{2}-S} - (2C-N+1) \binom{C+1}{\frac{N}{2}-S} \right\} \\
&= \sum_{S=0}^{N/2} \left\{ 4(C+1) \binom{C}{\frac{N}{2}+S} \binom{C}{\frac{N}{2}-S} - 2(2C-N+1) \binom{C}{\frac{N}{2}+S} \binom{C+1}{\frac{N}{2}-S} \right. \\
&\quad \left. - 2(N+1) \binom{C+1}{\frac{N}{2}+S+1} \binom{C}{\frac{N}{2}-S} + \frac{(N+1)(2C-N+1)}{C+1} \binom{C+1}{\frac{N}{2}+S+1} \binom{C+1}{\frac{N}{2}-S} \right\} \quad (\text{AII-13}) \\
&= 4(C+1) \sum_{S=0}^{N/2} \binom{C}{\frac{N}{2}+S} \binom{C}{\frac{N}{2}-S} - 2(2C-N+1) \sum_{S=0}^{N/2} \binom{C}{\frac{N}{2}+S} \binom{C+1}{\frac{N}{2}-S} \\
&\quad - 2(N+1) \sum_{S=0}^{N/2} \binom{C+1}{\frac{N}{2}+S+1} \binom{C}{\frac{N}{2}-S} + \frac{(N+1)(2C-N+1)}{C+1} \sum_{S=0}^{N/2} \binom{C+1}{\frac{N}{2}+S+1} \binom{C+1}{\frac{N}{2}-S}
\end{aligned}$$

Using the binomial expansion, it can be shown that

$$\sum_{S=0}^{N/2} \binom{C}{\frac{N}{2}+S} \binom{C}{\frac{N}{2}-S} = \frac{1}{2} \left\{ \binom{2C}{N} + \binom{C}{\frac{N}{2}} \binom{C}{\frac{N}{2}} \right\} \quad (\text{AII-14})$$

and that

$$\sum_{S=0}^{N/2} \binom{C+1}{\frac{N}{2}+S+1} \binom{C+1}{\frac{N}{2}-S} = \frac{1}{2} \binom{2C+2}{N+1} \quad (\text{AII-15})$$

Putting Eqs. (AII-10), (AII-12), (AII-14) and (AII-15) into Eq. (AII-13), we have

$$\begin{aligned} T &= (4C+4) \cdot \frac{1}{2} \left\{ \binom{2C}{N} + \binom{C}{\frac{N}{2}} \binom{C}{\frac{N}{2}} \right\} - (4C-2N+2) \frac{1}{2} \left\{ \binom{2C+1}{N} + \binom{C}{\frac{N}{2}} \binom{C}{\frac{N}{2}} \right\} \\ &\quad - (2N+2) \cdot \frac{1}{2} \left\{ \binom{2C+1}{N+1} + \binom{C}{\frac{N}{2}} \binom{C}{\frac{N}{2}} \right\} + \frac{(N+1)(2C-N+1)}{C+1} \cdot \frac{1}{2} \binom{2C+2}{N+1} \quad (\text{AII-16}) \\ &= \binom{2C}{N} = \frac{(2C)!}{(2C-N)! N!} \end{aligned}$$

From Eq. (AII-13), we have

$$\begin{aligned} \sum_{S=0}^{N/2} S T(S) &= \sum_{S=0}^{N/2} S \left\{ 4(C+1) \binom{C}{\frac{N}{2}+S} \binom{C}{\frac{N}{2}-S} - 2(2C-N+1) \binom{C}{\frac{N}{2}+S} \binom{C+1}{\frac{N}{2}-S} \right. \\ &\quad \left. - 2(N+1) \binom{C+1}{\frac{N}{2}+S+1} \binom{C}{\frac{N}{2}-S} + \frac{(N+1)(2C-N+1)}{C+1} \binom{C+1}{\frac{N}{2}+S+1} \binom{C+1}{\frac{N}{2}-S} \right\} \\ &= \sum_{S=0}^{N/2} \left\{ 4(C-\frac{N}{2})(C+1) \binom{C}{\frac{N}{2}+S} \binom{C}{\frac{N}{2}-S} - 4C(C+1) \binom{C-1}{\frac{N}{2}+S} \binom{C}{\frac{N}{2}-S} \right. \\ &\quad \left. - 2(2C-N+1)(C+1) \binom{C}{\frac{N}{2}+S} \binom{C}{\frac{N}{2}-S} + (2C-N+1)(2C-N+2) \binom{C}{\frac{N}{2}+S} \binom{C+1}{\frac{N}{2}-S} \right. \\ &\quad \left. - 2(N+1)(C+1) \binom{C}{\frac{N}{2}+S} \binom{C}{\frac{N}{2}-S} + (N+1)(N+2) \binom{C+1}{\frac{N}{2}+S+1} \binom{C}{\frac{N}{2}-S} \right. \\ &\quad \left. + (N+1)(2C-N+1) \binom{C}{\frac{N}{2}+S} \binom{C+1}{\frac{N}{2}-S} - \frac{(N+1)(2C-N+1)(\frac{N}{2}+1)}{C+1} \binom{C+1}{\frac{N}{2}+S+1} \binom{C}{\frac{N}{2}-S} \right\} \end{aligned}$$

$$\begin{aligned}
&= -2(c+1)(N+2) \sum_{S=0}^{N/2} \binom{C}{\frac{N}{2}+S} \binom{C}{\frac{N}{2}-S} - 4C(c+1) \sum_{S=0}^{N/2} \binom{C-1}{\frac{N}{2}+S} \binom{C}{\frac{N}{2}-S} \\
&\quad + (2C+3)(2C-N+1) \sum_{S=0}^{N/2} \binom{C}{\frac{N}{2}+S} \binom{C}{\frac{N}{2}-S} + (N+1)(N+2) \sum_{S=0}^{N/2} \binom{C+1}{\frac{N}{2}+S+1} \binom{C}{\frac{N}{2}-S} \\
&\quad - \frac{(2C-N+1)(N+1)(N+2)}{2(c+1)} \sum_{S=0}^{N/2} \binom{C+1}{\frac{N}{2}+S+1} \binom{C+1}{\frac{N}{2}-S} \\
&= -2(c+1)(N+2) \cdot \frac{1}{2} \left\{ \binom{2C}{N} + \binom{C}{\frac{N}{2}} \binom{C}{\frac{N}{2}} \right\} \\
&\quad - 4C(c+1) \cdot \frac{1}{2} \left\{ \binom{2C-1}{N} + \binom{C-1}{\frac{N}{2}} \binom{C-1}{\frac{N}{2}} \right\} \\
&\quad + (2C+3)(2C-N+1) \cdot \frac{1}{2} \left\{ \binom{2C+1}{N} + \binom{C}{\frac{N}{2}} \binom{C}{\frac{N}{2}} \right\} \\
&\quad + (N+1)(N+2) \cdot \frac{1}{2} \left\{ \binom{2C+1}{N+1} + \binom{C}{\frac{N}{2}} \binom{C}{\frac{N}{2}} \right\} \\
&\quad - \frac{(2C-N+1)(N+1)(N+2)}{2(c+1)} \cdot \frac{1}{2} \binom{2C+2}{N+1} \\
&= \left(N - \frac{N^2}{2C} + \frac{1}{2} \right) \binom{C}{\frac{N}{2}} \binom{C}{\frac{N}{2}} - \frac{1}{2} \binom{2C}{N}
\end{aligned}$$

(AII-17)

$$\therefore \langle S \rangle_{\infty} = \frac{\sum_{S=0}^{N/2} S T(S)}{\sum_{S=0}^{N/2} T(S)} = \frac{\left(N - \frac{N^2}{2C} + \frac{1}{2} \right) \binom{C}{\frac{N}{2}} \binom{C}{\frac{N}{2}} - \frac{1}{2} \binom{2C}{N}}{\binom{2C}{N}} \quad (\text{AII-18})$$