Cluster Expansion in the Heitler–London Approach to Many-Electron Problems*

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The Heitler–London method based on nonorthogonal atomic orbitals is applied to arrays of an infinitely large number of atoms. The electronic energy is given by a quotient with strongly divergent numerator and denominator, which until now has defied correct computation. By noticing some resemblance of this problem to the linked-cluster expansion in many-body problems, we have now developed a new method to compute the Heitler–London energy. Here, the numerator and denominator are divided simultaneously by a common factor, which leads to a set of recurrence relations between the normalization matrices **F**. The matrices **F** are essential parts of the quotient to be calculated. When an overlap integral $\langle k|h\rangle$ is represented by a line starting from h and ending at k, the calculation of **F** using the recurrence relations is carried out systematically by drawing diagrams consisting of connected loops. Since our present aim in applying the Heitler–London method is to compute spin-wave spectra, the calculation is carried out in the complete space of spin waves and the energy expression is given by a Hermitian matrix. This introduces additional matrices **A**. The computation of **A** is also carried out by the diagram technique, since **A** can be expanded into an asymptotic series using **F**. Finally the energy matrix is written as a sum over connected diagrams, in accordance with the speculation obtained from the linked-cluster expansion. An error introduced by truncating the series of diagrams is also calculated. The present method not only ensures that the energy density in the Heitler–London method is finite, but also provides an accurate and practical way to compute the Heitler–London energy, which has never been accomplished previously. To calculate the ground-state energy the technique is simplified since the computation of **A** can be completely eliminated.

I. INTRODUCTION

FOR many years, the concept of exchange coupling has played an important role in theories of chemical bond and magnetism. This concept was first introduced in the Heitler–London theory[1] of molecular binding and applied by Heisenberg[2] to ferromagnetism. Although the Heisenberg theory has been formulated in a very attractive form by Van Vleck[3] and Møller[4] and much theoretical work in magnetism has used this formalism, the method has been criticized in many respects.

In this paper, we will limit our discussion to one of the difficulties inherited in the Heitler–London approach to magnetic problems; that is, the nonorthogonality difficulty in calculating energy spectra. The other aspects of the difficulties will be found in, for example, review articles by Herring.[5]

The nonorthogonality difficulty can be stated as follows. If we assume that there are no spin-orbit terms in the Hamiltonian, the calculation of the Heitler–London energy of the form

$$E=\int\Psi^*\mathcal{H}\Psi d\tau\Big/\int\Psi^*\Psi d\tau \tag{1.1}$$

is reduced to that of the Heisenberg exchange Hamiltonian

$$\mathcal{H}_{\rm eff}=-2\sum_{i>j}J_{ij}\mathbf{S}_i\cdot\mathbf{S}_j, \tag{1.2}$$

provided the wave function Ψ of this system is constructed from *orthogonal* atomic orbitals.

The orthogonality of atomic orbitals makes the exchange integrals J_{ij} thus obtained all positive. Since a positive exchange integral in the Heisenberg theory corresponds to ferromagnetism, this approach leads to the obviously absurd conclusion that all substances are ferromagnetic.

To utilize the Heitler–London method to full advantage, nonorthogonal atomic orbitals should be used as the basis. However, the calculation of energy spectra becomes extremely difficult since both numerator and denominator of the energy expression (1.1) diverge when the number N of electrons involved increases. It is not at all obvious if it is permissible to discard, from the energy expression, terms of higher order in overlaps. Such terms may appear N times, N^2 times, or even more. Slater[6] and Inglis[7] pointed out this difficulty, which led to grave doubts as to the validity of the Heisenberg exchange Hamiltonian[8,9] (1.2).

Previously,[10] we have discussed this difficulty. (This paper will be referred to as paper I.) The remaining problems will also be examined in detail and will be published elsewhere.[11] The conclusions will be summarized as follows: The exact calculation of the Heitler–London energy can be converted to the eigenvalue problem of a spin Hamiltonian of the form

$$\mathcal{H}_{\rm spin}=\sum_P(-1)^P J_P P^\sigma, \tag{1.3}$$

where P is a permutation operator and P^σ the corresponding permutation of spin variables. The exchange energy J_P for a single interchange P of electrons is very nearly equal to the value one would compute by neglecting terms of higher order in overlaps. The con-

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tribution from the higher order terms in Hamiltonian $\sum_P'(-1)^P J_P P^\sigma$, where the summation $\sum_P'$ excludes all single interchanges, is small.

This gives a rigorous justification for using the Heisenberg exchange Hamiltonian in the calculation of thermodynamical functions.[12] However, we have not succeeded in evaluating the value of J_P when P is not a single interchange. Although we have bounded the total energy E as well as the exchange energy J_P for a single interchange by applying algebraic identities that exist between J_P's, the values of the bounds are merely first order in the approximation. The method cannot be extended immediately to narrow the bounds beyond the single interchange approximation. This implies that the accuracy of the Heitler–London method so far is limited up to that of the Heisenberg model.

If we would like to use the Heitler–London method as a rigorous mathematical tool to calculate many-electron systems, we have to provide an expansion technique with which the energy expression (1.1) as well as the expectation value of any observable quantity can be calculated up to a desired accuracy. This is the purpose of the present paper.

To achieve this goal, we have to carry out more detailed calculations of both the numerator and the denominator of (1.1). It is, of course, impossible to proceed with the calculation directly. However, we find that our problem has some resemblance to the linked cluster expansion for Green functions.[13] In either case, the quantity to be calculated is a quotient with divergent denominator and numerator. Use of Dyson's equation[14] reduces the numerator of a Green function to a factor multiplying all connected diagrams. Since the factor is exactly equal to the denominator and cancelled by it, the Green function consists of just the sum over all connected diagrams.

In the Heitler–London calculation, a set of recurrence relations (3.14) and (3.15) for the **F** matrices will take the place of Dyson's equation. Here the **F** matrices defined by (3.1) are the normalization matrices and the essential quantities to be calculated. Since the recurrence relations reduces the **F** matrices for N-electron systems to those for $N-1, N-2, \cdots$ electron systems, the successive application of the relations leads to the complete expansion of the **F** matrices in terms of overlaps. The expansion technique is similar to that used in both classical and quantum-theoretical treatments of many-body problems, and use of diagrams will facilitate the computation. It will be finally found that **F** is written as a sum over connected diagrams, when an overlap integral of the type $\langle\chi_k|\chi_h\rangle$ is denoted by a line starting from the center h of the atomic orbital χ_h and ending at k of χ_k. Following the prescriptions (i)–(iv) described in Sec. III(1b), diagrams for **F** can be drawn without knowledge of the expansion technique used. An error accompanied by truncating the expansion will be calculated by using a theorem which will be probed in the Appendix.

Since the energy matrix should be Hermitian, it is necessary to calculate, in addition to **F**, the matrix **A** defined by (3.2). The matrix **A** is to correct the deviation of **F** from Hermitian form. Although **A** is close to a unit matrix, the straight forward calculation is very difficult. In Sec. III(2), we shall, instead, develop an asymptotic expansion of **A** and discuss the convergence of the series. The calculation can also be carried out automatically by drawing diagrams.

By multiplying **F** by **A**, the energy matrix can be obtained and it will be found that the energy matrix is also written as a sum over connected diagrams.

The significance of the present method will be summarized as follows.

(1) By using this method, a rigorous calculation of the Heitler–London method including all overlaps can be carried out without difficulty. The effect of overlaps between distant atoms has been cancelled out rigorously. Such a calculation has never been performed for a many-electron system previously.[15,16] In fact, this has been considered impossible from the mathematical point of view.[8]

(2) The awesome task of calculating the inverse of the overlap matrix[17] is completely eliminated. The calculation can be carried out just by drawing diagrams. Even for a system with a small number of electrons, therefore, this method will be more convenient than inverting the overlap matrix directly.

(3) The fact that the energy matrix consists of just a sum over connected diagrams implies that the energy density is a finite number. This will, in practice, eliminate the nonorthogonality difficulties. Actually, a rigorous proof for this problem will be given in a forthcoming paper.[11]

So far, the calculation was carried out in the total space of the Heitler–London wave functions aiming at the computation of spin-wave spectra. The wave functions are naturally described by a vector in that space and the energy matrix is given in the form (2.26) or (2.27) rather than (1.1). This is why the matrix **A** appears. If, on the other hand, one is interested in the

[12] For a general review of the theory of direct exchange see C. Herring, in *Magnetism*, edited by G. Rado and H. Suhl (Academic Press Inc., New York, to be published).

[13] For instance, P. Nozières and D. Pines, Nuovo Cimento **9**, 47 (1958). J. Hubbard, Proc. Roy. Soc. (London) **A240**, 539 (1957) and **A243**, 336 (1957).

[14] F. J. Dyson, Phys. Rev. **75**, 486 (1949).

[15] The only exception is the calculation by F. Takano, J. Phys. Soc. Japan **14**, 348 (1959). He has calculated the energies of the ferromagnetic ground state and the excited states obtained from the ground state by reversing only one spin.

[16] Also see W. J. Carr, Phys. Rev. **92**, 28 (1953).

[17] The overlap matrix **D** in this paper is defined by (2.4). Here the ij element of **D** is given by the overlap between N-electron wave functions ψ_i and ψ_j. Under this definition of **D**, neither the inverse of **D** nor **D** itself has ever been calculated correctly when N is large. When the overlap matrix **Δ** is defined by overlaps between atomic orbitals so that its kh element is given by $\langle k|h\rangle$, the inverse $\mathbf{\Delta}^{-1}$ has been expanded into a power series of **Δ** by P. O. Löwdin, Advan. Phys. **5**, 1 (1956). However, there is very little relation between **Δ** and **D**.

ground state carrying a suitable spin function Θ, the wave function is simply written as (2.1) and the calculation of $\mathbf{A}$ can be bypassed. This will simplify the calculation considerably as we shall describe in Sec. IV.

Most of the present discussion will be carried out as if we are dealing with arrays of one-electron atoms. However, this limitation is merely an aid to keep track of the formulas and manipulations. In Sec. IV(3), we shall give a brief discussion of problems which arise when arrays of many-electron atoms are considered.

Before we start to calculate $\mathbf{F}$ and $\mathbf{A}$ in Sec. III, we shall review the method used in the previous paper I in Sec. II.

II. THE HEITLER–LONDON METHOD

Let us consider an array of N one-electron atoms. The Heitler–London wave function for this system is given by

$$\Psi=(N!)^{-1/2}\sum_{P}^{N!}(-1)^{P}P^{r}\Lambda(\mathbf{r}_1,\mathbf{r}_2,\cdots,\mathbf{r}_N)\times P^{\sigma}\Theta(\sigma_1,\sigma_2,\cdots,\sigma_N), \quad (2.1)$$

where $\Lambda(\mathbf{r}_1,\mathbf{r}_2,\cdots,\mathbf{r}_N)$ is a product of occupied atomic orbitals $\chi_h(\mathbf{r}_h)$,

$$\Lambda(\mathbf{r}_1,\mathbf{r}_2,\cdots,\mathbf{r}_N)=\chi_1(\mathbf{r}_1)\chi_2(\mathbf{r}_2)\cdots\chi_N(\mathbf{r}_N), \quad (2.2)$$

$\Theta(\sigma_1,\sigma_2,\cdots,\sigma_N)$ is an arbitrary function of the spin variables, and P^r and P^σ are permutations P of coordinate and spin variables. (P^r and P^σ are considered as corresponding to the same abstract permutation P.) The summation $\sum_P$ in (2.1) includes all $N!$ permutations P.

There are many ways to construct $\Theta(\sigma_1,\sigma_2,\cdots,\sigma_N)$ of N spins, but, in any case, we will find 2^N linearly independent and orthonormal functions Θ_1, Θ_2, $\cdots$. Starting from an orbital product $\Lambda(\mathbf{r}_1,\mathbf{r}_2,\cdots,\mathbf{r}_N)$, therefore it is possible to generate, in principle, 2^N linearly independent functions Ψ_1, Ψ_2, $\cdots$ of this array. Let $\boldsymbol{\Theta}$ be the row matrix $\boldsymbol{\Theta}=(\Theta_1,\Theta_2,\cdots)$, whose elements are 2^N linearly independent and orthonormal functions Θ_i of N spins. Similarly $\boldsymbol{\Psi}$ is the row matrix $\boldsymbol{\Psi}=(\Psi_1,\Psi_2,\cdots)$. Then the wave functions Ψ_i introduced by (2.1) are written as

$$\boldsymbol{\Psi}=(N!)^{-1/2}\sum_{P}^{N!}(-1)^{P}P^{r}\Lambda P^{\sigma}\boldsymbol{\Theta} \quad (2.3)$$

by using the matrix representation.

The wave functions $\boldsymbol{\Psi}=(\Psi_1,\Psi_2,\cdots)$ thus obtained are not normalized because of the nonorthogonality of the atomic orbitals χ_k used as basis. Instead, it will be found that the overlap between Ψ_i and Ψ_j is given by

$$D_{ij}\equiv\int\Psi_i^*\Psi_j d\tau=\int[\sum_P(-1)^P P^r\Lambda P^\sigma\Theta_i]^*\Lambda\Theta_j d\tau=\sum_P\langle P\Lambda|\Lambda\rangle\tilde{U}_{ij}(P), \quad (2.4)$$

where $\langle P\Lambda|\Lambda\rangle$ represents the integral over the coordinate variables

$$\langle P\Lambda|\Lambda\rangle\equiv\int P^r\Lambda(\mathbf{r}_1,\mathbf{r}_2,\cdots,\mathbf{r}_N)^*\Lambda(\mathbf{r}_1,\mathbf{r}_2,\cdots,\mathbf{r}_N)dv, \quad (2.5)$$

while the integral over the spin variables is denoted by $\tilde{U}_{ij}(P)$ as follows:

$$\tilde{U}_{ij}(P)\equiv(-1)^P\int P^\sigma\Theta_i^*\Theta_j d\sigma. \quad (2.6)$$

From (2.4), it is clear that the normalization constants D_{ii} can become very large, which leads to the difficulty of calculating the Heitler–London energy.

The overlap integral D_{ij} can be regarded as the ij element of the overlap matrix $\mathbf{D}$, and similarly $\tilde{U}_{ij}(P)$ as the ij element of matrix $\tilde{\mathbf{U}}(P)$. Using the matrix notation, Eqs. (2.4) and (2.6) are written as

$$\mathbf{D}\equiv\int\boldsymbol{\Psi}^\dagger\boldsymbol{\Psi}d\tau=\sum_P\langle P\Lambda|\Lambda\rangle\tilde{\mathbf{U}}(P), \quad (2.7)$$

and

$$\tilde{\mathbf{U}}(P)=(-1)^P\int P^\sigma\boldsymbol{\Theta}^\dagger\cdot\boldsymbol{\Theta}d\sigma. \quad (2.8)$$

It is easily proved that the matrix $\tilde{\mathbf{U}}(PQ)$ corresponding to the successive application of two permutations Q and P is given by the product of two matrices $\tilde{\mathbf{U}}(Q)$ and $\tilde{\mathbf{U}}(P)$ as follows[18,19]:

$$\tilde{\mathbf{U}}(PQ)=\tilde{\mathbf{U}}(Q)\tilde{\mathbf{U}}(P). \quad (2.9)$$

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[18] The matrix $\mathbf{U}(P)$ introduced by (2.8) is unitary and is a representation matrix of the permutation group. Use of representation matrices of permutation groups in the calculation of electronic energy levels is originally due to R. Serber [Phys. Rev. **45**, 461 (1934)] and T. Yamanouchi [Proc. Phys. Math. Soc. Japan **18**, 623 (1936)]. Also see the review by M. Kotani in *Table of Molecular Integrals*, edited by M. Kotani *et al.* (Maruzen Co., Ltd., Tokyo, 1955). In the present paper, however, we shall not use any group-theoretical argument except in (2.9) and (3.39). It is more convenient to understand that $\tilde{\mathbf{U}}(P)$ is merely a notation representing the integral appearing on the right of (2.8) and has the property described by (2.9).

[19] The relation (2.9) will be obtained as follows. Since 2^N linearly independent and orthonormal spin functions Θ_i, for $i=1, 2, \cdots, 2^N$, are complete in the spin space, we can expand $P^\sigma\Theta_i$ in terms of Θ_i as follows:

$$P^\sigma\Theta_i=(-1)^P\sum_j\Theta_j U_{ji}(P)^*, \quad (1)$$

where $U_{ji}(P)^*$ is merely an expansion coefficient but it is easily recognized that $U_{ji}(P)$ defined above is equivalent to $\tilde{U}_{ij}(P)$ introduced by (2.6). Here $\tilde{\mathbf{U}}(P)$ is the transpose of matrix $\mathbf{U}(P)$. Let us apply two permutations Q^σ and P^σ successively to Θ_i. Then

$$P^\sigma Q^\sigma\Theta_i=(-1)^Q\sum_k P^\sigma\Theta_k U_{ki}(Q)^*=(-1)^{PQ}\sum_j\sum_k\Theta_j U_{jk}(P)^*U_{ki}(Q)^*. \quad (2)$$

On the other hand, we can write this as follows:

$$P^\sigma Q^\sigma\Theta_i=(-1)^{PQ}\sum_j\Theta_j U_{ji}(PQ)^*. \quad (3)$$

Comparison of the above two equations yields

$$\mathbf{U}(PQ)=\mathbf{U}(P)\,\mathbf{U}(Q), \quad (4)$$

which is equivalent to (2.9).

The orthonormal wave functions Ψ_N of the array are then given by

$$\Psi_N=\Psi\mathbf{D}^{-1/2}. \tag{2.10}$$

Our problem is to calculate the Heitler–London energy of a Hamiltonian of the form

$$\mathcal{H}=\sum_{h=1}^{N} f(\mathbf{r}_h)+\tfrac{1}{2}\sum_{h_1=1}^{N}\sum_{h_2=1}^{N}{}' g(\mathbf{r}_{h_1},\mathbf{r}_{h_2}), \tag{2.11}$$

where the summation $\sum_{h_2=1}^{N}{}'$ excludes $h_2=h_1$. For this purpose, it is convenient to split off, from the N-electron wave function Ψ, one or several atomic orbitals, which are of particular interest for the manipulations we want to perform. This will be carried out as follows. An antisymmetric wave function of N electrons is constructed by taking the summation over $N!$ permutations P as is shown in (2.3). Here the $N!$ permutations P can be divided into two sets; the first set includes $(N-1)!$ permutations $Q[h]$ of $N-1$ electrons $1, 2, \cdots, h-1, h+1, \cdots, N$, while the second one consists of N permutations $P(k\leftarrow h)$ taking electron h to orbital k, where $k=1, 2, \cdots, N$. The original $N!$ permutations are given by $Q[h]\cdot P(k\leftarrow h)$ and the summation over $N!$ permutations P in (2.3) splits into two; the summations over $(N-1)!$ permutations $Q[h]$ and over k's. If we take the summation over $(N-1)!$ permutations $Q[h]$ after operating a particular permutation $P(k\leftarrow h)$, this portion of the wave function is antisymmetric with respect to electrons $1, 2, \cdots, h-1, h+1, \cdots, N$, but electron h always occupies orbital k. To emphasize this situation, let us denote the sum by $\chi_k(\mathbf{r}_h)\Psi_i[k(h)]$ where $i=1, 2, \cdots, N$. The original wave function Ψ is then written as

$$\Psi=N^{-1/2}\sum_k \chi_k(\mathbf{r}_h)\Psi[k(h)], \tag{2.12}$$

where $\Psi[k(h)]$ is the row matrix whose elements $\Psi_i[k(h)]$ are functions of $N-1$ orbitals and N spins as described above. More explicitly,

$$\Psi[k(h)]\equiv[(N-1)!]^{-1/2}\sum_{Q[h]}(-1)^{Q[h]P(k\leftarrow h)} \times Q^r[h]\Lambda[k(h)]Q^\sigma[h]P^\sigma(k\leftarrow h)\Theta, \tag{2.13}$$

and $\Lambda[k(h)]$ is a product of $N-1$ atomic orbitals, obtained from $\Lambda(\mathbf{r}_1,\mathbf{r}_2,\cdots,\mathbf{r}_N)$ by applying $P^r(k\leftarrow h)$ and deleting $\chi_k(\mathbf{r}_h)$ as follows:

$$\Lambda[k(h)]\equiv\frac{1}{\chi_k(\mathbf{r}_h)}P^r(k\leftarrow h)\Lambda(\mathbf{r}_1,\mathbf{r}_2,\cdots,\mathbf{r}_N). \tag{2.14}$$

Similarly we introduce

$$\Psi[k_1(h_1)k_2(h_2)],\ \cdots,\ \Psi[k_1(h_1)\cdots k_n(h_n)].$$

For example,

$$\Psi[k_1(h_1)k_2(h_2)] \equiv[(N-2)!]^{-1/2}\sum_{Q[h_1h_2]}(-1)^{Q[h_1h_2]P(k_1k_2\leftarrow h_1h_2)} \times Q^r[h_1h_2]\Lambda[k_1(h_1)k_2(h_2)]Q^\sigma[h_1h_2] \times P^\sigma(k_1k_2\leftarrow h_1h_2)\Theta, \tag{2.15}$$

where

$$\Lambda[k_1(h_1)k_2(h_2)] \equiv\frac{1}{\chi_{k_1}(\mathbf{r}_{h_1})\chi_{k_2}(\mathbf{r}_{h_2})}P^\sigma(k_1k_2\leftarrow h_1h_2) \times\Lambda(\mathbf{r}_1,\mathbf{r}_2,\cdots,\mathbf{r}_N), \tag{2.16}$$

and $Q[h_1h_2]$ represents $(N-2)!$ permutations not involving electrons h_1 and h_2, while $P(k_1k_2\leftarrow h_1h_2)$ is a permutation taking electrons h_1 and h_2 to orbitals k_1 and k_2. The functions

$$\Psi[k_1(h_1)k_2(h_2)],\quad \Psi[k_1(h_1)k_2(h_2)k_3(h_3)],$$

etc., are related to the original wave functions Ψ as follows:

$$\Psi=[N(N-1)]^{-1/2}\sum_{k_1}\sum_{k_2}{}'\chi_{k_1}(\mathbf{r}_{h_1})\chi_{k_2}(\mathbf{r}_{h_2}) \times\Psi[k_1(h_1)k_2(h_2)]=\text{etc.} \tag{2.17}$$

We further define the overlap matrices

$$S[k_1\cdots k_n|h_1\cdots h_n]$$

between the functions $\Psi[k_1(h_1)\cdots k_n(h_n)]$ as follows:

$$\mathbf{S}[k_1\cdots k_n|h_1\cdots h_n]\equiv\int\Psi[k_1(h_1)\cdots k_n(h_n)]^\dagger \times\Psi[k_1(h_1)\cdots k_n(h_n)]d\tau. \tag{2.18}$$

The method used in obtaining (2.4) is applied to the above matrices, which leads to

$$\mathbf{S}[k_1\cdots k_n|h_1\cdots h_n]=\sum_{Q[h_1\cdots h_n]}\langle Q[h_1\cdots h_n]\Lambda[k_1(h_1)\cdots k_n(h_n)|\Lambda[h_1(h_1)\cdots h_n(h_n)]\rangle \times\tilde{\mathbf{U}}(Q[h_1\cdots h_n]P(k_1\cdots k_n\leftarrow h_1\cdots h_n)). \tag{2.19}$$

Those overlap matrices are again related to the overlap matrix $\mathbf{D}$ between the original wave functions Ψ intro-

duced by (2.4) as follows:

$$\mathbf{D}=\mathbf{S}[h|h]+\sum_k{}'\langle k|h\rangle\mathbf{S}[k|h] \tag{2.20}$$

$$=\mathbf{S}[h_1h_2|h_1h_2]+\langle h_1|h_2\rangle\langle h_2|h_1\rangle\mathbf{S}[h_2h_1|h_1h_2]$$
$$+\sum_k{}'\{\langle k|h_1\rangle\mathbf{S}[kh_2|h_1h_2]+\langle k|h_2\rangle\mathbf{S}[h_1k|h_1h_2]+\langle k|h_2\rangle\langle h_2|h_1\rangle\mathbf{S}[h_2k|h_1h_2]+\langle k|h_1\rangle\langle h_1|h_2\rangle\mathbf{S}[kh_1|h_1h_2]\}$$
$$+\sum_{k_1k_2}{}''\langle k_1|h_1\rangle\langle k_2|h_2\rangle\mathbf{S}[k_1k_2|h_1h_2] \tag{2.21}$$

$$=\text{etc.},$$

where

$$\langle k|h\rangle=\int\chi_k(\mathbf{r}_h)^*\chi_h(\mathbf{r}_h)d\tau_h, \tag{2.22}$$

and $\sum_k{}'$ excludes $k=h$, and $\sum_{k_1k_2}{}''$ excludes $k_1=h_1$, $k_2=h_2$ and also $k_1=h_2$, $k_2=h_1$. These results can be proved by inserting (2.19) into (2.20) and (2.21).

More generally, it will be found that

$$\mathbf{S}[k_1\cdots k_{n-1}|h_1\cdots h_{n-1}]$$
$$=\delta(h_n\neq k_1,\cdots,k_{n-1})\mathbf{S}[k_1\cdots k_{n-1}h_n|h_1\cdots h_{n-1}h_n]$$
$$+\sum_{k_n}{}^{(n)}\langle k_n|h_n\rangle\mathbf{S}[k_1\cdots k_{n-1}k_n|h_1\cdots h_{n-1}h_n], \tag{2.23}$$

where

$$\delta(h_n\neq k_1,\cdots,k_{n-1})=1, \quad \text{if } h_n \text{ is not included in } k_1,\cdots,k_{n-1},$$
$$=0, \quad \text{otherwise}$$

and, in the summation $\sum_{k_n}{}^{(n)}$, we exclude $k_n=k_1, k_2, \cdots, k_{n-1}, h_n$. Furthermore, the following equality will hold:

$$\mathbf{S}[h_{i_1}h_{i_2}\cdots h_{i_n}|h_1h_2\cdots h_n]=\tilde{\mathbf{U}}(P_i)\mathbf{S}[h_1h_2\cdots h_n|h_1h_2\cdots h_n], \tag{2.24}$$

where P_i is a permutation in which $h_1h_2\cdots h_n$ are taken to orbitals $h_{i_1}h_{i_2}\cdots h_{i_n}$. This relation will be proved easily by replacing $P(k_1\cdots k_n\leftarrow h_1\cdots h_n)$ in (2.19) by P_i and by splitting matrices $\tilde{\mathbf{U}}(Q[h_1\cdots h_n]P_i)$ as $\tilde{\mathbf{U}}(P_i)\tilde{\mathbf{U}}(Q[h_1\cdots h_n])$ by using the relation (2.9).

Now we are ready to calculate the energy matrix of the Hamiltonian (2.11). Since the Hamiltonian is totally symmetric and commutes with the antisymmetrizer $\sum_P(-1)^PP$ in the wave functions (2.3), the method used in obtaining (2.4) is again applied to this calculation and it will be found that

$$\langle\Psi|\sum_h f(\mathbf{r}_h)|\Psi\rangle\equiv\int\Psi^\dagger\sum_h f(\mathbf{r}_h)\Psi d\tau$$
$$=\sum_h\langle h|f(\mathbf{r}_h)|h\rangle\mathbf{S}[h|h]$$
$$+\sum_h\sum_k{}'\langle k|f(\mathbf{r}_h)|h\rangle\mathbf{S}[k|h]. \tag{2.25}$$

The normalized expectation values $\langle\mathbf{f}\rangle$, calculated by using the orthonormal wave functions Ψ_N defined by (2.10), are given by

$$\langle\mathbf{f}\rangle\equiv\langle\Psi_N|\sum_h f(\mathbf{r}_h)|\Psi_N\rangle$$
$$=\sum_h\langle h|f(\mathbf{r}_h)|h\rangle\mathbf{D}^{-1/2}\mathbf{S}[h|h]\mathbf{D}^{-1/2}$$
$$+\sum_h\sum_k{}'\langle k|f(\mathbf{r}_h)|h\rangle\mathbf{D}^{-1/2}\mathbf{S}[k|h]\mathbf{D}^{-1/2}. \tag{2.26}$$

Similarly the expectation values $\langle\mathbf{g}\rangle$ of two-body interaction $\frac{1}{2}\sum_{h_1}\sum_{h_2}{}'g(\mathbf{r}_{h_1}\mathbf{r}_{h_2})$ are obtained by

$$\langle\mathbf{g}\rangle\equiv\langle\Phi_N|\tfrac{1}{2}\sum_{h_1}\sum_{h_2}{}'g(\mathbf{r}_{h_1}\mathbf{r}_{h_2})|\Phi_N\rangle$$
$$=\tfrac{1}{2}\sum_{h_1}\sum_{h_2}\sum_{k_1}\sum_{k_2}\langle k_1k_2|g(\mathbf{r}_{h_1}\mathbf{r}_{h_2})|h_1h_2\rangle$$
$$\times\mathbf{D}^{-1/2}\mathbf{S}[k_1k_2|h_1h_2]\mathbf{D}^{-1/2}, \tag{2.27}$$

where h_1 and h_2 are also included in the summations $\sum_{k_1}\sum_{k_2}{}'$ for simplicity.

Here $\langle\mathbf{f}\rangle$ and $\langle\mathbf{g}\rangle$ are both matrices and can be calculated if the normalization matrices $\mathbf{D}^{-1/2}\mathbf{S}[k|h]\mathbf{D}^{-1/2}$ and $\mathbf{D}^{-1/2}\mathbf{S}[k_1k_2|h_1h_2]\mathbf{D}^{-1/2}$ are evaluated explicitly. The calculation of the normalization matrices is the main subject of the present paper and will be carried out in the following section.

III. CALCULATION OF THE NORMALIZATION MATRICES

Here we shall expand the normalization matrices of the type $\mathbf{D}^{-1/2}\mathbf{S}[k_1\cdots k_n|h_1\cdots h_n]\mathbf{D}^{-1/2}$ in terms of $\tilde{\mathbf{U}}(P)$ and evaluate the expansion coefficients. To proceed with the problem, let us divide the expansion into two steps and first consider the calculation of matrices of the following form:

$$\mathbf{F}[k_1\cdots k_n|h_1\cdots h_n]\equiv\mathbf{S}[k_1\cdots k_n|h_1\cdots h_n]\mathbf{D}^{-1}$$
$$=\sum_P f_P[k_1\cdots k_n|h_1\cdots h_n]\tilde{\mathbf{U}}(P). \tag{3.1}$$

The second expansion to be calculated is of the form:

$$\mathbf{A}^{(1/2)}(R)\equiv\mathbf{D}^{-1/2}\tilde{\mathbf{U}}(R)\mathbf{D}^{1/2}=\sum_P a_P{}^{(1/2)}(R)\tilde{\mathbf{U}}(P). \quad (3.2)$$

The original matrix is thus expanded as

$$\begin{aligned}&\mathbf{D}^{-1/2}\mathbf{S}[k_1\cdots k_n|h_1\cdots h_n]\mathbf{D}^{-1/2}\\&=\mathbf{D}^{-1/2}\mathbf{S}[k_1\cdots k_n|h_1\cdots h_n]\mathbf{D}^{-1}\cdot\mathbf{D}^{1/2},\\&=\sum_Q f_Q[k_1\cdots k_n|h_1\cdots h_n]\mathbf{D}^{-1/2}\tilde{\mathbf{U}}(Q)\mathbf{D}^{1/2},\\&=\sum_P\sum_Q f_Q[k_1\cdots k_n|h_1\cdots h_n]a_P{}^{(1/2)}(Q)\tilde{\mathbf{U}}(P). \quad (3.3)\end{aligned}$$

Previously,[10,20] we have shown that, as long as atomic orbitals χ used as basis are linearly independent, the inverse $\mathbf{D}^{-1}$ exists and can be expanded as (24) of paper I, that is,

$$\mathbf{D}^{-1}=\sum_P T_P\tilde{\mathbf{U}}(P). \quad (3.4)$$

Multiplication of this expression with (2.19) yields (3.1). The second equation (3.2), which is similarly obtainable, has been introduced previously by (68) of paper I.

Our problem now is to expand the coefficients $f_P[k_1\cdots k_n|h_1\cdots h_n]$ and $a_P{}^{(1/2)}(R)$ in terms of overlap integrals so that f_P and $a_P{}^{(1/2)}(R)$ can be evaluated explicitly.

(1) Expansion of the F Matrices

(a) *The Recurrence Relations for the Expansion*

Let us first consider the matrices of the form $\mathbf{F}[h_1\cdots h_n|h_1\cdots h_n]$ and show that, by using the relations (2.20), (2.21), and (2.23), the matrices can be decomposed into a sum of products of two parts: The first ones denoted by $\Gamma[P]$ are made of overlaps between electrons $h_1\cdots h_n$ and the other electrons, and can be calculated up to any desired accuracy explicitly while the second parts are equivalent to the $\mathbf{F}$ matrices originally considered except that the new matrices are for a new array which can be obtained by removing electrons $h_1\cdots h_n$ from the original array. Therefore we can repeat the same calculation in the second parts. This expansion will converge since overlap between electron h and a distant electron decreases exponentially.

For example let us consider the simplest case, the matrix $\mathbf{F}[h|h]=\mathbf{S}[h|h]\mathbf{D}^{-1}$. By inserting (2.20) into $\mathbf{F}[h|h]$, we find that

$$\begin{aligned}\mathbf{F}[h|h]&=\mathbf{S}[h|h]\{\mathbf{S}[h|h]+\sum_k{}'\langle k|h\rangle\mathbf{S}[k|h]\}^{-1}\\&=(1+\mathbf{X}[h])^{-1},\end{aligned} \quad (3.5)$$

where

$$\mathbf{X}[h]\equiv\sum_k{}'\langle k|h\rangle\mathbf{S}[k|h]\mathbf{S}[h|h]^{-1}. \quad (3.6)$$

Repeated use of (2.23) in $\mathbf{X}[h]$ yields

$$\begin{aligned}\mathbf{X}[h]=&\sum_{k_1}{}'\langle h|k_1\rangle\langle k_1|h\rangle\mathbf{S}[k_1h|hk_1]\mathbf{S}[h|h]^{-1}\\&+\sum_{k_2}{}''\sum_{k_1}{}'\langle h|k_2\rangle\langle k_2|k_1\rangle\langle k_1|h\rangle\mathbf{S}[k_1k_2h|hk_1k_2]\mathbf{S}[h|h]^{-1}\\&+\sum_{k_3}{}'''\sum_{k_2}{}''\sum_{k_1}{}'\langle h|k_3\rangle\langle k_3|k_2\rangle\langle k_2|k_1\rangle\langle k_1|h\rangle\mathbf{S}[k_1k_2k_3h|hk_1k_2k_3]\mathbf{S}[h|h]^{-1}\\&+\cdots.\end{aligned} \quad (3.7)$$

Let us introduce the notation $\mathbf{F}_h[k_1\cdots k_n|k_1\cdots k_n]$ by defining

$$\mathbf{S}[hk_1\cdots k_n|hk_1\cdots k_n]\mathbf{S}[h|h]^{-1}\equiv\mathbf{F}_h[k_1\cdots k_n|k_1\cdots k_n]. \quad (3.8)$$

Use of this definition as well as (2.24) leads to

$$\begin{aligned}\mathbf{X}[h]=&\sum_{k_1}{}'\langle h|k_1\rangle\langle k_1|h\rangle\tilde{\mathbf{U}}(k_1h)\mathbf{F}_h[k_1|k_1]\\&+\sum_{k_2}{}''\sum_{k_1}{}'\langle h|k_2\rangle\langle k_2|k_1\rangle\langle k_1|h\rangle\tilde{\mathbf{U}}(k_1k_2h)\mathbf{F}_h[k_1k_2|k_1k_2]\\&+\sum_{k_3}{}'''\sum_{k_2}{}''\sum_{k_1}{}'\langle h|k_3\rangle\langle k_3|k_2\rangle\langle k_2|k_1\rangle\langle k_1|h\rangle\tilde{\mathbf{U}}(k_1k_2k_3h)\mathbf{F}_h[k_1k_2k_3|k_1k_2k_3]\\&+\cdots,\end{aligned} \quad (3.9)$$

where $(k_1k_2\cdots k_nh)$ is a cyclic permutation in which electrons $h, k_1, \cdots, k_{n-1}, k_n$ are shifted to orbitals $k_1, k_2, \cdots, k_n, h$. In (3.9), terms such as $\langle h|k_2\rangle\langle k_2|k_1\rangle\langle k_1|h\rangle\tilde{\mathbf{U}}(k_1k_2h)$ belong to the first part $\Gamma[P]$, while the matrices $\mathbf{F}_h[k_1\cdots k_n|k_1\cdots k_n]$ belonging to the second part are equivalent to $\mathbf{F}[k_1\cdots k_n|k_1\cdots k_n]$. For instance, $\mathbf{F}_h[k|k]$ can be calculated by (3.5) and (3.9) except that electron h should be excluded from the summations.

[20] The present method can be extended to the case where basic atomic orbitals are not linearly independent. See Sec. IV (3) and also Appendix B of paper I.

The equation (3.5) can be expanded formally as

$$\mathbf{F}[h|h]=1-\mathbf{X}[h]+\mathbf{X}[h]^2-\mathbf{X}[h]^3+\cdots. \tag{3.10}$$

This expansion converges as long as $\epsilon=\sum_P|x_P[h]|<1$ where $x_P[h]$ is the expansion coefficient of $\mathbf{X}[h]$:

$$\mathbf{X}[h]=\sum_P x_P[h]\tilde{\mathbf{U}}(P). \tag{3.11}$$

This will be proved in the Appendix.

Similarly $\mathbf{F}[h_1h_2|h_1h_2]$ is expanded as

$$\begin{aligned}\mathbf{F}[h_1h_2|h_1h_2]&=(1+\mathbf{X}[h_1h_2])^{-1}\\&=1-\mathbf{X}[h_1h_2]+\mathbf{X}[h_1h_2]^2-\mathbf{X}[h_1h_2]^3+\cdots,\end{aligned} \tag{3.12}$$

where

$$\begin{aligned}\mathbf{X}[h_1h_2]=&\langle h_1|h_2\rangle\langle h_2|h_1\rangle\tilde{\mathbf{U}}(h_1h_2)\\&+\sum_{k_1}\{\langle h_1|k_1\rangle\langle k_1|h_1\rangle\tilde{\mathbf{U}}(k_1h_1)+\langle h_2|k_1\rangle\langle k_1|h_2\rangle\mathbf{U}(k_1h_2)+\langle h_2|k_1\rangle\langle k_1|h_1\rangle\langle h_1|h_2\rangle\tilde{\mathbf{U}}(k_1h_2h_1)\\&\qquad+\langle h_1|k_1\rangle\langle k_1|h_2\rangle\langle h_2|h_1\rangle\tilde{\mathbf{U}}(h_2k_1h_1)\}\mathbf{F}_{h_1h_2}[k_1|k_1]\\&+\sum_{k_1k_2}\{\langle h_1|k_2\rangle\langle k_2|k_1\rangle\langle k_1|h_1\rangle\tilde{\mathbf{U}}(k_1k_2h_1)+\langle h_2|k_2\rangle\langle k_2|k_1\rangle\langle k_1|h_2\rangle\tilde{\mathbf{U}}(k_1k_2h_2)\\&\quad+\langle h_2|k_2\rangle\langle k_2|k_1\rangle\langle k_1|h_1\rangle\langle h_1|h_2\rangle\tilde{\mathbf{U}}(k_1k_2h_2h_1)+\langle h_1|k_2\rangle\langle k_2|k_1\rangle\langle k_1|h_2\rangle\langle h_2|h_1\rangle\tilde{\mathbf{U}}(h_2k_1k_2h_1)\\&\quad+\langle h_1|k_1\rangle\langle k_1|h_1\rangle\langle h_2|k_2\rangle\langle k_2|h_2\rangle\tilde{\mathbf{U}}((k_1h_1)(k_2h_2))\\&\quad+\langle h_1|k_2\rangle\langle k_2|h_2\rangle\langle h_2|k_1\rangle\langle k_1|h_1\rangle\tilde{\mathbf{U}}(k_1h_2k_2h_1)\}\mathbf{F}_{h_1h_2}[k_1k_2|k_1k_2]\\&+\cdots.\end{aligned} \tag{3.13}$$

The matrices $\mathbf{F}[h_1|h_1]$, $\mathbf{F}[h_1h_2|h_1h_2]$, $\cdots$, obtained by (3.9), (3.10), (3.12), and (3.13), can be inserted into replace (3.9) and (3.13). Thus the expansion develops further. These relations are more conveniently summarized by

$$\begin{aligned}\mathbf{F}[h(n)]&=(1+\mathbf{X}[h(n)])^{-1}\\&=1-\mathbf{X}[h(n)]+\mathbf{X}[h(n)]^2-\mathbf{X}[h(n)]^3+\cdots,\end{aligned} \tag{3.14}$$

and

$$\mathbf{X}[h(n)]=\sum_m\sum_k\Gamma[k(m)]\mathbf{F}_{h(n)}[k(m)], \tag{3.15}$$

where $h(n)$ and $k(n)$ are abbreviations of letters appearing in brackets of the matrices $\mathbf{F}[h_1\cdots h_n|h_1\cdots h_n]$, $\mathbf{X}[h_1\cdots h_n]$, etc., and n specifies the number of letters involved.

So far we consider matrices of the form $\mathbf{F}[h_1\cdots h_n|h_1\cdots h_n]$. More general ones $\mathbf{F}[k_1\cdots k_n|h_1\cdots h_n]$ introduced by (3.1) can also be reduced to the standard form by repeated use of (2.23). For instance,

$$\begin{aligned}\mathbf{F}[k|h]=&\langle h|k\rangle\tilde{\mathbf{U}}(hk)\mathbf{F}[hk|hk]\\&+\sum_{k_1}{}'\langle h|k_1\rangle\langle k_1|k\rangle\tilde{\mathbf{U}}(kk_1h)\mathbf{F}[hkk_1|hkk_1]\\&+\sum_{k_2}{}''\sum_{k_1}{}'\langle h|k_2\rangle\langle k_2|k_1\rangle\langle k_1|k\rangle\tilde{\mathbf{U}}(kk_1k_2h)\mathbf{F}[hkk_1k_2|hkk_1k_2]\\&+\cdots.\end{aligned} \tag{3.16}$$

(*b*) *Diagram Description*

To proceed with the calculation in practice, it is convenient to draw diagrams. Let us denote, by a solid line starting from point h_1 and ending at point h_2, the overlap integral $\langle h_2|h_1\rangle$ and similarly, by a broken line starting from h_1 going through $h_2,\cdots,h_n$ and coming back to h_1, a cyclic permutation $(h_2h_3\cdots h_nh_1)$. For example, the expansion (3.9) of $\mathbf{X}[h]$ is shown in Fig. 1, where, as a convenient way of explaining how diagrams are built up, points are classified *temporarily* as the following two kinds: a solid dot ● indicates the starting point of $\mathbf{X}[h]$ and no line comes back to this point any more in the course of expanding $\mathbf{X}[h]$, while an open dot ○ indicates that the expansion is not completed at

this point but a new $\mathbf{F}$ matrix starts from here. The first term has one open dot and therefore $\mathbf{F}_h[k_1|k_1]$ will follow. Two open dots of the second term show that $\mathbf{F}_h[k_1k_2|k_1k_2]$ follows. Since broken lines for permutations are the same as the solid lines, we have omitted them.

Similarly the expansion (3.13) of $\mathbf{X}[h_1h_2]$ is described in Fig. 2. There we have omitted terms obtained by interchanging h_1 and h_2.

To calculate $\mathbf{F}_h[k_1|k_1]$, $\mathbf{F}_h[k_1k_2|k_1k_2]$, etc., we further draw $\mathbf{X}_h[k_1|k_1]$, $\mathbf{X}_h[k_1k_2|k_1k_2]$, etc., starting from open dots. For example, the second term in Fig. 1 includes the series of diagrams in Fig. 3.

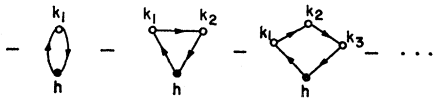


FIG. 1. The expansion of $\mathbf{X}[h]$ described by Eq. (3.9).

Solid lines can come into a point many times, but the representation of electron permutations should be reduced into the simplest form so that we can distinguish a permutation from others immediately. This implies that within one diagram, any one electron should not be shifted more than once, and hence a broken line can come into a point only once and come out only once. For instance, the second term in Fig. 3 represents the permutation $(k_1k_2)(k_1k_2h_1)$ which shifts electrons h_1, k_1, k_2 to k_1, k_2, h_1 and, after that, again interchanges k_1 and k_2, but this process is equivalent to a single interchange

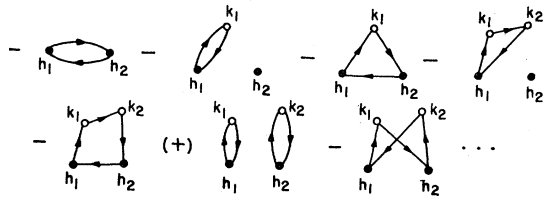


FIG. 2. The expansion of $\mathbf{X}[h_1h_2]$ described by Eq. (3.13).

of h_1 and k_2. Therefore the broken loop in this diagram illustrates the interchange (h_1k_2) only. The second term represents the quantity

$$|\langle k_1|k_2\rangle|^2\langle h_1|k_2\rangle\langle k_2|k_1\rangle\langle k_1|h_1\rangle\tilde{\mathbf{U}}(h_1k_2)\,.$$

Since $(k_1k_2h_1)(k_1k_2)=(h_1k_1)$ is a different permutation from the second term, it is important to remember the order in which these loops appear in a diagram.

In order to calculate $\mathbf{F}[h|h]$ by (3.14), we need to evaluate higher order terms $\mathbf{X}[h]^2$, $\mathbf{X}[h]^3$, $\cdots$. This will be carried out by multiplying diagrams we have generated. For instance, $\mathbf{X}[h]^2$ will be obtained from diagrams in Fig. 1. In case permutation $(k_1k_2h_1)$ appears first (on the left of $\mathbf{X}[h]\mathbf{X}[h]$) and then permutation (h_1k_1) follows it [(h_1k_1) appears on the right of $\mathbf{X}[h]\mathbf{X}[h]$], we obtain the diagram in Fig. 4, which corresponds to the quantity

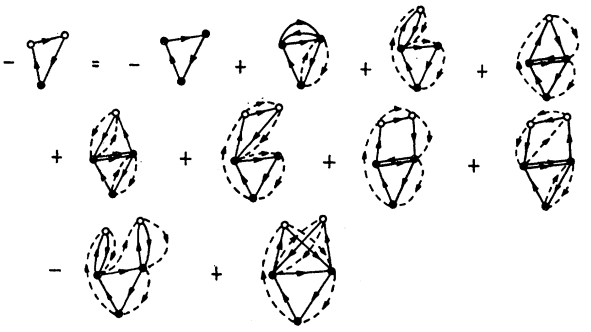
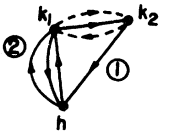


FIG. 3. Further expansion of the second term in Fig. 1.

$$|\langle h|k_1\rangle|^2\langle h|k_2\rangle\langle k_2|k_1\rangle\langle k_1|h\rangle\tilde{\mathbf{U}}(k_1k_2)\,.$$

Since all diagrams in $\mathbf{X}[h]$ start from h, solid lines come into h many times after the multiplication and the distinction between solid and open dots becomes obscure. Therefore, we shall not make this distinction in diagrams any more.

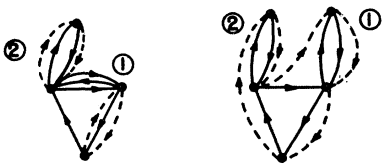
FIG. 4. The diagram of $\langle h|k_2\rangle\langle k_2|k_1\rangle \times\langle k_1|h\rangle\tilde{\mathbf{U}}(k_1k_2h)\times\langle h|k_1\rangle\langle k_1|h\rangle\tilde{\mathbf{U}}(k_1h)$. This term comes from $\mathbf{X}[h]^2$.



Similar multiplication should be added in those appearing in Fig. 3. Here we have drawn only $\mathbf{X}_h[k_1k_2|k_1k_2]$ instead of $\mathbf{F}_h[k_1k_2|k_1k_2]$. The expression will become complete if we include higher terms such as $\mathbf{X}_h[k_1k_2|k_1k_2]^2$, $\mathbf{X}_h[k_1k_2|k_1k_2]^3$, etc. The contribution from $\mathbf{X}_h[k_1k_2|k_1k_2]^2$ includes, for instance, the diagrams in Fig. 5. The first one is obtained by multiplication of the first and second diagrams in Fig. 2. The second one is obtained from two of the type appearing in the second term, but h_1 and h_2 are interchanged in the first one.

In (3.14), odd powered terms $\mathbf{X}[h(n)]^{2m+1}$ carry minus signs, which should also appear in diagrams. It is possible to associate a sign with the number of loops in a diagram. For instance, diagrams in Fig. 1 should have minus signs in $\mathbf{F}[h_1|h_1]$ since they are terms appearing in $\mathbf{X}[h_1]$. In fact, each of them consists of one loop. Those in Fig. 2 should also be minus. However, the fifth

FIG. 5. Some of the contributing terms from $\mathbf{X}_h[k_1k_2|k_1k_2]^2$.



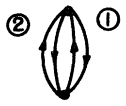


FIG. 6. The diagram of $\langle h|k_1\rangle\langle k_1|h\rangle\tilde{\mathbf{U}}(k_1h)\times\langle h|k_1\rangle\langle k_1|h\rangle\tilde{\mathbf{U}}(k_1h)$.

term consists of two loops. This will be explained as follows. The same diagram can be constructed from $\mathbf{X}[h_1h_2]^2$ by multiplying two of the type appearing in the second term in Fig. 2, as we have already explained in connection with Fig. 5. There are two ways to construct the diagram by the multiplication and both carry a plus sign. Therefore, the total sum is $2-1=1$ in accordance with the proposed criterion. Matrix $\mathbf{X}[h_1h_2h_3]$ will include diagrams with three loops. However, the same diagram will be constructed from $\mathbf{X}[h_1h_2h_3]^2$ 6 times with plus sign and from $\mathbf{X}[h_1h_2h_3]^3$ 6 times with minus sign. The total is $-1+6-6=(-1)^3$. We can test this rule further. Let us assume that, up to t loops, total sum of all possible contributions to a particular diagram with r loops is $(-1)^r$, where $r\leqslant t$. A diagram with $t+1$ loops is constructed by multiplying a diagram with χ loops by all possible diagrams with total $t-\chi+1$ loops. By considering all possible ways to construct diagrams each of which carries χ loops and by adding all possible cases starting from $\chi=1$ and counting up to $\chi=t+1$, we obtain the total sum of all possible contributions to the diagram with $t+1$ loops. We can construct $\binom{t+1}{\chi}$ diagrams, each of which carries χ loops, while the total sum of all possible contributions to a diagram with $t-\chi+1$ loops is $(-1)^{t-\chi+1}$. Therefore, the total sum of all possible contributions to the desired diagram carrying $t+1$ loops is

$$\sum_{\chi=1}^{t+1}(-1)^{t-\chi+1}\binom{t+1}{\chi}=(-1)^{t+1}.$$

This proves the criterion on assigning signs to diagrams: *We count the number t of loops in solid lines in a diagram. The diagram should carry sign* $(-1)^t$.

Thus we have expanded the matrix $\mathbf{F}[h_1\cdots h_n|h_1\cdots h_n]$ in terms of overlap integrals and $\tilde{\mathbf{U}}(P)$. Comparison of the expansion with (3.1) yields that

$$f_P[h_1\cdots h_n|h_1\cdots h_n]$$
$$=\sum_{t=1}^{\infty}\sum_{P_1P_2\cdots P_t}^{P}(-1)^tS_{P_1}S_{P_2}\cdots S_{P_t},\quad(3.17)$$

where P_i is a cyclic permutation and $S_{P_i}=\int P_i\Lambda^*\Lambda dv$ represents a loop. The summation takes all possible $P_1, P_2, \cdots, P_t$ under the condition $P=P_tP_{t-1}\cdots P_1$ and, at least, P_1 will include some of $h_1h_2\cdots h_n$.

From (3.17), we can calculate $f_P[h_1\cdots h_n|h_1\cdots h_n]$ for any P. The computation will be simplified if we draw diagrams as follows:

(i) We start from a point in $h_1h_2\cdots h_n$, and draw a loop. A loop must never go through a point more than once and always come back to the starting point.

(ii) By adding more loops, we can calculate terms in high order. Loops appear by successive expansion (Fig. 3) of $\mathbf{F}$ and by multiplication (Figs. 4 and 5) of $\mathbf{X}$. Number the loops according to the order with which the loops appear and attach sign $(-1)^t$ to the diagram, where t is the number of loops in the diagram.

(iii) After completing solid lines in a diagram, we describe the electron permutation by broken lines. The broken lines never go through one point more than once in a diagram and always come back to the starting point. If the line is equal to P, retain the diagram. Otherwise discard it.

(iv) We can draw all different diagrams, including differences in ordering of loops. If, however, loops are commutative, we should take only one of the diagrams we find by numbering the loops in different ways. An example of such a case is the second diagram in Fig. 5, where we have already counted all contributions when $(-1)^t$ was assigned to it. Another example is shown in Fig. 6, which, in fact, appears only once in the expansion.

(c) *Accuracy of the Expansion Technique*

In practice, the expansion described in this section cannot be carried out indefinitely and it is necessary to truncate the series. The upper bound to an error introduced by such truncation of the series can be calculated by using the inequality (A7) for sum L_n of absolute values of the expansion coefficients $f_P[h(n)]$.

Let us consider, for example, the series in Fig. 1. The first term represents

$$\langle h|k_1\rangle\langle k_1|h\rangle\mathbf{U}(k_1h)\mathbf{F}_h[k_1|k_1].$$

Suppose we do not pursue the expansion beyond point k_1 any more. This implies that we approximate $\mathbf{F}_h[k_1|k_1]$ by 1, and hence it introduces an error to the series. From (A7), it is easily found that the error is less than

$$\sum_{k_1}\langle h|k_1\rangle\langle k_1|h\rangle[(1-O(\Delta\Delta_0))^{-1}-1].$$

From the second term in Fig. 1, we get an error of

$$\sum_{k_1}\sum_{k_2}\langle h|k_2\rangle\langle k_2|k_1\rangle\langle k_1|h\rangle[(1-O(\Delta\Delta_0))^{-2}-1],$$

by not taking further expansion terms beyond k_1 and k_2, and so on. Here the factor $[(1-O(\Delta\Delta_0))^{-m}-1]$ will increase when m increases, and the first term $(1-O(\Delta\Delta_0))^{-m}$ will eventually become dominant. Under such circumstances, there is no reason to write the large loop without further expansion, since the loop is merely a minority term in the further expansion. They should be neglected altogether. For instance, if we neglect, in

the series in Fig. 1, the fourth term and higher, the error will be

$$\Delta^5(1-O(\Delta\Delta_0))^{-4}+\Delta^6(1-O(\Delta\Delta_0))^{-5}+\Delta^7(1-O(\Delta\Delta_0))^{-6}+\cdots.$$

A similar observation can be made for the series in Fig. 3. If we retain the first term and neglect all the others, the error will be

$$\Delta^3[(1-O(\Delta\Delta_0))^{-2}-1].$$

If we consider all diagrams that appear in Fig. 3 and neglect the higher orders, we have to estimate the error for each diagram one by one. This process is not so difficult. The first two diagrams are complete and therefore introduce no error. The next three carry an error $[(1-O(\Delta\Delta_0))^{-1}-1]$ times their values and so on. In addition, an error will be introduced by not considering terms such as $X_h[k(2)]^2$, $X_h[k(2)]^3$, etc.

In any case, it is possible to calculate the upper bound to an error introduced by truncation of an expansion of **F**.

(2) Calculation of the A Matrices

(a) *Evaluation of* $\mathbf{A}^{(1)}(R)$

The calculation of matrix $\mathbf{A}^{(1/2)}(R)$ introduced by (3.2) involves more difficulties. In the present subsection, we shall compute, instead of $\mathbf{A}^{(1/2)}(R)$, the matrix $\mathbf{A}^{(1)}(R)$ defined by

$$\mathbf{A}^{(1)}(R)\equiv\mathbf{D}^{-1}\tilde{\mathbf{U}}(R)\mathbf{D}=\sum_P a_P{}^{(1)}(R)\tilde{\mathbf{U}}(P). \quad (3.18)$$

In subsection (b), the matrix $\mathbf{A}^{(1/2)}(R)$ will be calculated by using the expansion coefficients $a^{(1)}(R)$ obtained here.

We shall proceed with the calculation of $\mathbf{A}^{(1)}(R)$ by observing from (3.18) that $\mathbf{A}^{(1)}(R)$ can be expanded in terms of matrices **F** and consequently $a_P{}^{(1)}(R)$ in terms of f_P. To facilitate the expansion of $\mathbf{A}^{(1)}(R)$ in terms of **F**, we shall consider the Hermitian conjugate of the expression (3.18), that is,

$$\mathbf{A}^{(1)}(R^{-1})^\dagger=\mathbf{D}\tilde{\mathbf{U}}(R)\mathbf{D}^{-1}=\sum_P a_P{}^{-1(1)}(R^{-1})^*\tilde{\mathbf{U}}(P). \quad (3.19)$$

Let us first consider a case where R is a simple interchange (h_1h_2). Use of the expansion (2.21) of **D** in $\mathbf{D}\tilde{\mathbf{U}}(R)\mathbf{D}^{-1}$ decomposes the matrix $\mathbf{A}^{(1)}(h_1h_2)^\dagger$ into a sum of matrices of the type

$$\langle k_1|h_1\rangle\mathbf{S}[k_1h_2|h_1h_2]\tilde{\mathbf{U}}(h_1h_2)\mathbf{D}^{-1}. \quad (3.20)$$

When the method used in obtaining the expansion (3.16) is applied in $\mathbf{S}[k_1h_2|h_1h_2]$, the above expression is rewritten as

$$\begin{aligned}
&\langle h_1|k_1\rangle\langle k_1|h_1\rangle\tilde{\mathbf{U}}(h_1k_1)\mathbf{S}[h_1h_2k_1|h_1h_2k_1]\tilde{\mathbf{U}}(h_1h_2)\mathbf{D}^{-1}\\
&\quad+\sum_{k_2}{}''\langle h_1|k_2\rangle\langle k_2|k_1\rangle\langle k_1|h_1\rangle\tilde{\mathbf{U}}(h_1k_1k_2)\mathbf{S}[h_1h_2k_1k_2|h_1h_2k_1k_2]\tilde{\mathbf{U}}(h_1h_2)\mathbf{D}^{-1}\\
&\quad+\sum_{k_3}{}'''\sum_{k_2}{}''\langle h_1|k_3\rangle\langle k_3|k_2\rangle\langle k_2|k_1\rangle\langle k_1|h_1\rangle\tilde{\mathbf{U}}(h_1k_1k_2k_3)\mathbf{S}[h_1h_2k_1k_2k_3|h_1h_2k_1k_2k_3]\tilde{\mathbf{U}}(h_1h_2)\mathbf{D}^{-1}\\
&\quad+\cdots\\
&=\langle h_1|k_1\rangle\langle k_1|h_1\rangle\tilde{\mathbf{U}}(h_1k_1h_2)\mathbf{F}[h_1h_2k_1|h_1h_2k_1]\\
&\quad+\sum_{k_2}{}'''\langle h_1|k_2\rangle\langle k_2|k_1\rangle\langle k_1|h_1\rangle\tilde{\mathbf{U}}(h_1k_1k_2h_2)\mathbf{F}[h_1h_2k_1k_2|h_1h_2k_1k_2]\\
&\quad+\sum_{k_3}{}''''\sum_{k_2}{}'''\langle h_1|k_3\rangle\langle k_3|k_2\rangle\langle k_2|k_1\rangle\langle k_1|h_1\rangle\tilde{\mathbf{U}}(h_1k_1k_2k_3h_2)\mathbf{F}[h_1h_2k_1k_2k_3|h_1h_2k_1k_2k_3]\\
&\quad+\cdots. \qquad (3.21)
\end{aligned}$$

Similarly **D** in the expression $\tilde{\mathbf{U}}(h_1h_2)\mathbf{D}\mathbf{D}^{-1}$ is expanded, where a term corresponding to (3.20) yields a series similar to (3.21), but $\tilde{\mathbf{U}}(h_1h_2k_1)$, $\tilde{\mathbf{U}}(h_1h_2k_1k_2)$, etc., will appear instead of $\tilde{\mathbf{U}}(h_1k_1h_2)$, $\tilde{\mathbf{U}}(h_1k_1k_2h_2)$, etc., in (3.21). The matrix

$$\langle k_1|h_2\rangle\mathbf{S}[h_1k_1|h_1h_2]\tilde{\mathbf{U}}(h_1h_2)\mathbf{D}^{-1}$$

will also produce an expansion obtained from (3.21) by interchanging h_1 and h_2.

By calculating all matrices appearing in the expansion of **D** and by taking the difference between $\mathbf{D}\tilde{\mathbf{U}}(h_1h_2)\mathbf{D}^{-1}$

and $\tilde{\mathbf{U}}(h_1h_2)\mathbf{D}\mathbf{D}^{-1}=\tilde{\mathbf{U}}(h_1h_2)$, it will finally be found that

$$\begin{aligned}\mathbf{A}^{(1)}(h_1h_2)^\dagger&=\mathbf{D}\tilde{\mathbf{U}}(h_1h_2)\mathbf{D}^{-1}\\&=\tilde{\mathbf{U}}(h_1h_2)+\sum_{k_1}{}'(\langle h_1|k_1\rangle\langle k_1|h_1\rangle-\langle h_2|k_1\rangle\langle k_1|h_2\rangle)[\tilde{\mathbf{U}}(h_1k_1h_2)-\tilde{\mathbf{U}}(h_2k_1h_1)]\mathbf{F}[h_1h_2k_1|h_1h_2k_1]\\&\quad+\sum_{k_1}{}''(\langle h_1|k_1\rangle\langle k_1|h_2\rangle\langle h_2|h_1\rangle-\langle h_2|k_1\rangle\langle k_1|h_1\rangle\langle h_1|h_2\rangle)[\tilde{\mathbf{U}}(h_2k_1)-\tilde{\mathbf{U}}(h_1k_1)]\mathbf{F}[h_1h_2k_1|h_1h_2k_1]\\&\quad+\sum_{k_2}{}'''\sum_{k_1}{}''(\langle h_1|k_2\rangle\langle k_2|k_1\rangle\langle k_1|h_1\rangle-\langle h_2|k_2\rangle\langle k_2|k_1\rangle\langle k_1|h_2\rangle)\\&\qquad\times[\tilde{\mathbf{U}}(h_1k_1k_2h_2)-\tilde{\mathbf{U}}(h_2k_1k_2h_1)]\mathbf{F}[h_1h_2k_1k_2|h_1h_2k_1k_2]\\&\quad+\cdots\\&\quad+\sum_{k_2}{}'''\sum_{k_1}{}''(\langle h_1|k_2\rangle\langle k_2|k_1\rangle\langle k_1|h_2\rangle\langle h_2|h_1\rangle-\langle h_2|k_2\rangle\langle k_2|k_1\rangle\langle k_1|h_1\rangle\langle h_1|h_2\rangle)\\&\qquad\times[\tilde{\mathbf{U}}(h_2k_1k_2)-\tilde{\mathbf{U}}(h_1k_1k_2)]\mathbf{F}[h_1h_2k_1k_2|h_1h_2k_1k_2]\\&\quad+\cdots\\&\quad+\tfrac{1}{2}\sum_{k_2}{}'''\sum_{k_1}{}''(\langle h_1|k_1\rangle\langle k_1|h_1\rangle\langle h_2|k_2\rangle\langle k_2|h_2\rangle-\langle h_2|k_1\rangle\langle k_1|h_2\rangle\langle h_1|k_2\rangle\langle k_2|h_1\rangle)\\&\qquad\times[\tilde{\mathbf{U}}(h_1k_1h_2k_2)-\tilde{\mathbf{U}}(h_2k_1h_1k_2)]\mathbf{F}[h_1h_2k_1k_2|h_1h_2k_1k_2]\\&\quad+\cdots\\&\quad+\tfrac{1}{2}\sum_{k_2}{}'''\sum_{k_1}{}''(\langle h_1|k_1\rangle\langle k_1|h_2\rangle\langle h_2|k_2\rangle\langle k_2|h_1\rangle-\langle h_2|k_1\rangle\langle k_1|h_1\rangle\langle h_1|k_2\rangle\langle k_2|h_2\rangle)\\&\qquad\times[\tilde{\mathbf{U}}((h_1k_2)(h_2k_1))-\tilde{\mathbf{U}}((h_1k_1)(h_2k_2))]\mathbf{F}[h_1h_2k_1k_2|h_1h_2k_1k_2]\\&\quad+\cdots.\end{aligned}\tag{3.22}$$

By using the expansion technique of the $\mathbf{F}$ matrices developed in the previous subsection (1), therefore, the matrix $\mathbf{A}^{(1)}(h_1h_2)$ can be calculated. The inequality (A7) ensures the convergence even if higher order terms in n of $\mathbf{F}[h(n)]$ are neglected.

Let us insert (3.1) and (3.17) into (3.22) and write the series in terms of loops S_P and $\mathbf{U}(P)$ as follows:

$$\begin{aligned}&\mathbf{A}^{(1)}(h_1h_2)^\dagger\\&\quad=\tilde{\mathbf{U}}(h_1h_2)+\sum_P\sum_t\sum_{P_0P_1\cdots P_n}^{P}(-1)^tC[(h_1h_2);P_0]\\&\qquad\times S_{P_1}S_{P_2}\cdots S_{P_t}\tilde{\mathbf{U}}(P),\end{aligned}\tag{3.23}$$

where the summation $\sum_{P_0P_1\cdots P_t}{}^P$ takes all possible $P_0P_1\cdots P_t$ which satisfy the relation

$$P=P_tP_{t-1}\cdots P_2P_1(h_1h_2)P_0,\tag{3.24}$$

and $C[(h_1h_2);P_0]$ represents a quantity in parentheses in (3.22). For instance,

$$\begin{aligned}&C[(h_1h_2);(h_1k_1)]=\langle h_1|k_1\rangle\langle k_1|h_1\rangle-\langle h_2|k_1\rangle\langle k_1|h_2\rangle,\\&C[(h_1h_2);(h_1h_2k_1)]=\langle h_1|k_1\rangle\langle k_1|h_2\rangle\langle h_2|h_1\rangle\\&\qquad-\langle h_2|k_1\rangle\langle k_1|h_1\rangle\langle h_1|h_2\rangle.\end{aligned}\tag{3.25}$$

Comparison of (3.23) with (3.19) yields that

$$\begin{aligned}&a_{P^{-1}}{}^{(1)}(h_1h_2)^*\\&\quad=\delta_{(h_1h_2),P^{-1}}+\sum_t\sum_{P_0P_1\cdots Pt}^{P}(-1)^tC[(h_1h_2);P_0]\\&\qquad\times S_{P_1}S_{P_2}\cdots S_{P_t}.\end{aligned}\tag{3.26}$$

By noting the relation $S_P{}^*=S_{P^{-1}}$, the above equation can be rewritten as

$$\begin{aligned}&a_P{}^{(1)}(h_1h_2)=\delta_{(h_1h_2),P}\\&\qquad+\sum_t\sum_{P_0P_1\cdots P_n}^{P}{}'(-1)^tC[(h_1h_2);P_0]^*\\&\qquad\times S_{P_1}{}^{-1}S_{P_2}{}^{-1}\cdots S_{P_t}{}^{-1},\end{aligned}\tag{3.27}$$

where the summation $\sum_{P_0P_1\cdots P_t}{}'$ takes all possible $P_0, P_1\cdots P_t$ under the condition

$$P=P_0{}^{-1}(h_1h_2)P_1{}^{-1}P_2{}^{-1}\cdots P_t{}^{-1}.\tag{3.28}$$

The equation (3.27), however, is less convenient than (3.26). To evaluate the electron permutation P as given by (3.28), we have to start from the last loop S_{P_t} and to count the cyclic permutations in reverse order. On the other hand, computation of $a_{P^{-1}}{}^{(1)}(h_1h_2)^*$ by (3.26) and (3.24) is exactly the same as the expansion (3.17) of $f_P[h(n)]$ and the electron permutation P can be obtained by multiplying cyclic permutations following the same order in which the loops appear. It is easily found that, after completing a diagram of $\mathbf{A}_{P^{-1}}{}^{(1)}(h_1h_2)^*$ by (3.26), a corresponding diagram for $\mathbf{A}_P{}^{(1)}(h_1h_2)$ can be obtained by reversing the direction of arrows in all solid lines as well as broken lines.

The calculation of $\mathbf{A}^{(1)}(R)$ just described can be extended to any permutation R, and it will be found that

$$\begin{aligned}&a_{P^{-1}}{}^{(1)}(R^{-1})^*=\delta_{R,P}+\sum_t\sum_{P_0P_1\cdots Pt}^{P}(-1)^tC[R;P_0]\\&\qquad\times S_{P_1}S_{P_2}\cdots S_{P_t}.\end{aligned}\tag{3.29}$$

Diagrams for $a_P^{(1)}(R^{-1})$ can be constructed from those obtained by (3.29), by simply reversing directions of arrows in all solid lines and broken lines.

The only problem here is to develop $\mathbf{A}^{(1)}(R^{-1})^\dagger$ in terms of $\mathbf{F}$ and get an equation similar to (3.22), which, in return, gives explicit expressions of $C[R; P_0]$. This can also be carried out automatically by drawing diagrams of $C[R; P_0]$ as follows: Let R be a cyclic permutation $R=(h_1h_2\cdots h_s)$ and consider all possible permutations P_0 which start from a point on the loop $(h_1h_2\cdots h_s)$. The permutations P_0 may consist of many unconnected loops $P_{01}, P_{02}, \cdots, P_{0r}$, but each of the loops must have at least one common point with the original loop $(h_1h_2\cdots h_s)$. The desired coefficients $C[R; P_0]$ will be given by

$$C[R; P_0]=S_{P_{01}}S_{P_{02}}\cdots S_{P_{0r}} -S_{R^{-1}P_{01}R}S_{R^{-1}P_{02}R}\cdots S_{R^{-1}P_{0r}R}, \quad (3.30)$$

where $P_0=P_{0r}P_{0r-1}\cdots P_{02}P_{01}$.

In case R is a single interchange, we had the relation

$$C[R; P_0]=-C[R; R^{-1}P_0R], \quad (3.31)$$

which leads to factorizations of the type

$$C[R; P_0][\tilde{\mathbf{U}}(R^{-1}P_0)-\tilde{\mathbf{U}}(P_0R^{-1})], \quad (3.32)$$

as has been shown in (3.22). When R is a permutation involving more than two electrons, the relation (3.31) is no longer valid and each matrix $\tilde{\mathbf{U}}(R^{-1}P_0)$ may carry a distinct coefficient $C[R; P_0]$. Therefore $\mathbf{A}^{(1)}(R^{-1})^\dagger$ will not be written in the form (3.32).

Use of the inequality (A7) in (3.22) leads to the conclusion that the sum

$$L_b^{(2)}=\sum_P |a_P^{(1)}(h_1h_2)-\delta_{(h_1h_2),P}| \quad (3.33)$$

is also bounded and small as compared with unity as long as Δ is small. However, the quantity

$$L_b^{(s)}=\sum_P |a_P^{(1)}(R_s^{-1})-\delta_{R_s^{-1},P}| \quad (3.34)$$

will increase in proportion to the number s of electrons involved in the permutations R_s. This will be seen if we calculate some of the dominant terms in $\mathbf{A}^{(1)}(R_s^{-1})^\dagger$. For instance, let R_s be a loop $(h_1h_2\cdots h_s)$ of equally spaced s electrons in a crystal with translational symmetry. The matrix $\mathbf{A}^{(1)}(R_s^{-1})^\dagger$ will include s terms of the form

$$C[R_s; (h_ik_i)]\mathbf{U}(R_s^{-1}(h_ik_i)), \quad \text{for} \quad i=1, 2, \cdots, n,$$

whose s coefficients

$$C[R_s; (h_ik_i)]=\langle h_i|k_i\rangle\langle k_i|h_i\rangle-\langle h_{i+1}|k_i\rangle\langle k_i|h_{i+1}\rangle,$$

are equal to each other. Terms of the form

$$C[R_s; (h_ik_i)(h_jk_j)]\mathbf{U}(R_s^{-1}(h_ik_i)(h_jk_j))$$

will appear $\frac{1}{2}s(s-1)$ times in $A^{(1)}(R_s^{-1})^\dagger$, since all possible relative positions of loops (h_ik_i) and (h_jk_j) should be considered here.

This divergence of $L_b^{(s)}$ will lead to difficulties in proving the convergence of the expansion of $\mathbf{A}^{(1/2)}(R)$ as is seen in the following subsection (b). The origin of the divergence is due to the fact that diagrams in $\mathbf{A}^{(1)}(R_s^{-1})^\dagger$ are not connected with solid lines (overlaps). It is expected that, if the quantity $S_{R_s}\mathbf{A}^{(1)}(R_s)^\dagger$ is considered instead of $\mathbf{A}^{(1)}(R_s^{-1})^\dagger$, the sum of the absolute values of the expansion coefficients $S_{R_s}a_P^{(1)}(R_s^{-1})$

$$M_b^{(s)}=\sum_P |S_{R_s}[a_P^{(1)}(R_s^{-1})-\delta_{R_s^{-1}P}]| \leqslant |S_{R_s}| L_b^{(s)} \quad (3.35)$$

will converge and be very small. In fact, there is no essential difference between $\mathbf{A}^{(1)}(R_s^{-1})^\dagger$ and $\mathbf{F}[h(n)]$, and their expansion coefficients are calculated similarly by (3.17) and (3.26). Therefore the argument used in Appendix for bounding $F[h(n)]$ will be applied to $\mathbf{A}^{(1)}(R_s^{-1})^\dagger$ too.

(b) *Asymptotic Expansion of* $\mathbf{A}^{(1/2)}(B)$.

The expansion coefficients $a_P^{(1)}(R)$ obtained in the preceding subsection (a) are related to the desired ones $a_P^{(1/2)}(R)$ by

$$a_P^{(1)}(R)=\sum_Q a_Q^{(1/2)}(R)a_P^{(1/2)}(Q). \quad (3.36)$$

This relation is proved as follows. The matrix $\mathbf{A}^{(1)}(R)$ defined by (3.18) can also be expanded as

$$\begin{aligned}\mathbf{A}^{(1)}(R)&=\mathbf{D}^{-1/2}\mathbf{D}^{-1/2}\tilde{\mathbf{U}}(R)\mathbf{D}^{1/2}\mathbf{D}^{1/2}\\ &=\sum_Q a_Q^{(1/2)}(R)\mathbf{D}^{-1/2}\tilde{\mathbf{U}}(Q)\mathbf{D}^{1/2}\\ &=\sum_P\sum_Q a_Q^{(1/2)}(R)a_P^{(1/2)}(Q)\tilde{\mathbf{U}}(P). \quad (3.37)\end{aligned}$$

Comparison of (3.37) with (3.18) yields (3.36).

Let $a_P^{(1/2)}(R)$ and $a_P^{(1)}(R)$ be RP elements of matrices $\mathbf{a}^{(1/2)}$ and $\mathbf{a}^{(1)}$, respectively, and rewrite Eq. (3.36) in terms of the matrix representation as follows:

$$\mathbf{a}^{(1)}=\mathbf{a}^{(1/2)}\mathbf{a}^{(1/2)}. \quad (3.38)$$

Use of the orthogonality relation of the irreducible representation matrices $\tilde{\mathbf{U}}(P)$ in (3.2) leads to[21,22]

$$a_P^{(1/2)}(R)=\sum_{\rho km}\frac{f_\rho}{N!}(D^{-1/2})_{kk}^{(\rho)}\tilde{U}_{km}^{(\rho)}(R) \times(D^{1/2})_{mm}^{(\rho)}\tilde{U}_{km}^{(\rho)}(P)^*, \quad (3.39)$$

[21] As we shall show in (4.1) and (4.2), it is always possible to consider a representation where $\mathbf{D}$ is diagonal.

[22] The $N!$ matrices $\tilde{\mathbf{U}}(P)$ introduced by (2.8) are representation matrices of the permutation group. By choosing a suitable set of N-spin functions Θ_i as basis, $\tilde{\mathbf{U}}(P)$'s can be made irreducible. Let $\tilde{\mathbf{U}}^{(\rho)}(P)$ be the matrix in the irreducible representation ρ. The km

where f_ρ is the dimension of the subspace (ρ). Since $(D^{-1/2})_{kk}{}^{(\rho)}$ and $(D^{1/2})_{mm}{}^{(\rho)}$ are real, we find the relation

$$a_P{}^{(1/2)}(R)=a_R{}^{(1/2)}(P)^*, \tag{3.40}$$

which shows that the matrices $\mathbf{a}^{(1/2)}$ and $\mathbf{a}^{(1)}$ are both Hermitian. Hence, there exists a unitary matrix $\mathbf{V}$ with which $\mathbf{a}^{(1/2)}$ and $\mathbf{a}^{(1)}$ are simultaneously diagonalized such that

$$\mathbf{V}^\dagger\mathbf{a}^{(1)}\mathbf{V}=\mathbf{1}+\boldsymbol{\eta}, \quad \text{diagonal}, \tag{3.41}$$

$$\mathbf{V}^\dagger\mathbf{a}^{(1/2)}\mathbf{V}=(\mathbf{1}+\boldsymbol{\eta})^{1/2}, \quad \text{diagonal}. \tag{3.42}$$

Eigenvalues $1+\eta_K$ and $(1+\eta_K)^{1/2}$ of matrices $\mathbf{a}^{(1)}$ and $\mathbf{a}^{(1/2)}$ are all positive, and there is no case where $(\mathbf{1}+\boldsymbol{\eta})^{1/2}$ on the right of (3.42) carries a minus sign. This will be proved as follows. Let us introduce matrix $\mathbf{A}^{(1/4)}(R)$ and the expansion coefficients $a_P{}^{(1/4)}(R)$ by

$$\mathbf{A}^{(1/4)}(R)\equiv\mathbf{D}^{-1/4}\tilde{\mathbf{U}}(R)\mathbf{D}^{1/4}=\sum_P a_P{}^{(1/4)}(R)\tilde{\mathbf{U}}(P). \tag{3.43}$$

As before, a Hermitian matrix $\mathbf{a}^{(1/4)}$ will be constructed from the expansion coefficients $a_P{}^{(1/4)}(R)$, and the following relation between $\mathbf{a}^{(1/4)}$ and $\mathbf{a}^{(1/2)}$ will be found

$$\mathbf{a}^{(1/2)}=\mathbf{a}^{(1/4)}\mathbf{a}^{(1/4)}. \tag{3.44}$$

This relation shows that $\mathbf{a}^{(1/4)}$ is also brought into a diagonal form by the unitary matrix $\mathbf{V}$ used in (3.41) and (3.42), and that the eigenvalues are square roots of eigenvalues of $\mathbf{a}^{(1/2)}$. This implies that, if some eigenvalues of $\mathbf{a}^{(1/2)}$ carried minus signs, the corresponding eigenvalues of $\mathbf{a}^{(1/4)}$ would have to be imaginary. This is contradictory to the theorem that the eigenvalues of a Hermitian matrix are real. Therefore, eigenvalues $1+\eta_K$ and $(1+\eta_K)^{1/2}$ in (3.41) and (3.42) must be all positive.

Since off-diagonal elements $a_P{}^{(1)}(R)$ are small, the relations (3.41) and (3.42) suggest that the perturbation technique can be applied to calculate the eigenvalues $1+\eta_K$ and the unitary matrix $\mathbf{V}$ of $\mathbf{a}^{(1)}$. The desired matrix $\mathbf{a}^{(1/2)}$ can then be obtained from

$$\mathbf{a}^{(1/2)}=\mathbf{V}(\mathbf{1}+\boldsymbol{\eta})^{1/2}\mathbf{V}^\dagger. \tag{3.45}$$

It turned out that this approach is not practical since the matrix $\mathbf{a}^{(1)}$ has an infinite order of degeneracy. For instance, diagonal elements $a_{(h_ik_i)}{}^{(1)}(h_ik_i)$, for $i=1, 2, \cdots, N$, are all equal to each other, if we consider a crystal with translational symmetry.

To eliminate this difficulty, it is more convenient to use an asymptotic expansion. Let us expand $(\mathbf{1}+\boldsymbol{\eta})^{1/2}$ in (3.45) in a power series of $\boldsymbol{\eta}$. The matrix $\mathbf{a}^{(1/2)}$ is then written formally as

$$\begin{aligned}\mathbf{a}^{(1/2)}&=\mathbf{V}(\mathbf{1}+\tfrac{1}{2}\boldsymbol{\eta}-\tfrac{1}{2}\times\tfrac{1}{4}\boldsymbol{\eta}^2+\tfrac{1}{2}\times\tfrac{1}{4}\times(3/6)\boldsymbol{\eta}^3-\cdots)\mathbf{V}^\dagger\\&=\mathbf{1}+\tfrac{1}{2}\mathbf{b}-\tfrac{1}{2}\times\tfrac{1}{4}\mathbf{b}^2+\tfrac{1}{2}\times\tfrac{1}{4}\times(3/6)\mathbf{b}^3-\cdots,\end{aligned} \tag{3.46}$$

where

$$\mathbf{b}\equiv\mathbf{V}\boldsymbol{\eta}\mathbf{V}^\dagger=\mathbf{a}^{(1)}-\mathbf{1}. \tag{3.47}$$

These equations (3.46) and (3.47) are written more explicitly as

$$a_P{}^{(1/2)}(R)=\delta_{RP}+\tfrac{1}{2}b_{RP}-\tfrac{1}{2}\times\tfrac{1}{4}\sum_Q b_{RQ}b_{QP}+\cdots, \tag{3.48}$$

and

$$b_{RP}=a_P{}^{(1)}(R)-\delta_{RP}. \tag{3.49}$$

Since b_{RP} is obtained by (3.29) and (3.49), the expansion coefficients $a_P{}^{(1/2)}(R)$ can be calculated by (3.48) provided the series converges.

In practice, there will not be any difficulty in using the expansion (3.48) for the calculation of $a_P{}^{(1/2)}(R)$. This will be explained as follows: Since it is not possible to calculate b_{RP} for all R and P exactly, we need to truncate and approximate the matrix b by neglecting permutations involving $s+1$ electrons or more. Let b^0 be the truncated matrix. The RP element $b_{RP}{}^0$ is then given by an approximate b_{RP} when R and P are both permutations of s electrons or less, while $b_{RP}{}^0=0$ if either R or P involves $s+1$ electrons or more. Here s is chosen so that $L_b{}^{(s)}$ as defined by (3.34) is less than one. This implies that

$$\sum_P|b_{RP}{}^0|\leqslant\epsilon<1, \quad \text{for all } R. \tag{3.50}$$

When all of b_{RP} in (3.48) are replaced by $b_{RP}{}^0$, the series (3.48) converges and the quantities $a_P{}^{(1/2)\,(0)}(R)$ thus calculated satisfy the following inequality:

$$\sum_P|a_P{}^{(1/2)\,(0)}(R)|\leqslant 2-(1-\epsilon)^{1/2}<(1-\epsilon)^{-1/2}. \tag{3.51}$$

The relation (3.51) will be proved in exactly the same way as (A6) has been obtained.

When the number s increases, however, the value of $L_b{}^{(s)}$ increases indefinitely, and the convergence of (3.48) will not be proved easily by an exact language of algebra.[11] Nevertheless, it is expected that the series (3.48), multiplied by S_R

$$\begin{aligned}S_Ra_P{}^{(1/2)}(R)=&S_R\delta_{RP}+\tfrac{1}{2}S_Rb_{RP}\\&-\tfrac{1}{2}\times\tfrac{1}{4}\sum_Q S_Rb_{RQ}b_{QP}+\cdots\end{aligned} \tag{3.52}$$

converges, for the following reasons. Quantities such as S_Rb_{RP} or $\sum_Q S_Rb_{RQ}$ will be finite and small as we have discussed in (3.35). Higher terms $\sum_Q S_Rb_{RQ}b_{QP}$, $\sum_{Q_2}\sum_{Q_1}S_Rb_{RQ_1}b_{Q_1Q_2}b_{Q_2P}$, etc., consist of connected dia-

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element of matrix $\mathbf{A}^{(1/2)}(R)$ in this representation is then written as

$$[A^{(1/2)}(R)]_{km}{}^{(\rho)}\equiv(D^{-1/2})_{kk}{}^{(\rho)}\tilde{\mathbf{U}}_{km}{}^{(\rho)}(R)\,(D)_{mm}{}^{(\rho)}=\sum_Q a_Q{}^{(1/2)}(R)\tilde{\mathbf{U}}_{km}{}^{(\rho)}(Q). \tag{1}$$

Because of the orthogonality relation of the irreducible representation matrices

$$\sum_{\rho km}(f_\rho/N!)\tilde{\mathbf{U}}_{km}{}^{(\rho)}(Q)\tilde{\mathbf{U}}_{km}{}^{(\rho)}(P)^*=\delta_{QP}, \tag{2}$$

we will find (3.39) when multiplying (1) by $\tilde{\mathbf{U}}_{km}{}^{(\rho)}(P)^*$ and summing over ρ, k and m.

grams, which build up over $S_R b_{RQ}$. This implies the convergence of the series provided the same diagrams do not accumulate. When a diagram appears repeatedly, we can count the number of times the diagram appears as we did for the $\mathbf{F}$ matrix in Sec. III (1b), and it will be finally found that they cancel each other in the course of the summation in (3.52), so the net contribution is a small finite number.

The calculation of $\sum_Q S_R b_{RQ} b_{QP}$ is, in fact, very similar to that of $S_{R_n}\mathbf{F}[h(n)]$ described by (3.15) or (3.9), where b_{RQ} corresponds to $\Gamma[k(n)]$ and b_{QP} to $\mathbf{F}_{h(n)}[k(m)]$. $S_{R_n}F[h(n)]$ may contain very large terms $\mathbf{F}_{h(n)}[k(m)]$ when m is large, but those are connected by $S_{R_n}\Gamma[k(m)]$. Large terms $b_{Q_m P}$ for large m are also connected by $S_R b_{RQ_m}$. To evaluate higher terms $\sum_{Q_2}\sum_{Q_1} S_R b_{RQ_1} b_{Q_1Q_2} b_{Q_2P}$, etc., corresponds to expanding $\mathbf{F}_{h(n)}[k(m)]$ in terms of $\mathbf{F}_{h(n)k(m)}[l(s)]$, etc. As we have discussed in the Appendix, the value of $S_{R_n}\mathbf{F}[h(n)]$ vanishes when n becomes large.

The higher order contribution, for which $L_b^{(s)}>1$, can also be calculated by combining a perturbation

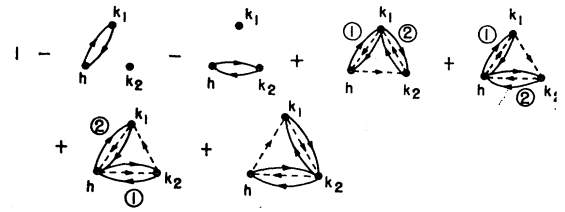

FIG. 7. The expansion of $\mathbf{F}[h|h]$.

technique with the asymptotic expansion described here. We shall not describe the details but we will again reach the same conclusion that $S_R\mathbf{A}^{(1/2)}(R)$ is expanded in terms of connected diagrams.

(c) *Role of* $\mathbf{A}^{(1/2)}(R)$

We have described the matrix $\mathbf{A}^{(1/2)}(R)$ as being very close to one and merely a correction factor of the $\mathbf{F}$ matrix. Here we shall illustrate, by an example, an essential role of $\mathbf{A}^{(1/2)}$ in our calculation.

Let us consider a Hermitian matrix

$$\mathbf{S}_N=\mathbf{D}^{-1/2}\mathbf{S}[h|h]\mathbf{D}^{-1/2},$$

which, according to (3.3), is expanded as

$$\mathbf{S}_N=\mathbf{D}^{-1/2}\mathbf{S}[h|h]\mathbf{D}^{-1/2}$$
$$=\sum_P\sum_Q f_Q[h|h]a_P{}^{(1/2)}(Q)\tilde{\mathbf{U}}(P). \quad (3.53)$$

By using the prescription (i)–(iv) in Sec. III (1b) for drawing diagrams of matrix $\mathbf{F}[h|h]$, we find that $\mathbf{F}[h|h]$ contains among others the diagrams illustrated in Fig. 7.

If we set $\mathbf{A}^{(1/2)}(R)=1$ and hence $a_P{}^{(1/2)}(R)=\delta_{RP}$, the matrix $\mathbf{S}_N$ becomes equivalent to $\mathbf{F}[h|h]$ described in Fig. 7, which is not Hermitian. For example, Hermitian

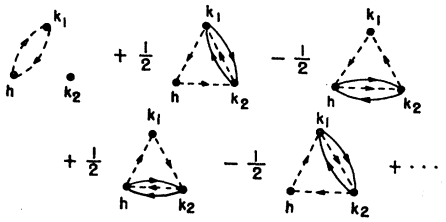

FIG. 8. The expansion of $\mathbf{A}^{(1/2)}(hk_1)$.

conjugates of the fourth and seventh diagrams become equivalent to, respectively, the second and fourth diagrams in Fig. 9. However, those diagrams cannot appear in $\mathbf{F}[h|h]$, since, to draw either of them, we have to start from loop (k_1k_2). All diagrams in $\mathbf{F}[h|h]$, however, should start from h.

On the other hand, matrix $\mathbf{A}^{(1/2)}(hk_1)$ includes the diagrams in Fig. 8. Diagrams for $\mathbf{A}^{(1/2)}(hk_2)$ are similar to those in Fig. 8 and obtained from them by interchanging k_1 and k_2. If we multiply $\mathbf{A}^{(1/2)}(hk_1)$ by the second term in Fig. 7 and $\mathbf{A}^{(1/2)}(hk_2)$ by the third, we obtain the expression for $\mathbf{S}_N$, which is similar to the series in Fig. 7, but the fourth and seventh terms are replaced by those in Fig. 9, and matrix $\mathbf{S}_N$ becomes Hermitian.

The present example clearly shows that the matrix $\mathbf{A}^{(1/2)}(R)$ is essential for retaining the Hermitian property of the energy matrix.

IV. DISCUSSION

(1) Evaluation of the Expectation Values

According to the description in Sec. III, any matrix containing an operator $f(\mathbf{r}_h)$ or $g(\mathbf{r}_{h_1}\mathbf{r}_{h_2})$ can now be evaluated by drawing diagrams. Let us denote an integral of the form $\langle k|f(\mathbf{r}_h)|h\rangle$ by a heavy line starting from h and ending at k plus a wavy line indicating the operator $f(\mathbf{r}_h)$ as shown in Fig. 10, where the second one corresponds to $\langle h|f(\mathbf{r}_h)|h\rangle$. The integral

$$\langle k_1k_2|g(\mathbf{r}_{h_1}\mathbf{r}_{h_2})|h_1h_2\rangle$$

is also written by diagrams as in Fig. 11. Here the second one represents a Coulomb interaction, the third one an exchange interaction.

From (3.16) and (3.17) together with the discussion at the end of Sec. III (2b), it is clear that any expectation value $\langle\mathbf{f}\rangle$ or $\langle\mathbf{g}\rangle$ given by (2.26) or (2.27) can be written as a sum of connected diagrams. This provides another indication that the nonorthogonality difficulties do not appear and that the Heitler–London

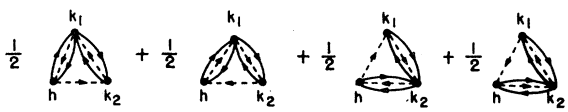

FIG. 9. Terms appearing in the expansion of $\mathbf{S}_N=\mathbf{D}^{-1/2}\mathbf{S}[h|h]\mathbf{D}^{-1/2}$.

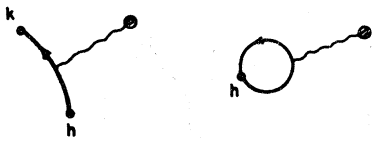

FIG. 10. Diagrams for $\langle k|f(\mathbf{r}_h)|h\rangle$ and $\langle h|f(\mathbf{r}_h)|h\rangle$.

method can be used rigorously in calculating energy spectra or other quantities.

The calculation can be carried out as follows:

(i) First, we shall write an interaction term $\langle k|f(\mathbf{r})|h\rangle$ or $\langle k_1k_2|g(\mathbf{r}_{h_1}\mathbf{r}_{h_2})|h_1h_2\rangle$ by using notations introduced in Figs. 10 and 11.

(ii) The matrix $\mathbf{D}^{-1/2}\mathbf{S}[k|h]\mathbf{D}^{-1/2}$ or

$$\mathbf{D}^{-1/2}S[k_1k_2|h_1h_2]\mathbf{D}^{-1/2}$$

should follow the diagram just obtained in (i). These matrices are expanded in terms of $f_P[h(n)]$ and $a_P{}^{(1/2)}(R)$.

(iii) Diagrams for $f_P[h(n)]$ are all constructed according to the prescriptions (i)–(iv) in Sec. III (1b).

(iv) Before computing $a_P{}^{(1/2)}(R)$, we need to draw diagrams for $a_P{}^{(1)}(R)$. This will be accomplished according to the instructions appearing between (3.29) and (3.30).

(v) The desired coefficients $a_P{}^{(1/2)}(R)$ are computed by the asymptotic expansion (3.48) and (3.49).

(vi) Finally, the matrix $\mathbf{D}^{-1/2}\mathbf{S}[k|h]\mathbf{D}^{-1/2}$ or

$$\mathbf{D}^{-1/2}\mathbf{S}[k_1k_2|h_1h_2]\mathbf{D}^{-1/2}$$

is calculated by (3.3).

(vii) Repeat the process for all k. Thus, the calculation of $\langle\mathbf{f}\rangle$ or $\langle\mathbf{g}\rangle$, including the inverse of the overlap, is now completed.

(2) Calculation of the Ground-State Energy

So far, our aim was to calculate spin-wave spectra of the Heitler–London space. The wave function $\mathbf{\Psi}$ defined by (2.3), therefore, was a vector in the complete space G of spin waves, and the energy matrix had the dimensions of the space G. This matrix representation has introduced the matrices $\mathbf{A}^{(1/2)}(R)$, which are difficult to calculate.

If, on the other hand, we want to compute the ground state of the Heitler–London method by assuming a definite spin function Θ^0 for the system,[23] we can bypass the difficult calculation of $\mathbf{A}^{(1/2)}(R)$ and we need to compute the $\mathbf{F}$ matrices in one dimension, only.

The 2^N wave functions Ψ_i defined by (2.3) can be regarded as orthogonal and the overlap matrix $\mathbf{D}$ as diagonal. If $\mathbf{D}$ is not diagonal, there exists a unitary matrix $\mathbf{V}$ with which $\mathbf{D}$ can be brought into diagonal form such that

$$\mathbf{D}'=\mathbf{V}^\dagger\mathbf{D}\mathbf{V}=\int(\mathbf{\Psi}\mathbf{V})^\dagger(\mathbf{\Psi}\mathbf{V})d\tau. \tag{4.1}$$

This implies that, instead of $\mathbf{\Psi}$, we should use the orthogonal wave functions $\mathbf{\Psi}\mathbf{V}$ defined by

$$\mathbf{\Psi}\mathbf{V}=(N!)^{-1/2}\sum_P(-1)^P P^r X(\mathbf{r}_1,\mathbf{r}_2,\cdots,\mathbf{r}_N)\times P^\sigma\mathbf{\Theta}(\sigma_1,\sigma_2,\cdots,\sigma_N)\mathbf{V}, \tag{4.2}$$

and, instead of $\mathbf{\Theta}$, spin functions $\mathbf{\Theta}\mathbf{V}$ should be used as basis.

Use of the diagonal matrix $\mathbf{D}$ in (2.26) and (2.27) leads to

$$\langle f\rangle_{ii}=\sum_h\langle h|f(\mathbf{r}_h)|h\rangle S[h|h]_{ii}D_{ii}{}^{-1}+\sum_h\sum_k{}'\langle k|f(\mathbf{r}_h)|h\rangle S[k|h]_{ii}D_{ii}{}^{-1}, \tag{4.3}$$

and

$$\langle g\rangle_{ii}=\tfrac{1}{2}\sum_{h_1}\sum_{h_2}{}'\sum_{k_1}\sum_{k_2}{}'\langle k_1k_2|g(\mathbf{r}_{h_1}\mathbf{r}_{h_2})|h_1h_2\rangle\times S[k_1k_2|h_1h_2]_{ii}D_{ii}{}^{-1}, \tag{4.4}$$

where $S[k|h]_{ii}D_{ii}{}^{-1}$ and $S[k_1k_2|h_1h_2]_{ii}D_{ii}{}^{-1}$ are diagonal elements of $\mathbf{F}[k|h]$ and $\mathbf{F}[k_1k_2|h_1h_2]$. This shows that, to calculate $\langle f\rangle_{ii}$ and $\langle g\rangle_{ii}$, we need to compute the $\mathbf{F}$ matrices only.

The overlap matrices $\mathbf{D}$ and $\mathbf{S}$ introduced by (2.7) and (2.18) can be regarded as if they are one dimensional. Hence matrices $\mathbf{F}$ and $\mathbf{X}$ introduced in Sec. III are all one dimensional and $\mathbf{U}(P)$ is a number defined by (2.6) where $i=j$. The description of drawing diagrams of the $\mathbf{F}$ matrices in Sec. III (1b) is now applied to this "one dimensional" case, and the calculation will be simplified considerably.

(3) Intra-Atomic Terms

As we have remarked in the end of Sec. I, our method can be applied to a case where each of the atoms carries more than one electron. We need to make only two short remarks for this case.

Since atomic orbitals centered at a nucleus are orthogonal to each other, overlap integrals between them vanish and we need to draw lines between those belonging to different atoms. It is convenient, therefore,

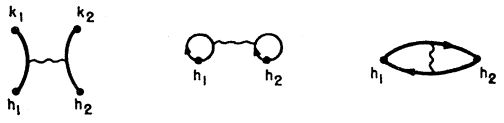

FIG. 11. Diagrams for $\langle k_1k_2|g(\mathbf{r}_{h_1}\mathbf{r}_{h_2})|h_1h_2\rangle$, $\langle h_1h_2|g(\mathbf{r}_{h_1}\mathbf{r}_{h_2})|h_1h_2\rangle$ and $\langle h_2h_1|g(\mathbf{r}_{h_1}\mathbf{r}_{h_2})|h_1h_2\rangle$.

[23] For a ferromagnet or an ionic crystal with closed-shell structure, the spin function for the ground state is known and we can use this simplified method without introducing further approximations. For any other type of ground state, we have to assume a model function Θ^0 for the spins to compute $\tilde{\mathbf{U}}(P)$, since the exact function Θ is not known. This introduces an additional approximation to the wave function Ψ defined by (2.3). In (2.3), we have specified the product Λ of atomic orbitals, but Θ can, in principle, be obtained by solving the spin Hamiltonian of the type (1.2).

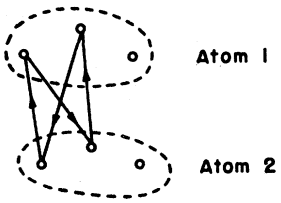

FIG. 12. An example of diagrams for arrays of many-electron atoms.

to group electrons belonging to a single atom and draw lines only between groups as is shown in Fig. 12. Of course *heavy* lines introduced in Figs. 10 and 11 representing interactions can connect electrons belonging to one atom.

The second remark concerns the case where two electrons occupy the same orbital with up and down spins. Here the overlap matrix $\mathbf{D}$ no longer has an inverse when the entire space G is considered. As we have discussed in Appendix B of paper I, however, there is a smaller space in which $\mathbf{D}^{-1}$ exists and our method can be used without any further difficulty. The smaller space is in fact a complete space of spin wave spectra for this case. We also do not need to consider $N!$ permutations but take one out of those generated from each other by simply permuting electrons in the same orbitals. For example, we need to consider only one of the diagrams in Fig. 13 when h_1 and h_2 are the same atomic orbital. Detailed discussion of such techniques will be found elsewhere[24] and therefore we shall not discuss it any further.

ACKNOWLEDGMENTS

In the course of developing the present work, the author has received great benefits from numerous communications with Dr. C. Herring. In fact, Dr. C. Herring has originally suggested the theorem described in the Appendix. Thanks are due to Dr. T. L. Gilbert for many discussions.

APPENDIX: EXPANSION OF $(1+\mathbf{X}[h(n)])^{-1}$

In this Appendix, we shall discuss the convergence of the expansion (3.14) or (3.10). First, it will be shown that, if the inequality

$$\epsilon=\sum_P |x_P[h(n)]|<1 \tag{A1}$$

is valid, the series (3.14) converges.

Both sides of (3.14) can be expanded in terms of $\tilde{\mathbf{U}}(P)$ and it will be found that

$$f_P[h(n)]=\delta_{EP}-(x[h(n)])_P+(x[h(n)]^2)_P-\cdots, \tag{A2}$$

where

$$(x[h(n)]^m)_P=\sum_{Q_1}\cdots\sum_{Q_{m-1}} x_{Q_1}[h]x_{Q_2Q_1^{-1}}[h]\cdots x_{PQ_{m-1}^{-1}}[h]. \tag{A3}$$

Taking the sum of absolute values of $(x[h(n)]^m)_P$, we find that

$$\sum_P |(x[h(n)]^m)_P|\leqslant[\sum_Q |x_Q[h(n)]|]^m=\epsilon^m. \tag{A4}$$

Inserting (A4) into (A2), we obtain

$$f_P[h(n)]\leqslant\delta_{EP}+\epsilon+\epsilon^2+\cdots=\delta_{EP}+\epsilon(1-\epsilon)^{-1}. \tag{A5}$$

and also

$$\sum_P |f_P[h(n)]|\leqslant(1-\epsilon)^{-1}. \tag{A6}$$

These results prove the original statement. If we truncate the series after the mth term of (3.14), errors in $f_P[h(n)]$ and $\mathbf{F}[h(n)]$ will both be smaller than $\epsilon^m(1-\epsilon)^{-1}$.

In the forthcoming paper, we shall introduce the theorem that the sum L_n of absolute values of the expansion coefficients $f_P[h(n)]$ is bounded as

$$[1+O(\Delta\Delta_0)]^{-n}\leq L_n\leq[1-O(\Delta\Delta_0)]^{-n}, \tag{A7}$$

where

$$L_n=\text{max on } h\text{'s of } \sum_P |f_P[h_1\cdots h_n|h_1\cdots h_n]|, \tag{A8}$$

$$\Delta=\text{max on } h \text{ of } \sum_{j\neq h} |\langle j|h\rangle|, \tag{A9}$$

$$\Delta_0=\text{max of } |\langle j|h\rangle|, \tag{A10}$$

and

$$O(\Delta\Delta_0)=\frac{\Delta\Delta_0}{1-\Delta}\left\{1+\frac{1}{4}\frac{4\Delta\Delta_0}{(1-\Delta)^2}+\frac{1.3}{4.6}\left[\frac{4\Delta\Delta_0}{(1-\Delta)^2}\right]^2+\cdots\right\}. \tag{A11}$$

Here we shall show briefly how this theorem can be proved. The expansion formula (2.23) of matrices S leads to

$$\mathbf{F}[\cdots h_n|\cdots h_n]=\mathbf{F}[\cdots h_nh_{n+1}|\cdots h_nh_{n+1}]+\sum_h{}^{(n+1)}\langle h|h_{n+1}\rangle\mathbf{F}[\cdots h_nh|\cdots h_nh_{n+1}], \tag{A12}$$

and

$$\mathbf{F}[\cdots h_{n+1}|\cdots h_n]=\langle h_n|h_{n+1}\rangle\mathbf{F}[\cdots h_{n+1}h_n|\cdots h_nh_{n+1}]+\sum_h{}^{(n+1)}\langle h|h_{n+1}\rangle\mathbf{F}[\cdots h_{n+1}h|\cdots h_nh_{n+1}], \tag{A13}$$

where $\cdots$ in the square brackets indicates $h_1h_2\cdots h_{n-1}$. When the matrices $\mathbf{F}$ in (A12) are expanded in terms of f_P and $\tilde{\mathbf{U}}(P)$, the equation is converted into a set of $N!$ equations for f_P as follows:

$$f_P[\cdots h_n|\cdots h_n]=f_P[\cdots h_nh_{n+1}|\cdots h_nh_{n+1}]+\sum_h{}^{(n+1)}\langle h|h_{n+1}\rangle f_P[\cdots h_nh|\cdots h_nh_{n+1}], \tag{A14}$$

[24] M. Kotani *et al.*, Ref. 18, also see T. Arai, J. Phys. Soc. Japan **18**, 718 (1963).

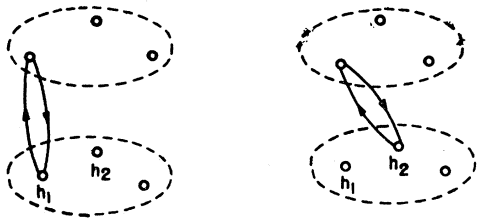

FIG. 13. An example of a case of two equivalent diagrams. Here electrons h_1 and h_2 occupy the same atomic orbital with up and down spins. We need to consider only one of them.

for all P. By taking absolute values of each term in (A14) and summing over $N!$ permutations P, we obtain that

$$\sum_P |f_P[\cdots h_n|\cdots h_n]|$$

$$\leqslant \sum_P |f_P[\cdots h_n h_{n+1}|\cdots h_n h_{n+1}]| + \sum_h{}^{(n+1)} |\langle h|h_{n+1}\rangle| \times \sum_P |f_P[\cdots h_n h|\cdots h_n h_{n+1}]| . \quad \text{(A15)}$$

Since the above inequality is valid for any h's, we find that

$$L_n \leq L_{n+1} + \Delta l_{n+1}{}^1, \quad \text{(A16)}$$

where

$$l_n{}^1 = \max \text{ on } h\text{'s of } \sum_P |f_P[\cdots h_n h|\cdots h_n h_{n+1}]| , \quad \text{(A17)}$$

and h is not involved among $h_1\cdots h_n h_{n+1}$.

Similarly transposition of (A12) leads to

$$L_{n+1} \leq L_n + \Delta l_{n+1}{}^1, \quad \text{(A18)}$$

and, from (A13), we also find that

$$l_n{}^1 \leq \Delta_0 L_{n+1} + \Delta l_{n+1}{}^1. \quad \text{(A19)}$$

If the relation

$$l_{n+1}{}^1 \leq [O(\Delta\Delta_0)/\Delta] L_{n+1} \quad \text{(A20)}$$

is valid for any n, the present theorem will be proved. In fact, use of (A20) in (A16) and (A18) leads to

$$[1+O(\Delta\Delta_0)]^{-1} L_n \leq L_{n+1} \leq [1-O(\Delta\Delta_0)]^{-1} L_n \quad \text{(A21)}$$

for any n. If n becomes zero, the matrix $\mathbf{F}$ becomes $\mathbf{D}\mathbf{D}^{-1}=1$ and $L_0=1$. Inserting this result in (A21) when $n=0$, we find the desired bound for L_1. Repeated use of (A21), by increasing n one by one, will lead to the expression (A7).

The relation (A20) will be proved by an inductive unraveling process as follows. When $n=N-1$, Eq. (A19) becomes

$$l_{N-1}{}^1 \leq \Delta_0 L_N, \quad \text{(A22)}$$

since the second term on the right of (A13) vanishes. From (2.19), it is clear that $\mathbf{F}[\cdots h_{N-1}|\cdots h_{N-1}] = \mathbf{F}[\cdots h_{N-1}h_N|\cdots h_{N-1}h_N]$, and hence $L_{N-1}=L_N$. This implies that (A22) is written as

$$l_{N-1}{}^1 \leq \Delta_0 L_{N-1}. \quad \text{(A23)}$$

Since Δ_0 is smaller than $O(\Delta\Delta_0)/\Delta$, the above relation proves the inequality (A20) when $n=N-1$.

Let us assume that (A20) is valid for $n=n_0$. Use of (A20) in (A18) and (A19) yields

$$[1-O(\Delta\Delta_0)] L_{n_0+1} \leq L_{n_0} \quad \text{(A24)}$$

and

$$l_{n_0}{}^1 \leq [\Delta_0 + O(\Delta\Delta_0)] L_{n_0+1}. \quad \text{(A25)}$$

From (A24) and (A25), we obtain

$$l_{n_0}{}^1 \leq [\Delta_0 + O(\Delta\Delta_0)][1-O(\Delta\Delta_0)]^{-1} L_{n_0}. \quad \text{(A26)}$$

Inserting the expression (A11) for $O(\Delta\Delta_0)$ into (A26), we will find that the coefficient

$$[\Delta_0 + O(\Delta\Delta_0)][1-O(\Delta\Delta_0)]^{-1}$$

on the right of (A26) is equivalent to $O(\Delta\Delta_0)/\Delta$. Hence (A20) is also valid for $n=n_0-1$. This shows that (A20) is valid for any n. Thus the present theorem is proved.

Use of the inequality (A7) in (3.9) leads to

$$\epsilon = \sum_P |x_P[h]| < \Delta^2(1-O(\Delta\Delta_0))^{-1} + \Delta^3(1-O(\Delta\Delta_0))^{-2} + \Delta^4(1-O(\Delta\Delta_0))^{-3} + \cdots. \quad \text{(A27)}$$

Therefore, the inequality (A1) is satisfied when $n=1$ and the expansion (3.10) is valid as long as Δ is small as compared with one.

Use of the inequality (A7) in (3.13) will lead in the case $n=2$ to the same conclusion and it will be found that the series (3.12) converges. If, on the other hand, n increases, the upper bound $(1-O(\Delta\Delta_0))^{-n}$ and ϵ increase indefinitely and therefore the expansion (3.14) is no longer valid. However, it will be found that, in calculating an expectation value $\langle \mathbf{f}\rangle$ or $\langle \mathbf{g}\rangle$, the matrix $\mathbf{F}[h(n)]$ appears in the form $S_{R_n}\mathbf{F}[h(n)]$, which vanishes when n increases indefinitely since

$$S_{R_n}\mathbf{F}[h(n)] < \Delta^n(1-O(\Delta\Delta_0))^{-n} \to 0 \quad \text{(A28)}$$

as long as Δ is small as compared with unity. Here R_n is a cyclic permutation with which electrons $h_1, h_2, \cdots, h_{n-1}, h_n$ are shifted to orbitals $h_2, h_3, \cdots, h_n, h_1$ and S_{R_n} is an overlap of the type $\int R_n\Lambda^*\Lambda dv$.