The Variational Solution of the Schrödinger Equation of Finite Fermion Systems

I. Hartree-Fock Approximation and Independent Pair Model

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In this and the succeeding communication we outline a method for obtaining the variational solution of the Schrödinger equation for finite Fermion systems. We consider the Schrödinger equation

$$\psi = E \psi \tag{1}$$

where $\psi$ is in general a non-local, translation invariant, symmetric potential without hard core. This includes the Tabakin-potential $^1$ for nucleons or the Coulomb potential for electrons in an atom; the system under study may be a finite nucleus or the electrons of an atom. The new method is based on a trial function (called correlated wave function) of the form $^2$

$$\psi = \psi_V + \psi_C \tag{2}$$

where $\psi_V$ is the Hartree-Fock (HF) wave function built from the orbitals $\Phi_1, \ldots, \Phi_n$ and

$$\psi_C = \sum_{i<j}^{n} f_{ij}^2 (ij) + \sum_{i<j}^{n} f_{ij}^3 (ij) + \ldots \tag{3}$$

In this finite sum the successive terms represent two-, three-, $\ldots$-particle correlations where e. g.

$$f_{ij}^3 (ij) = A (\Phi_i (1) 2 D_1^3 (i j) 1 2) \tag{4}$$

and $\Phi_i, \Phi_j, \ldots$ are arbitrary, antisymmetric correlation functions, $D_1^3 (i j)$ is the $(A - 2)$ determinant obtained from $\psi_V$ by striking out the rows containing $\Phi_i$ and $\Phi_j$ and the coordinates $1$ and $2$; $A$ is an antisymmetrizer. All properties of $(3)$ along with the matrix components of the Hamiltonian in $(1)$ can be obtained as straightforward generalizations of the Coulomb case developed earlier by one of us. $^3$

We define the HF energy as $E_F = \langle \psi_V | H | \psi_V \rangle$ and the energy of the $n$-particle approximation $E^{(n)} (2 \leq n \leq A)$ as

$$E^{(n)} = \text{Min.} \{ \langle \psi_V | H | \psi_V \rangle / \langle \psi_V | \psi_V \rangle \} \tag{5}$$

where $\psi_V$ contains all terms in $(3)$ up to and including the $n$-particle correlated functions $f_{ij}$. The method consists of computing successively $E_F$, $E^{(2)}, E^{(3)}, \ldots, E^{(A)}$ where the energy at each step, is an upper limit to the true eigenvalue of $(1)$, i.e.

$$E_F > E^{(2)} > E^{(3)} \ldots \ldots > E^{(A)} \geq E \tag{6}$$

Defining the correlation energy of the $n$-particle approximation by $E^{(n)} = E^{(n)} - E^{(n-1)}$ where $2 \leq n \leq A$ and $E^{(1)} = E_F$ we get the variational solution as

$$E_V = E_F + \sum_{n=2}^{A} E^{(n)} \tag{7}$$

In the present note we outline the calculation of $E_F$ and $E^{(2)}$. For $E_F$ the energy minimum principle leads to the HF equations $H \Phi_i = \varepsilon_i \Phi_i$ where $H = H_0 + \sum U_i$ and $U_i$ is the (non-local) HF potential related to $\Phi_i$; the HF energy is given as $E_F = \sum \varepsilon_i - \sum \varepsilon_i j$ where

$$\varepsilon_i j = \langle \Phi_i | U | \Phi_j \rangle \tag{8}$$

The calculation of $E^{(2)}$ is done by using the idea of the independent-pair model $^4$ which was first suggested by Brueckner $^3$, extended and refined by Bethe $^3$, and clearly by Gomes, Walecka and Weisskopf $^3$. We assume that each $\Phi_i j$ can be computed independently, one at a time; in the formula for $E^{(2)}$ however, we do not make any approximations. Let $\varepsilon_i j$ be the correlation energy of one pair. We get the equation for $\Phi_i j$ by varying $\varepsilon_i j$; the results will depend on the subsidiary conditions. It can be shown that the “strong” orthogonality condition $\int \Phi_i^* (1) \Phi_j (2) \mathrm{d}^3 r = 0$ (for $s = 1, 2, \ldots, A; s \neq i, j$) which is called the partial-orthogonality is non-restrictive $^5$. With this condition we get

$$(H_i j + P_{12} O_{12}) \Phi_j = \varepsilon_i j \Phi_i j + (\varepsilon_i j - P_{12} O_{12}) \mu_{ij} \tag{9}$$

where $H_i j \equiv H (1) + H (2) - \varepsilon_i - \varepsilon_j$

and

$$O_{12} \equiv v_{12} - U_1 (1) - U_2 (2) - U_1 (1) + U_2 (2) + \varepsilon_i j \tag{10}$$

For $P_{12}$ we have $P_{12} = P_1 P_2$ where $P_1$ is a projection operator removing the HF orbitals except $\Phi_i$ and $\Phi_j$ and $\mu_{ij} \equiv \text{det} [\Phi_i \Phi_j]$. Using $(5)$ we get for the correlation energy

$$E^{(2)} = \sum_{i<j} (\varepsilon_i j N_{ij} + X_{ij}) / N_{ij}^2 \tag{11}$$

where $N_{ij}$ is the normalization constant if only the pair $(i j)$ is correlated, $N_{ij}$ is the full normalization constant and $X_{ij}$ contains the off-diagonal matrix components of the Hamiltonian with respect to $\Phi_i j$ with different orbital indices. $^6$

A different equation is obtained for $\Phi_i j$ if the slightly restrictive so-called total orthogonality condition

$$\Phi_i (1) | \Phi_j (2) = 0 \tag{12}$$

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II. Three-Particle Correlations and Higher Order Effects

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In the preceding note \(^1\) we outlined a method for obtaining the variational solution of the Schrödinger equation of finite Fermion systems \(^2\). The energy of the system was written in the form \( E_V = E_F + \sum_{n=2} A \tilde{E}^{(n)} \) where \( E_F \) is the Hartree-Fock energy and \( \tilde{E}^{(n)} \) is the correlation energy of the \( n \)-particle approximation (\( 2 \leq n \leq A \)). In the preceding note \(^1\) (referred to as I) we outlined the calculation of \( E_F \) and \( \tilde{E}^{(2)} \). In order to get the 3-rd order correlation energy we minimize the energy of the system using the trial function

\[
\psi = \psi_F + \sum_{i<j<k} f^{(3)}(i j k)
\]

where the notation is the same as in I. This method may be called the method of "independent triplets" \(^3\); the results again depend on the subsidiary conditions. If the 3-particle functions \( \Phi_{ijk} \) satisfy the non-restrictive partial orthogonality condition \(^4\) (strong-orthogonal to all HF orbitals except \( \Phi_i, \Phi_j, \Phi_k \)) we get the equation

\[
[H_{ijk} + P_{123} O_{ijk}] \Phi_{ijk} = \tilde{\epsilon}_{ijk} \Phi_{ijk} + [\tilde{\epsilon}_{ijk} - P_{123} O_{ijk}] \mu_{ijk}
\]

where \( \tilde{\epsilon}_{ijk} \) is the correlation energy of one triplet (relative to \( E_F \)) and the symbols are the logical generalizations of the symbols used in Eq. (5) of I. Using the \( \Phi_{ijk} \)'s computed from (2), one at a time, one gets

\[
\tilde{E}^{(3)} = \sum_{i<j<k} \tilde{\epsilon}_{ijk} N_{ijk} + \chi_3 - \tilde{E}^{(2)} (N_3 - N_2)
\]

where \( N_{ijk} \) is the normalization constant if only the triplet \( (ijk) \) is correlated, \( N_2 \) and \( N_3 \) are the full normalization constants in the two- and three-particle approximations; \( \chi_3 \) contains the off-diagonal matrix components of the Hamiltonian between 2- and 3-particle functions.

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\(^3\) Generalization of the "independent pair" model. See Ref. \(^3\) in I.


If \( \Phi_{ijk} \) in (1) is subjected to the slightly restrictive total orthogonality (strong orthogonal to all HF orbitals) then we obtain an equation similar to (2) but a closer investigation shows that it has only the trivial solutions \( \tilde{\epsilon}_{ijk} = 0 \). Therefore, in the case of total orthogonality the energy has to be minimized with respect to the trial function

\[
\psi = \psi_F + \sum_{i<j} f^{(3)}(ij) + f^{(3)}(ijk)
\]

and we get, assuming that \( \psi_F \) and the \( f^{(3)} \)'s are known from the preceding step the equation for \( \Phi_{ijk} \):

\[
[H_{ijk} + P_{123} O_{ijk}] \Phi_{ijk} = (\tilde{\epsilon}_{ijk} + \tilde{E}^{(2)}) \Phi_{ijk} - P_{123} L_{ijk},
\]

where the symbols are the same as in (2) except the projection operators now remove all HF orbitals; the function \( L_{ijk} \) contains the \( \Phi_{ijk} \)'s which are present in the equation because of (4). Using the \( \Phi_{ijk} \)'s, computed from (5), one at a time, we get

\[
\tilde{E}^{(3)} = \sum_{i<j<k} \tilde{\epsilon}_{ijk} N_{ijk} + \chi_3 - \tilde{E}^{(2)} (N_3 - N_2)
\]

where \( N_{ijk} \) is the normalization constant of (4), \( N_3 \) is the full normalization constant in the three-particle approximation and \( \chi_3 \) contains the off-diagonal matrix components of the Hamiltonian with respect to \( \Phi_{ijk} \)'s with different orbital indices.

Beginning with the 4-particle approximation the correlation function has to be written as the sum of real \( n \)-particle collisions ("linked clusters") plus simultaneous 2-, 3-, etc. particle collisions ("unlinked clusters"). We put \( \Phi_{ijkl} = \Phi_{ijkl}^U + \Phi_{ijkl}^L \) where the first is the "real" 4-particle collision, the second is the product of simultaneous two-particle collisions. By putting \( \Phi^U = 0 \) first, one gets \( \Phi^L \) in the same way as in the 3-particle case; then adding \( \Phi^U \) one gets the complete \( \tilde{E}^{(4)} \). (One can assume that \( \Phi^U \) is built from 2-particle \( \Phi_{ij} \)'s). Using total orthogonality we get

\[
\tilde{E}^{(4)} = \sum_{i<j<k<l} \tilde{\epsilon}_{ijkl} N_{ijkl} + \sum_{i<j<k,l} A_{ijkl}^U + A_{ijkl}^L
\]

\[
+ \chi_4 - \tilde{E}^{(2)} (N_4 - N_3)
\]

where \( \tilde{\epsilon}_{ijkl} \), \( N_{ijkl} \), \( N_4 \) and \( \chi_4 \) are similar to the corresponding symbols in (6); \( A_{ijkl}^U \) and \( X_4 \) are the diagonal elements of the matrix functions.