# 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 SCHROEDINGER equation for finite Fermion systems. We consider the Schroedinger equation

$$\left\{ \sum_{i=1}^{A} t_i + \tfrac{1}{2} \sum_{i<j=1}^{A} v_{ij} \right\} \psi = E\, \psi \tag{1}$$

where $v_{ij}$ 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]

$$\psi = \psi_{\mathrm{F}} + \psi_{\mathrm{C}} \tag{2}$$

where $\psi_{\mathrm{F}}$ is the Hartree-Fock (HF) wave function built from the orbitals $\Phi_1 \dots \Phi_A$ and

$$\psi_{\mathrm{C}} = \sum_{i<j} f^{(2)}(ij) + \sum_{i<j<l} f^{(3)}(ijl) + \dots \qquad \dots f^{(A)}(1, 2, \dots, A). \tag{3}$$

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

$$f^{(2)}(i\,j) = \tilde{A}\,\{\Phi_{ij}(1\,2)\; D^{(A-2)}(i\,j \mid 1\,2)\} \tag{4}$$

and $\Phi_{ij}$, $\Phi_{ijl} \dots$ etc. are arbitrary, antisymmetric correlation functions, $D^{(A-2)}$ is the $(A-2)$ determinant obtained from $\psi_{\mathrm{F}}$ by striking out the rows containing $\Phi_i$ and $\Phi_j$ and the coordinates 1 and 2; $\tilde{A}$ 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[2].

We define the HF energy as $E_{\mathrm{F}} = \langle \psi_{\mathrm{F}} \mid H \mid \psi_{\mathrm{F}} \rangle$ and the energy of the *n-particle approximation* $E^{(n)}$ $(2 \leqq n \leqq A)$ as

$$E^{(n)} = \mathrm{Min.} \{ \langle \psi^{(n)} \mid H \mid \psi^{(n)} \rangle / \langle \psi^{(n)} \mid \psi^{(n)} \rangle \}$$

where $\psi^{(n)}$ contains $\psi_{\mathrm{F}}$ plus all terms in (3) up to and including the $n$-particle correlated functions $f^{(n)}$. The method consist of computing successively $E_{\mathrm{F}}$, $E^{(2)}, E^{(3)}, \dots, E^{(A)}$ where the energy at each step, is an upper limit to the true eigenvalue of (1), i. e.

$$E_{\mathrm{F}} > E^{(2)} > E^{(3)} \dots \quad \dots > E^{(A)} \geqq E\,.$$

Defining the correlation energy of the $n$-particle approximation by $\tilde{E}^{(n)} = E^{(n)} - E^{(n-1)}$ where $2 \leqq n \leqq A$ and $E^{(1)} \equiv E_{\mathrm{F}}$ we get the variational solution as

$$E_{\mathrm{V}} = E_{\mathrm{F}} + \sum_{n=2}^{A} \tilde{E}^{(n)}.$$

In the present note we outline the calculation of $E_{\mathrm{F}}$ and $\tilde{E}^{(2)}$. For $E_{\mathrm{F}}$ the energy minimum principle leads to the HF equations $H_{\mathrm{F}}\, \Phi_i = \varepsilon_i\, \Phi_i$ where $H_{\mathrm{F}} = t + \sum_i U_i$ and $U_i$ is the (non-local) HF potential related to $\Phi_i$; the HF energy is given as $E_{\mathrm{F}} = \sum_i \varepsilon_i - \frac{1}{2} \sum_{ij} \varepsilon_{ij}$ where $\varepsilon_{ij} = \langle \Phi_i \mid U_j \mid \Phi_i \rangle$. The calculation of $\tilde{E}^{(2)}$ is done by using the idea of the independent-pair model[3] which was first suggested bz BRUECKNER[3], extended and refined by BETHE[3], BETHE and GOLDSTONE[3] and most clearly by GOMES, WALECKA and WEISSKOPF[3]. We assume that each $\Phi_{ij}$ can be computed independently, one at a time; in the formula for $\tilde{E}^{(2)}$ however, we do not make any approximations. Let $\bar{\varepsilon}_{ij}$ be the correlation energy of one pair. We get the equation for $\Phi_{ij}$ by varying $\bar{\varepsilon}_{ij}$; the results will depend on the subsidiary conditions. It can be shown that the "strong" orthogonality condition $\int \Phi_s^*(1)\; \Phi_{ij}(1\,2)\; dq_1 = 0$ (for $s = 1, 2, \dots, A;\ s \neq i\,j$) which is called the *partial-orthogonality* is non-restrictive[2]. With this condition we get

$$(H_{ij} + P_{12}\, O_{ij})\; \Phi_{ij} = \bar{\varepsilon}_{ij}\, \Phi_{ij} + (\bar{\varepsilon}_{ij} - P_{12}\, O_{ij})\; \mu_{ij} \tag{5}$$

where

$$H_{ij} \equiv H_{\mathrm{F}}(1) + H_{\mathrm{F}}(2) - \varepsilon_i - \varepsilon_j$$

and

$$O_{ij} \equiv v_{12} - U_i(1) - U_i(2) - U_j(1) - U_j(2) + \varepsilon_{ij}\,.$$

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 $\mu_{ij} \equiv \det[\Phi_i\, \Phi_j]$. Using (5) we get for the correlation energy

$$\tilde{E}^{(2)} = \sum_{i<j} \frac{\bar{\varepsilon}_{ij}\, N_{ij}}{N_2} + \frac{X_2}{N_2}\,, \tag{6}$$

where $N_{ij}$ is the normalization constant if only the pair $(i\,j)$ is correlated, $N_2$ is the full normalization constant and $X_2$ contains the off-diagonal matrix components of the Hamiltonian with respect to $\Phi_{ij}$'s with different orbital indices.

A different equation is obtained for $\Phi_{ij}$ if the slightly restrictive so-called *total orthogonality* condition

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[1] F. TABAKIN, Ann. Phys. (N.Y.) **30**, 51 [1964].

[2] Generalization of a method developed previously for Coulomb forces: L. SZASZ, Z. Naturforsch. **14 a**, 1014 [1959]; **15 a**, 909 [1960]; Phys. Rev. **126**, 169 [1962]; **132**, 936 [1963]; J. Math. Phys. **3**, 1147 [1962].

[3] K. A. BRUECKNER and C. A. LEVINSON, Phys. Rev. **97**, 1344 [1955]; H. A. BETHE, ibid. **103**, 1353 [1956]; J. GOLDSTONE, Proc. Roy. Soc. London **A 239**, 267 [1957]; H. A. BETHE and J. GOLDSTONE, ibid. **A 238**, 551 [1957]; L. C. GOMES, J. D. WALECKA, and W. F. WEISSKOPF, Ann. Phys. (N.Y.) **3**, 241 [1958].

$\int \Phi_s^*(1)\, \Phi_{ij}(1\,2)\, dq_1 = 0$ [for $s = 1, 2, \dots, A$, with $(i\,j)$ included] is introduced[4]. In this case one gets[4]

$$(H_{ij} + P_{12}\, O_{ij})\, \Phi_{ij} = \bar{\varepsilon}_{ij}\, \Phi_{ij} - P_{12}\, O_{ij}\, \mu_{ij} \qquad (7)$$

where the symbols mean the same as in (5) except now $P_1$ removes all HF orbitals. For the correlation energy one gets again an expression like (6) but with slightly different meaning for $N_{ij}$, $N_2$ and $X_2$; the form of $X_2$ is simpler with total orthogonality.

[4] O. Sinanoglu, J. Chem. Phys. **36**, 706, 3198 [1962].

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# The Variational Solution of the Schrödinger Equation of Finite Fermion Systems

## 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 sytems[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 ($2 \leqq n \leqq A$). 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

$$\psi = \psi_F + f^{(3)}(i\,j\,k) \qquad (1)$$

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[2] (strong-orthogonal to all HF orbitals except $\Phi_i$, $\Phi_j$, $\Phi_k$) we get the equation

$$[H_{ijk} + P_{123}\, O_{ijk}]\, \Phi_{ijk} = \bar{\varepsilon}_{ijk}\, \Phi_{ijk} + [\bar{\varepsilon}_{ijk} - P_{123}\, O_{ijk}]\, \mu_{ijk} \qquad (2)$$

where $\bar{\varepsilon}_{ijk}$ 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

$$\tilde{E}^{(3)} = \sum_{i<j<k} \frac{\bar{\varepsilon}_{ijk}\, N_{ijk}}{N_3} + \frac{\chi_3}{N_3} - \tilde{E}^{(2)} \left( \frac{N_3 - N_2}{N_3} \right) \qquad (3)$$

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.

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 $\bar{\varepsilon}_{ijk} = 0$. Therefore, in the case of total orthogonality the energy has to be minimized with respect to the trial function

$$\psi = \psi_F + \sum_{i<j} f^{(2)}(ij) + f^{(3)}(ijk), \qquad (4)$$

and we get, assuming that $\psi_F$ and the $f^{(2)}$'s are known from the preceding step the equation for $\Phi_{ijk}$:

$$[H_{ijk} + P_{123}\, O_{ijk}]\, \Phi_{ijk} = (\bar{\varepsilon}_{ijk} + \tilde{E}^{(2)})\, \Phi_{ijk} - P_{123}\, L_{ijk}, \qquad (5)$$

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

$$\tilde{E}^{(3)} = \sum_{i<j<k} \frac{\bar{\varepsilon}_{ijk}\, N_{ijk}}{N_3} + \frac{\chi_3}{N_3}, \qquad (6)$$

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 $\Phi_{ijkl} = \Phi^{L}_{ijkl} + \Phi^{U}_{ijkl}$ 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

$$\tilde{E}^{(4)} = \sum_{i,j,k,l} \frac{\bar{\varepsilon}_{ijkl}\, N_{ijkl}}{N_4} + \sum_{i,j,k,l} \frac{A^{U}_{ijkl} + A^{U}_{ijkl}}{N_4} + \frac{X^{L}_4 + X^{LU}_4 + X^{U}_4}{N_4}, \qquad (7)$$

where $\bar{\varepsilon}_{ijkl}$, $N_{ijkl}$, $N_4$ and $X^{L}_4$ are similar to the corresponding symbols in (6); $A^{U}_{ijkl}$ and $X^{U}_4$ are the dia-

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[1] L. Szasz and J. Schroeder, Z. Naturforsch. **24 a**, 1855 [1969].

[2] The method is an improved generalization of a theory previously developed for Coulomb forces: L. Szasz, Z. Naturforsch. **14 a**, 1014 [1959]; **15 a**, 909 [1960]; Phys. Rev. **126**, 163 [1962]; **132**, 936 [1963]; J. Math. Phys. **3**, 1147 [1962].

[3] Generalization of the "independent pair" model. See Ref. [3] in I.