Derivation of the Dirac Vector Model for a Solid

WILLIAM J. MULLIN
Aerospace Research Laboratories, Wright-Patterson Air Force Base, Ohio
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A cluster expansion derivation of the Dirac vector model, which has important applications in the theory of ferromagnetic and antiferromagnetic materials, is given for the case of a solid with a wave function which is a linear combination of Slater determinants, each corresponding to a different spin configuration. It is assumed that the single-particle wave functions are nonorthogonal, with one particle per lattice site. It is shown that there is no "nonorthogonality catastrophe" and that Carr's condition for the validity of the vector model applies in this case, as he has conjectured. Expressions are given for the direct energy and exchange integral.

I. INTRODUCTION

ONE of the most useful techniques in the theory of ferromagnetic and antiferromagnetic substances is that of the Dirac vector model. In this formulation the energy of the solid is given by finding the eigenvalues of the effective spin Hamiltonian,

$$H_S=E_0-\sum_{i<j}J_{ij}(P_{ij}{}^{ji})_S. \tag{1}$$

The spin permutation operator for particles i and j is

$$(P_{ij}{}^{ji})_S=\tfrac{1}{2}(1+\boldsymbol{\sigma}_i\cdot\boldsymbol{\sigma}_j);$$

$\boldsymbol{\sigma}_i$ and $\boldsymbol{\sigma}_j$ are the Pauli spin matrices. The "direct" energy E_0 is the expectation value of the system Hamiltonian obtained without antisymmetrizing the wave function; J_{ij} is called the "exchange" integral. The eigenfunctions of Eq. (1) can be taken to be linear combinations of products of single-particle spin functions. (Spin-wave theory, for example, approximates these eigenfunctions.)

If the number of particles N is a very large number, and if the single-particle wave functions are not orthogonal, there is difficulty involved in the justification of Eq. (1). Analyses of this problem have been made by Van Vleck,[1] Carr,[2] and Mizuno and Izuyama.[3] In Sec. II we will show that the energy is the ratio of two polynomials in N. The resolution of the difficulty introduced by this apparent breakdown of the energy expression, the "nonorthogonality catastrophe," rests on the fact that these polynomials cancel one another in a way such that the energy is actually of order N. Van Vleck was able to demonstrate this in several special cases. Carr gave conditions under which the energy took the vector model form when the wave function was a single Slater determinant. There is no apparent reason, as Carr argues, why similar conditions should not hold for a sum of Slater determinants. However, he did not show this explicitly. We will use a cluster expansion technique to demonstrate that Carr's conditions for the applicability of the Dirac vector model do indeed hold for a wave function which is a sum of Slater determinants. Mizuno and Izuyama show that no "nonorthogonality catastrophe" occurs in the general case, but do not give an explicit series development for the energy as we shall do. This problem has also been treated in a different way by Arai.[4]

II. ENERGY EXPECTATION VALUE

We consider a Hamiltonian of the form

$$H=\sum_{\gamma=1}^{N}H_1(\gamma)+\sum_{1\leqslant\gamma<\delta\leqslant N}H_2(\gamma,\delta). \tag{2}$$

The N particles described by this Hamiltonian may be the electrons responsible for the magnetic behavior of the solid, or they may be the nuclei which give rise to a nuclear magnetism, as in the case of solid He^3. In either case each particle will be localized about a lattice site with one particle per lattice site. If Eq. (2) describes electrons, then $H_1(\gamma)$ and $H_2(\gamma,\delta)$ will each contain a dependence on the lattice site positions because of nucleus-nucleus and electron-nucleus Coulomb interactions.

A suitable trial wave function for the Hamiltonian (2) is a linear combination of Slater determinants made up of single particle spatial wave functions, $\phi_i(\mathbf{x}_\alpha)$ (i.e., particle α is localized about lattice site i), and single-particle spin functions $\xi_{\mu_i}(\alpha)$, where μ_i is $+1$ or -1 if the spin of particle α is up or down, respectively. Let the set $\mu_1, \mu_2, \cdots\mu_N$ be designated simply by μ, with no subscript. Then the wave function is

$$\Psi=\sum_{\mu}A_\mu\Phi_\mu(\mathbf{x}), \tag{3}$$

where normalization requires $\sum_\mu|A_\mu|^2=1$. The symbol $\mathbf{x}$ stands for the N space and spin variables. We have

$$\Phi_\mu(\mathbf{x})=\begin{vmatrix}\phi_1(\mathbf{x}_1)\xi_{\mu_1}(1)&\cdots&\phi_N(\mathbf{x}_1)\xi_{\mu_n}(1)\\ \vdots&\ddots&\vdots\\ \phi_1(\mathbf{x}_N)\xi_{\mu_1}(N)&\cdots&\phi_N(\mathbf{x}_N)\xi_{\mu_n}(N)\end{vmatrix}. \tag{4}$$

Thus, the sum over μ is a sum over all spin configurations.

[1] J. H. Van Vleck, Phys. Rev. **49**, 232 (1936).
[2] W. J. Carr, Phys. Rev. **92**, 28 (1953).
[3] Y. Mizuno and T. Izuyama, Progr. Theoret. Phys. (Kyoto) **22**, 344 (1959).
[4] T. Arai, Phys. Rev. **126**, 471 (1962); **134**, A824 (1964).

We can also write (4) as a sum of permutations,

$$\Phi_\mu(\mathbf{x})=\sum_\mu(-1)^{p_\nu}P_\nu\Phi_{\mu 0}(\mathbf{x}), \tag{5}$$

where

$$\Phi_{\mu 0}(\mathbf{x})=\prod_i \phi_i(\mathbf{x}_i)\xi_{\mu_i}(i).$$

The operator P_ν interchanges the particle states, i.e., the indices. It can be written as a product of a spatial permutation operator $P_{\nu 0}$, and a spin permutation operator $P_{\nu S}$. The sum over ν is a sum over all possible permutations of the N states, p_ν being the "parity" of the νth permutation.

The energy expectation value is

$$E=\int\Psi^*(\mathbf{x})H\Psi(\mathbf{x})d\mathbf{x}\Big/\int\Psi^*(\mathbf{x})\Psi(\mathbf{x})d\mathbf{x}.$$

We have let $d\mathbf{x}=d\mathbf{x}_1\cdots d\mathbf{x}_N$. The integration also implies a summation over all spin coordinates. Using Eq. (3),

$$E=\frac{\sum_{\mu,\mu'}A_\mu^*A_{\mu'}\int\Phi_\mu^*(\mathbf{x})H\Phi_{\mu'}(\mathbf{x})d\mathbf{x}}{\sum_{\mu,\mu'}A_\mu^*A_{\mu'}\int\Phi_\mu^*(\mathbf{x})\Phi_{\mu'}(\mathbf{x})d\mathbf{x}},$$

we can show that

$$\frac{\int\Phi_\mu^*(\mathbf{x})H\Phi_{\mu'}(\mathbf{x})d\mathbf{x}}{\int\Phi_\mu^*(\mathbf{x})\Phi_{\mu'}(\mathbf{x})d\mathbf{x}}=\frac{N!\int\Phi_{\mu 0}^*(\mathbf{x})H\Phi_{\mu'}(\mathbf{x})d\mathbf{x}}{N!\int\Phi_{\mu 0}^*(\mathbf{x})\Phi_{\mu'}(\mathbf{x})d\mathbf{x}}.$$

As is stated in Ref. 2, this follows because each of the $N!$ permutations of $\Phi_{\mu 0}$ in Φ_μ gives the same result since H is assumed symmetric in the particle coordinates. Thus we have

$$E=\frac{\sum_\nu(-1)^{p_\nu}\sum_{\mu,\mu'}A_\mu^*A_{\mu'}\int\Phi_{\mu 0}^*(\mathbf{x})H(P_\nu\Phi_{\mu' 0}(\mathbf{x}))d\mathbf{x}}{\sum_\nu(-1)^{p_\nu}\sum_{\mu,\mu'}A_\mu^*A_{\mu'}\int\Phi_{\mu 0}^*(\mathbf{x})(P_\nu\Phi_{\mu' 0}(\mathbf{x}))d\mathbf{x}}$$
$$=\frac{\sum_\nu(-1)^{p_\nu}\int\phi_0^*H(P_{\nu 0}\phi_0)d\mathbf{x}\langle P_{\nu S}\rangle}{\sum_\nu(-1)^{p_\nu}\int\phi_0^*(P_{\nu 0}\phi_0)d\mathbf{x}\langle P_{\nu S}\rangle}. \tag{6}$$

We have separated P_ν into spatial and spin parts $P_\nu=P_{\nu 0}P_{\nu S}$; $\phi_0=\prod_i\phi_i(\mathbf{x})$; and $\langle P_{\nu S}\rangle$ is the expectation value of the spin permutation operator, i.e.,

$$\langle P_{\nu S}\rangle=\sum_{\text{spin}}\Big[\Big\{\sum_\mu A_\mu\prod_i\xi_{\mu_i}(i)\Big\}^*P_{\nu S}\Big\{\sum_{\mu'}A_{\mu'}\prod_j\xi_{\mu_j'}(j)\Big\}\Big].$$

From Eq. (6) it can be seen that E is the ratio of two polynomials in N. This is clear from the numerator of Eq. (6) if, as an example, we consider the following: There is one term in which no particle states are exchanged; there are $\sim N$ terms in which the states of two particles are exchanged; there are $\sim N^2$ terms in which two particle states are exchanged and simultaneously the states of two other particles are exchanged; and so on. It is this apparent breakdown of the energy expression for large N which Van Vleck, Carr, Mizuno, and Izuyama, and Arai have discussed, and which was mentioned in Sec. I.

III. THE CLUSTER EXPANSION

We follow the procedure of Iwamoto and Yamada[5] and introduce a "generalized normalization integral," which we define by

$$I_N(\beta)=\sum_\nu(-1)^{p_\nu}\int\phi_0^*e^{\beta H}(P_{\nu 0}\phi_0)d\mathbf{x}\langle P_{\nu S}\rangle,$$

so that

$$E=(\partial/\partial\beta)\ln I_N(\beta)|_{\beta=0}. \tag{7}$$

Define the "subnormalization integrals,"

$$I_i=(i|f(1)|i),$$
$$I_{ij}=(ij|f(1)f(2)g(1,2)\{|ij)-|ji)\langle(P_{ij}{}^{ji})_S\rangle\},$$
$$I_{ijk}=(ijk|f(1)f(2)f(3)g(1,2)g(2,3)g(3,1)\{|ijk)-|jik)\langle(P_{ij}{}^{ji})_S\rangle-|kji)\langle(P_{ik}{}^{ki})_S\rangle$$
$$-|ikj)\langle(P_{jk}{}^{kj})_S\rangle+|jki)\langle(P_{ijk}{}^{jki})_S\rangle+|kij)\langle(P_{ijk}{}^{kij})_S\rangle\}, \tag{8}$$
$$\cdots$$
$$I_{i_1\cdots i_n}=\sum_\nu(-1)^{p_\nu}(i_1\cdots i_n|f(1)\cdots f(n)\prod_{1\leqq\gamma<\delta\leqq n}g(\gamma,\delta)P_{\nu 0}|i_1\cdots i_n)\langle P_{\nu S}\rangle,$$

where

$$f(1)=\exp(\beta H_1(1)),\quad g(1,2)=\exp(\beta H_2(1,2)),$$

[5] F. Iwamoto and M. Yamada, Progr. Theoret. Phys. (Kyoto) **17**, 543 (1957); **18**, 345 (1957).

and, for example,

$$(ij|f(1)f(2)g(1,2)\{|ij)-|ji)\langle(P_{ij}{}^{ji})_S\rangle\}\equiv\int\phi_i{}^*(1)\phi_j{}^*(2)f(1)f(2)g(1,2)\{\phi_i(1)\phi_j(2)-\phi_j(1)\phi_i(2)\langle(P_{ij}{}^{ji})_S\rangle\}d\mathbf{x}_1d\mathbf{x}_2.$$

$\langle(P_{ij}{}^{ji})_S\rangle$, is the expectation value of the spin permutation operator for particles i and j.

Using the subnormalization integrals, we define the cluster integrals,[5]

$$X_i=I_i,\quad X_{ij}=I_{ij}-X_iX_j,\quad X_{ijk}=I_{ijk}-X_{ij}X_k-X_{ik}X_j-X_{jk}X_i-X_iX_jX_k,\text{ etc.}$$

We find

$$\begin{aligned}
X_i&=(i|f(1)|i),\\
X_{ij}&=(ij|f(1)f(2)h(1,2)|ij)-(ij|f(1)f(2)h(1,2)|ji)\langle(P_{ij}{}^{ji})_S\rangle-(ij|f(1)f(2)|ji)\langle(P_{ij}{}^{ji})_S\rangle,\\
X_{ijk}&=(ijk|f(1)f(2)f(3)h(1,2)h(2,3)h(3,1)|ijk)\\
&\quad+(ijk|f(1)f(2)f(3)[h(1,2)h(3,1)+h(1,2)h(2,3)+h(2,3)h(3,1)]|ijk)\\
&\quad-(ijk|f(1)f(2)f(3)g(1,2)[h(2,3)h(3,1)+h(2,3)+h(3,1)]|jik)\langle(P_{ij}{}^{ji})_S\rangle\\
&\quad-(ijk|f(1)f(2)f(3)g(2,3)[h(1,2)h(3,1)+h(1,2)+h(3,1)]|ikj)\langle(P_{jk}{}^{kj})_S\rangle\\
&\quad-(ijk|f(1)f(2)f(3)g(3,1)[h(1,2)h(2,3)+h(1,2)+h(2,3)]|kji)\langle(P_{ik}{}^{ki})_S\rangle\\
&\quad+(ijk|f(1)f(2)f(3)g(1,2)g(2,3)g(3,1)|jki)\langle(P_{ijk}{}^{jki})_S\rangle\\
&\quad+(ijk|f(1)f(2)f(3)g(1,2)g(2,3)g(3,1)|kij)\langle(P_{ijk}{}^{kij})_S\rangle,
\end{aligned}\tag{9}$$

where

$$h(\gamma,\delta)=g(\gamma,\delta)-1.$$

We note that terms containing more than one factor of $h(\gamma,\delta)=\exp(\beta H_2(\gamma,\delta))-1$ will not contribute to the final result whose derivation will involve taking the β derivative of each term followed by setting $\beta=0$. Thus, we keep only terms which are zeroth and first order in β, and we have

$$\begin{aligned}
X_{ijk}&=-(ijk|f(1)f(2)f(3)[h(2,3)+h(3,1)]|jik)\langle(P_{ij}{}^{ji})_S\rangle-(ijk|f(1)f(2)f(3)[h(1,2)+h(3,1)]|ikj)\langle(P_{jk}{}^{kj})_S\rangle\\
&\quad-(ijk|f(1)f(2)f(3)[h(1,2)+h(2,3)]|kji)\langle(P_{ik}{}^{ki})_S\rangle\\
&\quad+(ijk|f(1)f(2)f(3)[1+h(1,2)+h(2,3)+h(3,1)]|jki)\langle(P_{ijk}{}^{jki})_S\rangle\\
&\quad+(ijk|f(1)f(2)f(3)[1+h(1,2)+h(2,3)+h(3,1)]|kji)\langle(P_{ijk}{}^{kji})_S\rangle.
\end{aligned}\tag{10}$$

Note that Eq. (10) contains no direct energy terms. Indeed, we can prove a theorem stating that a general n-index cluster integral $X_{i_1\cdots i_n}$ $(n>2)$ contains only terms which are nth and $(n-1)$th order in the "overlap integral" $S_{ij}=\int\phi_i{}^*(1)\phi_j(1)d\mathbf{x}_1$ if we consider only terms of zeroth and first order in β. We will also show that the terms which are $(n-1)$th order in S_{ij} are also first order in β. If the wave functions $\phi_i(\mathbf{x}_\alpha)$ are sufficiently localized, the overlap integral S_{ij} will be small $(i\neq j)$ and the cluster integrals will form a converging sequence. We will use this theorem in the remainder of this section, but delay proof of it until Sec. IV.

Iwamoto and Yamada,[5] and also Wu,[6] show that

$$I_N(\beta)=\prod_i X_ie^G,\tag{11}$$

where

$$G=\tfrac{1}{2}\sum_{(i,j)}x_{ij}-\tfrac{1}{4}\sum_{(i,j)}x_{ij}{}^2-\tfrac{1}{2}\sum_{(i,j,k)}x_{ij}x_{jk}+\tfrac{1}{6}\sum_{(i,j,k)}x_{ijk}+\frac{1}{24}\sum_{(i,j,k,l)}x_{ijkl}+\cdots,\tag{12}$$

and $x_{ij}=X_{ij}/X_iX_j$, etc. The parentheses on the summation indices in Eq. (12) mean omit those terms from the sums for which two or more indices are equal. To find the order of magnitude of the terms in this series we must demonstrate two points: (a) All indices in a term of the cluster expansion (12) are "linked" or "connected" to one another. This "connectedness" means that the sums over the indices of an expansion term are not independent of one another. When summed over all indices the term will then be of order N, and there will be no "nonorthogonality catastrophe." In the next section, while demonstrating the theorem mentioned above, we will prove a lemma which states that all indices of a given cluster integral X, or equivalently, of an x, are connected either by exchanges or by an $h(\gamma,\delta)$. However, many terms in the cluster expansion are products of a number of x's. Wu[6] has shown that the indices of these product terms are connected by having indices in common, as the index j is common to both x's in $x_{ij}x_{jk}$. (b) From the derivation of Iwamoto and Yamada (or of Wu) it is evident that succeeding groups of terms in the expansion (12) have increasing numbers of indices. Hence, they are of increasingly higher order in the overlap integral S. For example, x_{ij} has a term of order S^0 (which is also first order in β) and terms of order S^2; $x_{ij}{}^2$, which is considered to have four indices,

[6] F. Y. Wu, J. Math. Phys. 4, 1438 (1963).

has terms of order S^2 and S^4 (dropping terms in β^2); x_{ijk} has terms of order S^2 and S^3, etc. In general, then, using our theorem, a term having n indices is of order S^{n-2} or higher (dropping noncontributing terms of order β^2 or higher).

From (a) and (b) it is clear that when summed over all values of the indices, an n-index term will be at least of order $NZ_1Z_2^{n-2}S^{n-2}$, where Z_1 is the number of particles in the range of $H_2(\gamma,\delta)$,and Z_2 is the number of neighboring wave functions which have appreciable overlap with a given single-particle wave function. There is only one factor of N because the sums over the indices are not independent. There is only one factor of Z_1 because $h(\gamma,\delta)$ is first order in β so each expansion term can contain at most a single $h(\gamma,\delta)$, or, equivalently, a single $H_2(\gamma,\delta)$. The factor $Z_2^{n-2}S^{n-2}$ is a result of the discussion in (b). If $Z_2S<1$, the expansion for G, and hence for E, will converge. If $Z_2S\ll 1$, then the vector model (1) is valid. These are essentially the conditions of Ref. 2.

An expression for the exchange integral J_{ij} can be gotten from Eqs. (7), (11), and (12). Denoting differentiation with respect to β by a prime we have

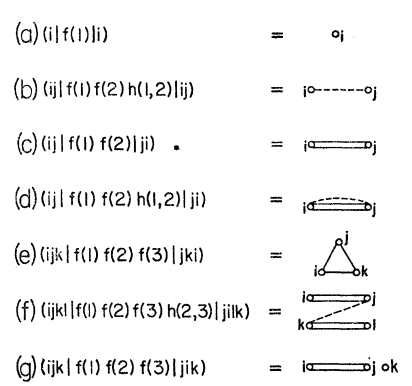

FIG. 1. Examples of the graphical representation of matrix elements.

$$E=[\sum_i X_i'+\tfrac{1}{2}\sum_{(i,j)} x_{ij}'-\tfrac{1}{2}\sum_{(i,j)} x_{ij}'x_{ij}-\sum_{(i,j,k)} x_{ij}'x_{jk}+\tfrac{1}{6}\sum_{(i,j,k)} x_{ijk}'+\cdots]_{\beta=0}.$$

If we keep terms of order no higher than S^2,

$$E=[\sum_i (i|H_1(1)|i)+\tfrac{1}{2}\sum_{(i,j)}(ij|H_2(1,2)|ij)]+[\sum_{(i,j)} S_{ij}S_{ji}(i)|H_1(1)|i)\langle(P_{ij}{}^{ji})_S\rangle - \sum_{(i,j)} S_{ji}(i|H_1(1)|j)\langle(P_{ij}{}^{ji})_S\rangle-\tfrac{1}{2}\sum_{(i,j)} S_{ij}S_{ji}(ij|H_2(1,2)|ij)\langle(P_{ij}{}^{ji})_S\rangle-\sum_{(i,j)}(ij|H_2(1,2)|ji)\langle(P_{ij}{}^{ji})_S\rangle + \sum_{(i,j,k)} S_{ik}S_{ki}(ij|H_2(1,2)|ij)\langle(P_{ik}{}^{ki})_S\rangle-\sum_{(i,j,k)} S_{ji}(ik|H_2(1,2)|jk)\langle(P_{ij}{}^{ji})_S\rangle]. \quad (13)$$

The first term in square brackets is the direct energy E_0, the second is $-\sum_{i<j} J_{ij}\langle(P_{ij}{}^{ji})_S\rangle$. This result, which is valid for any linear combination of Slater determinants, is identical with Carr's result for a single determinant [Ref. 2, Eq. (29)]. In comparing the two results note that our definition of $H_2(\gamma,\delta)$ differs by a factor of 2 from Carr's.

IV. PROOF OF THE THEOREM OF SEC. III

In Sec. III we used the following theorem: a general n-index cluster integral $X_{i_1\cdots i_n}$ $(n>2)$ contains only terms which are nth and $(n-1)$th order in the overlap integral $S_{ij}=\int\phi_i^*(1)\phi_j(1)d\mathbf{x}_1$, if we consider only terms of zeroth and first order in β. Furthermore, the terms $(n-1)$th order in S are also first order in β.

The proof of this theorem is facilitated by introduction of a graphical representation of the terms in the cluster integrals. Those indices of a matrix element connected by exchange, as i and j in $(i|f(1)|j)$, will be joined by a solid line; indices connected by an $h(\gamma,\delta)$, as i and j in $(ij|f(1)f(2)h(1,2)|ij)$, will be joined by a dashed line. The number of solid lines in a graph is the order of the matrix element in the overlap integral S. Examples of matrix elements and the graphs representing them are shown in Fig. 1.

Note that in matrix element (f) of Fig. 1 there is ambiguity as to whether it is indices j and k or i and l which are joined by $h(2,3)$. We define, as being joined by an h, those indices which were joined previous to the permutations.

We note that every index must have zero or two solid lines ending on it. This rule occurs because permutations never occur singly; for example, $i\rightarrow j$ always requires $j\rightarrow$ (some index$\neq j$).

Except for that of matrix element (g) of Fig. 1, all graphs shown are said to be "connected." That is, it is possible to get from an index to any other index by following either solid or dashed lines. The graph of matrix element (g) in Fig. 1 is "disconnected."

We now show the following lemma which was mentioned in Sec. III: the n-index cluster integral $X_{i_1\cdots i_n}$ contains all matrix elements of n indices whose graphs are connected, and only those matrix elements. The lemma is true for X_i, X_{ij}, and X_{ijk} by inspection of Eqs. (9). We proceed by induction. Assume the lemma is true for all m-index cluster integrals with $m<n$. We form cluster integrals according to the formula

$$X_{i_1\cdots i_n}=I_{i_1\cdots i_n}-\sum_{m,p,\cdots q\leqslant n} X_{i_1\cdots i_m}X_{i_{m+1}\cdots i_p}\cdots X_{i_{q+1}\cdots i_n}. \quad (14)$$

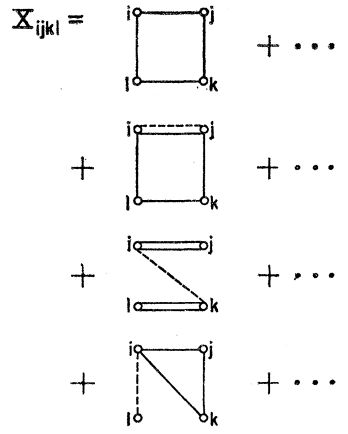

FIG. 2. The graphical representation of Eq. (15).

If we use $g(\gamma,\delta)=h(\gamma,\delta)+1$ and write

$$\prod_{1\leqslant\gamma<\delta\leqslant n} g(\gamma,\delta)=1+\sum_{1\leqslant\gamma<\delta\leqslant n} h(\gamma,\delta) +\sum h(\gamma,\delta)h(\mu,\nu)+\cdots$$

in Eq. (8), we see that $I_{i_1\cdots i_n}$ contains all diagrams, both connected and disconnected, of n indices. Since a cluster integral $X_{i_1\cdots i_m}$ $(m<n)$ is assumed to contain all the m-index connected diagrams and no more, then the sum $\sum X_{i_1\cdots i_m}\cdots X_{i_{q+1}\cdots i_n}$ in Eq. (14) contains all possible n-index disconnected diagrams, and no more. Thus, on the right-hand side of Eq. (13), only the n-index connected diagrams do not cancel. Since the lemma holds for the one-, two-, and three-index cluster integrals by induction, it holds for the general one.

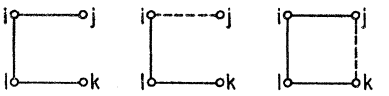

FIG. 3. Examples of four-index connected graphs which violate the rule that zero or two solid lines must end on every index.

All terms in

$$\prod_{1\leqslant\gamma<\delta\leqslant n} g(\gamma,\delta)=1+\sum_{1\leqslant\gamma<\delta\leqslant n} h(\gamma,\delta)+\cdots,$$

which are signified by the dots, are at least second order in β and will not contribute to the final result. They can then be dropped. However, the only kinds of connected diagrams of n indices $(n>2)$ which have only a 1 or a single $h(\gamma,\delta)$ in them, and which satisfy the rule that only zero or two solid lines end on an index, are of order n or $n-1$ in the overlap integral. For $n>2$, they are one of the following forms: (1) n indices connected by n solid lines only—of order n in the overlap integral; (2) n indices connected by n solid lines with a single pair of them also connected by a dotted line—of order n in the overlap integral; (3) m indices all connected by m solid lines, $n-m$ indices all connected by n—m solid lines, with the two sets connected together by only a dashed line—of order n in the overlap integral; (4) $n-1$ indices all connected by $n-1$ solid lines, one index connected to the rest by only a dashed line—of order $n-1$ in overlap integral and first order in β. This completes the proof.

As an illustration we consider X_{ijkl}. The theorem gives

$$\begin{aligned}X_{ijkl}=(ijkl|\,f(1)f(2)f(3)f(4)\,|\,jkli)\langle(P_{ijkl}{}^{jkli})_S\rangle+\cdots+(ijkl|\,f(1)f(2)f(3)f(4)h(1,2)\,|\,jkli)\langle(P_{ijkl}{}^{jkli})_S\rangle+\cdots\\ +(ijkl|\,f(1)f(2)f(3)f(4)h(1,3)\,|\,jilk)\langle(P_{ijkl}{}^{jilk})_S\rangle+\cdots\\ +(ijkl|\,f(1)f(2)f(3)f(4)h(1,4)\,|\,jkil)\langle(P_{ijk}{}^{jki})_S\rangle+\cdots,\end{aligned}\quad(15)$$

where the dots represent other terms of the same type as preceded them. The graphical representation of X_{ijkl} is shown in Fig. 2. In Fig. 3 we illustrate some four index connected graphs which are not present because they violate our rule that zero or two solid lines must end on every index.

The one- and two-index cluster integrals are special cases for which the theorem does not hold; the one-index integral has only a term of order S^0, and the two-index integral has terms of order S^0 (which is also first order in β) and S^2. We have taken this into account in the discussion of Sec. III.

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