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Formulation of the Quantum-Mechanical Many-Body Problem in Terms of One- and Two-Particle Functions

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A self-consistent procedure is presented for the determination of the properties of a many-fermion system, taking into account all two-particle correlations. We consider a system of N fermions, interacting through two-body forces and write the wave function in the form, $\Psi=\Psi_0+\Sigma_{ij} f^{(2)}(ij)$, where Ψ_0 is a determinant of one-particle wave functions and $f^{(2)}(ij)$ is an antisymmetrized product of $(N-2)$ one-particle functions and of one two-particle function. By introducing two-particle functions for each electron pair, all two-particle correlations are taken into account. It is shown that for the best one- and two-particle functions a system of coupled integrodifferential equations can be derived. These equations are derived by varying the expectation value of the Hamiltonian with respect to the one- and two-particle functions, taking into account the normalization and orthogonality as subsidiary conditions. After eliminating the Lagrangian multipliers, we have obtained the following result. We obtained N one-particle equations for the N one-particle wave functions and one-particle orbital parameters. These equations are characterized by a potential (and exchange operator) in which, besides the Hartree-Fock type potential terms, there are also the potentials arising from the two-particle functions, where the latter occur in diagonal, as well as in nondiagonal form. For the two-particle functions and the orbital parameters associated with them, we have obtained two-particle equations in which the equation for the function ϕ_{ij} contains all one-particle functions and all the other two-particle functions. It is shown that the system of coupled one- and two-particle equations can be solved with a self-consistent procedure. The method can be applied to systems with any number of particles.

I. INTRODUCTION

THE first step toward the solution of the quantum-mechanical many-body problem is the independent-particle (or Hartree-Fock) approximation.[1] In this approximation the wave function of the system is written as an antisymmetrized product of one-particle wave functions which means that the correlation between the particles is not taken into account. In order to introduce correlation into the treatment of the quantum-mechanical many-body problem a new theory has been developed by this writer.[2-5] In this "theory of correlated wave functions" the solution of the Schrödinger equation for N-interacting particles is written in the form

$$\Psi=\Psi_0+\sum_{ij} f^{(2)}(ij)+\sum_{ijl} f^{(3)}(ijl)+\cdots+f^{(N)}(1,2,\cdots N). \quad (1.1)$$

Here the first term which represents the independent-particle approximation is a Slater determinant built from the one-particle orbitals $\varphi_1, \varphi_2, \cdots, \varphi_N$:

$$\Psi_0=[\tilde{A}/(N!)^{1/2}]\{\varphi_1(q_1)\varphi_2(q_2)\cdots\varphi_N(q_N)\}, \quad (1.2)$$

where $\tilde{A}$ is the antisymmetrizer operator and q_i stands for the space and spin coordinates of the ith particle. The subsequent terms of (1.1) are introduced in order to take into account the correlation between the particles. This is done in such a way that the correlation effects are decomposed into 2-particle, 3-particle, $\cdots$, n-particle correlations which are represented by the 2nd, 3rd, $\cdots$, nth sums of (1.1), respectively. The function $f^{(2)}(ij)$ occurring in the second term of (1.1) is defined in the following way:

$$\begin{aligned} f^{(2)}(ij) &= [\tilde{A}/(N!)^{1/2}]\{\varphi_1(q_1)\varphi_2(q_2)\cdots\varphi_{i-1}(q_{i-1})\varphi_{i+1}(q_{i+1})\cdots \\ &\quad \times\varphi_{j-1}(q_{j-1})\varphi_{j+1}(q_{j+1})\cdots\varphi_N(q_N)\phi_{ij}(q_iq_j)\}, \quad (1.3)\end{aligned}$$

where $\phi_{ij}(q_1q_2)$ is an arbitrary, antisymmetric *two-particle function*. As we see from (1.2) and (1.3), the 2-particle correlation is introduced into the wave function by replacing the one-particle orbitals φ_i and φ_j by the two-particle function ϕ_{ij}. The second term of (1.1) is a sum for all particle pairs, therefore it contains all 2-particle correlations. The functions $f^{(3)}\cdots f^{(N)}$, which represent higher order correlation effects[6] are defined similarly to $f^{(2)}$.

The summations in the 3rd$\cdots n$th terms of (1.1) are to be taken over all possible 3-particle, $\cdots$, n-particle combinations; therefore, they contain all many-electron correlations.

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[2] L. Szasz, Z. Naturforsch. **14a**, 1014 (1959); **15a**, 909 (1960).

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[4] L. Szasz, J. Math. Phys. **3**, 1147 (1962); Phys. Letters **3**, 263 (1963).

[5] In recent years, considerable attention has been given to the problem of particle correlation in the quantum-mechanical many-body problem. We do not attempt to compare our method with the other methods which have been put forward in recent years. It should be noted, however, that the first attempt to develop a method for the treatment of correlation was made by V. Fock, M. Vesselov, and M. Petrashen [Zh. Eksperim. i Teor. Fiz. **10**, 723 (1940)]. Fock *et al.* have considered an atom with N core electrons and two valence electrons and have written the wave function in such a form that the N-core electrons were represented by a determinantal wave function whereas for the valence electrons a *two-electron function* was introduced, thereby allowing them to take into account the correlation between the two valence electrons. An extensive discussion of this theory may be found also in the first paper of Ref. 2.

[6] We call the function $f^{(n)}$ a correlated wave function of nth order $(2\leqq n\leqq N)$.

For the various approximations which may be obtained from (1.1) we have adapted[3] the following definitions:

(1) The first term of (1.1) is the independent-particle (Hartree-Fock) approximation;

(2) The function

$$\Psi=\Psi_0+\sum_{ij} f^{(2)}(ij)\,, \tag{1.4}$$

in which all two-particle correlations are taken into account, is called the two-particle approximation;

(3) The function

$$\Psi=\Psi_0+\sum_{ij} f^{(2)}(ij)+\cdots+\sum_{ijl\cdots m} f^{(n)}(ijl\cdots m) \tag{1.5}$$

is called the *n*-particle approximation.

The properties of the function (1.1) were investigated in detail[3] and will not be discussed here. We mention only two important facts:

(1) The two-particle approximation (1.4) is equivalent to a superposition of configurations in which all single- and double-substitution configurations are included;

(2) If all terms are included, (1.1) has the form of the exact solution of the Schrödinger equation. This should be understood in the following way: if we expand all many-electron functions in terms of complete sets of Slater determinants, (1.1) becomes identical with the exact solution of the Schrödinger equation.[7]

In the present paper we investigate the two-particle approximation. The importance of this approximation is evident since pair correlations play an important role in several fields of physics, for instance, in the theory of atomic structure,[8] in the theory of nuclear matter,[9] and in the theory of superconductivity.[10] The purpose of the present paper is to determine the equations from which the *best two-particle approximation* may be obtained. As is well known, the best independent-particle approximation may be obtained from the Hartree-Fock equations. Those equations were derived by Fock[1] by varying the expectation value of the energy with respect to the one-particle orbitals which occur in the determinantal wave function Ψ_0. The basic wave function of the two-particle approximation which is given by (1.4) consists of N one-particle functions $\varphi_1, \varphi_2, \cdots, \varphi_N$ (similarly to the Hartree-Fock approximation), but, in addition to these, it contains also $\frac{1}{2}N(N-1)$ two-particle functions $\phi_{12}, \phi_{13}, \cdots, \phi_{N-1,N}$. The equations for the best one- and two-particle functions will be derived by varying the expectation value of the energy with respect to the one- and two-particle functions. It should be emphasized that in the derivation of these equations: (1) No orthogonality condition will be introduced which restricts the generality of the wave function[11]; (2) No term will be neglected in the energy expressions.

In view of the absence of any restrictive conditions the theory presented in this paper may be considered as a model, in which all two-particle correlations are fully included. If we consider the Hartree-Fock approximation as the first step toward the solution of the quantum-mechanical many-body problem, then, since the model presented here is the logical extension of the Hartree-Fock theory, it may be considered as the logical second step toward the exact solution of the many-body problem. The results presented here are valid for any system of fermions which can be described by a Hamiltonian given below [Eq. (2.1)].

II. THE VARIATION PRINCIPLE

We consider a system of N fermions and assume that its Hamiltonian is of the form

$$H=\sum_{i=1}^{N} H_0(i)+\tfrac{1}{2}\sum_{i=1}^{N}\sum_{j=1}^{N} v(ij)\,, \tag{2.1}$$

where $H_0(i)$ is a one-particle operator and $v(ij)$ is the interaction between the ith and jth particle. We assume that $v(ij)=v(ji)$ and that v is not an operator.

We represent the system by the wave function

$$\Psi=\Psi_0+\sum_{i=1}^{N}\sum_{j=i+1}^{N} f^{(2)}(ij)\,, \tag{2.2}$$

in which all two-particle correlations are included. As we see from the definitions of Ψ_0 and $f^{(2)}(ij)$ [Eqs. (1.2) and (1.3)] the wave function (2.2) consist of N one-particle orbitals $\varphi_1\cdots\varphi_N$ and of $\frac{1}{2}N(N-1)$ two-particle functions $\phi_{12}, \phi_{13}, \cdots, \phi_{N-1,N}$. Our goal is to determine the ***best set*** of one- and two-particle wave functions, which is defined as that which brings the energy of the system to a minimum. In order to obtain the equations for the best set we apply the variation principle.

Let us denote the expectation value of the Hamiltonian (2.1) with respect to the wave function (2.2) by A, and the normalization integral by B; then the energy of the system is

$$E=A/B\,. \tag{2.3}$$

The sum of all subsidiary conditions (which must be taken into account when we apply the variation

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[7] The proof is given in Ref. 3, Sec. 2.

[8] According to the recent investigations of L. C. Allen and H. M. Gladney (to be published), the correlation energy of atoms with nuclear charge $Z\leqq 12$ and number of electrons $N\leqq 10$, can be looked upon as arising mostly from *two-electron correlations*.

[9] The investigations of R. D. Puff [Ann. Phys. (N. Y.) **13**, 317 (1961)] on the properties of nuclear matter indicate that the effects of higher order correlations are small compared to the two-particle correlations.

[10] J. Bardeen, L. Cooper, and J. Schrieffer, Phys. Rev. **108**, 1175 (1957).

[11] A general discussion of the orthogonality conditions is given in Ref. 3, Sec. 3.

principle) multiplied by the appropriate Lagrangian multipliers, will be denoted by E_0. According to the basic theorem of the variation calculus, the energy minimum is determined by the equation

$$\delta(E+E_0)=0\,, \tag{2.4}$$

where δ means variation with respect to the one-particle, or with respect to the two-particle functions. Considering (2.3), we obtain from (2.4) that form of the variation principle which will be used in this paper,

$$\delta A-E\delta B+B\delta E_0=0\,. \tag{2.5}$$

III. THE FORMULAS FOR A, B, AND E_0

General formulas for the integrals A and B were given in our previous papers.[12] Our goal now is to write these quantities in such a form that will be convenient for obtaining the variations δA and δB. The quantities A and B are, by definition, given by the formulas[13,14]

$$\begin{aligned}A=&\int\Psi_0^*H\Psi_0dq+\sum_{ij}\int\Psi_0^*Hf(ij)dq\\&+\sum_{ij}\int f^*(ij)H\Psi_0dq+\sum_{ij}\int f^*(ij)Hf(ij)dq\\&+\sum_{ijl}\int f^*(ij)Hf(jl)dq+\sum_{ijkl}\int f^*(ij)Hf(kl)dq\\&\equiv A_1+A_2+A_3+A_4+A_5+A_6\,,\end{aligned} \tag{3.1}$$

$$\begin{aligned}B=&\int\Psi_0^*\Psi_0dq+\sum_{ij}\int\Psi_0^*f(ij)dq\\&+\sum_{ij}\int f^*(ij)\Psi_0dq+\sum_{ij}\int f^*(ij)f(ij)dq\\&+\sum_{ijl}\int f^*(ij)f(jl)dq+\sum_{ijkl}\int f^*(ij)f(kl)dq\\&\equiv B_1+B_2+B_3+B_4+B_5+B_6\,.\end{aligned} \tag{3.2}$$

The formulas for A_i and B_i are derived under the following subsidiary conditions:

(1) The one-particle orbitals are orthonormal:

$$\int\varphi_i^*\varphi_kdq=\delta_{ik}\,,\quad(i,k=1,2,\cdots,N)\,; \tag{3.3}$$

(2) The two-particle functions are normalized:

$$\int|\phi_{ij}|^2dq=1\,,\quad[\text{for all }(ij)\text{ pairs }i,j=1,2,\cdots,N]\,; \tag{3.4}$$

(3) The one-particle and two-particle functions are orthogonal to each other in the following sense:

$$\int\varphi_s^*(1)\phi_{ij}(1,2)dq_1\equiv0\,,\quad[\text{for all }(ij)\text{ pairs }s=1,2,\cdots,\text{N},\ s\neq i,j]\,. \tag{3.5}$$

It is easy to show that none of the above conditions put a restriction on the total wave function (2.2). It is particularly important to realize that the condition (3.5) can be satisfied without restricting the generality of the total wave function. This can be shown in the following way.[15] Let us consider an arbitrary two-particle function ϕ_{ij}^0 and let us consider the *orthogonality projection operator* $\Omega_{ij}(1,2)$ which is defined in the following way:

$$\Omega_{ij}(1,2)\equiv\Omega_{ij}(1)+\Omega_{ij}(2)-\Omega_{ij}(1)\Omega_{ij}(2)\,, \tag{3.6}$$

where

$$\Omega_{ij}(1)f(1)=\sum_{\substack{s=1\\(s\neq ij)}}^{N}\varphi_s(1)\int\varphi_s^*(2)f(2)dq_2\,. \tag{3.7}$$

Let us now consider the orthogonalized two-particle function

$$\phi_{ij}(1,2)=[1-\Omega_{ij}(12)]\phi_{ij}^0(1,2)\,. \tag{3.8}$$

It is easy to see that ϕ_{ij} satisfies the condition (3.5) regardless of the form of ϕ_{ij}^0. Furthermore, it is easy to prove that if we replace an arbitrary two-particle function ϕ_{ij}^0 by the orthogonalized two-particle function ϕ_{ij}, which is defined by (3.8), then *the total wave function $f(ij)$ does not change.* In formula

$$\begin{aligned}f(ij)&=[\tilde{A}/(N!)^{1/2}][\varphi_1(q_1)\cdots\varphi_N(q_N)\phi_{ij}^0(q_iq_j)]\\&=[\tilde{A}/(N!)^{1/2}][\varphi_1(q_1)\cdots\varphi_N(q_N)\phi_{ij}(q_iq_j)]\,.\end{aligned} \tag{3.9}$$

Therefore, we can assume, without restricting the generality of the total wave function $f(ij)$, that the two-particle functions satisfy the orthogonality condition (3.5).

We proceed now to the presentation of the formulas for A and B. Let us introduce first a few notations. Let

$$\mu_{ab}(1,2)\equiv[\varphi_a(1)\varphi_b(2)-\varphi_a(2)\varphi_b(1)]\,, \tag{3.10}$$

$$\phi_{abc}(123)\equiv\tilde{A}[\phi_{ab}(12)\varphi_c(3)]\,, \tag{3.11a}$$

$$\tilde{\phi}_{abc}(123)\equiv\tilde{A}[\varphi_a(1)\phi_{bc}(23)]\,, \tag{3.11b}$$

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[12] They were first given in the second paper of Ref. 2 and may be found also in the first paper of Ref. 4. General formulas involving correlated wave functions of any order were given in Ref. 3.

[13] Here, and throughout the paper the symbol dq indicates integration with respect to *all* coordinates which occur in the integrand of an integral. If the integrand depends on a number of variables, and the integration has to be carried out only with respect to some of them, this will be indicated explicitly, for instance, the symbol dq_{234} means integration with respect to q_2, q_3 and q_4, i.e., $dq_{234}=dq_2dq_3dq_4$.

[14] Since we consider only the two-particle approximation, we have dropped the superscript from the symbol $f(ij)$.

[15] See Sec. 3 of Ref. 3.

$$\phi_{abcd}(1234)\equiv\tilde{A}[\phi_{ab}(12)\mu_{cd}(34)], \tag{3.11c}$$

$$\tilde{\phi}_{abcd}(1234)\equiv\tilde{A}[\mu_{ab}(12)\phi_{cd}(34)], \tag{3.11d}$$

where $\tilde{A}$ is an operator which makes the functions in the square brackets antisymmetric, taking into account that ϕ and u are antisymmetrized already. We introduce the Hartree-Fock type potential function and exchange operator

$$V_s(1)\equiv\int v(1,2)|\varphi_s(2)|^2dq_2, \tag{3.12}$$

$$A_s(1)f(1)\equiv\int v(1,2)\varphi_s(1)\varphi_s^*(2)f(2)dq_2, \tag{3.13}$$

where f is an arbitrary function. Let

$$H_{ijl\cdots m}(1)\equiv H_0(1)+\sum_{\substack{s=1\\(s\neq ijl\cdots m)}}^{N}[V_s(1)-A_s(1)], \tag{3.14}$$

$$H_{ijl\cdots m}(1,2,\cdots n)\equiv\sum_{s=1}^{n}H_{ijl\cdots m}(s)+\tfrac{1}{2}\sum_{s=1}^{n}\sum_{t=1}^{n}v(s,t),\qquad (n=2,3,\cdots N), \tag{3.15}$$

$$\bar{H}_{ijl\cdots m}(1,2,\cdots n)\equiv H_{ijl\cdots m}(1,2,\cdots,n)+\epsilon_{ijl\cdots m}-E,\qquad (n=2,3,\cdots N), \tag{3.16}$$

where

$$\epsilon_{ijl\cdots m}\equiv\sum_{s=1}^{N}T_{ss}+\tfrac{1}{2}\sum_{s=1}^{N}\sum_{t=1}^{N}U_{st},\quad (s,t\neq ijl\cdots m), \tag{3.17}$$

and

$$T_{ab}\equiv\int\varphi_a^*H_0\varphi_bdq, \tag{3.18}$$

$$\begin{aligned}U_{ab}\equiv\int v(1,2)[&|\varphi_b(2)|^2|\varphi_a(1)|^2\\&-\varphi_b(1)\varphi_b^*(2)\varphi_a(2)\varphi_a^*(1)]dq_{12}\\&=\int\varphi_a^*[V_b-A_b]\varphi_adq,\end{aligned} \tag{3.19}$$

and E is the total energy $E=A/B$.

As we see from (2.5) we shall need the quantities A and B in the combination $A-EB$. Therefore, we give the formulas for the integrals A_i-EB_i $(i=1,\cdots 6)$. Taking into account the subsidiary conditions (3.3)–(3.5), we obtain, from the formulas (2.2)–(2.4), (4.5)–(4.7), and (4.11)–(4.13) of the first paper of Ref. 4,

$$A_1-EB_1=\sum_{s=1}^{N}T_{ss}+\tfrac{1}{2}\sum_{s,t=1}^{N}U_{st}-E, \tag{3.20}$$

$$A_2-EB_2=\sum_{ij}\tfrac{1}{2}\int\mu_{ij}^*(12)\bar{H}_{ij}(12)\phi_{ij}(1,2)dq_{12}, \tag{3.21}$$

$$A_3-EB_3=\sum_{ij}\tfrac{1}{2}\int\phi_{ij}^*(12)\bar{H}_{ij}(12)u_{ij}(1,2)dq_{12}, \tag{3.22}$$

$$A_4-EB_4=\sum_{ij}\tfrac{1}{2}\int\phi_{ij}^*(1,2)H_{ij}(12)\phi_{ij}(1,2)dq_{12}+\sum_{ij}\tfrac{1}{2}(\epsilon_{ij}-E), \tag{3.23}$$

$$A_5-EB_5=\sum_{ijl}\tfrac{1}{2}\int\phi_{ij}^*(12)\varphi_l^*(3)\bar{H}_{ijl}(123)\tilde{\phi}_{ijl}(123)dq, \tag{3.24}$$

$$A_6-EB_6=\sum_{ijkl}\tfrac{1}{4}\int\phi_{ij}^*(12)u_{kl}^*(34)\bar{H}_{ijkl}(1234)\times\tilde{\phi}_{ijkl}(1234)dq. \tag{3.25}$$

Our next task will be to express the conditions (3.3)–(3.5) in the form of subsidiary conditions for the variation principle (2.5). In order to do this we introduce the Lagrangian multipliers $-\lambda_{ik}$ and $-E_{ik}/2$ for the conditions (3.3) and (3.4), respectively. Following Fock *et al.*[16] we treat the orthogonality condition (3.5) in such a way that we multiply each of the orthogonality integrals by a Lagrangian multiplier which is a function, and integrate over all space. We must also remember that since the one- and two-particle functions are, in general, complex, we shall have to vary each one- and two-particle function and their complex conjugate independently.[17] This can be done easily in the expressions (3.20)–(3.25) since these contain the functions and their complex conjugate in a symmetrical fashion; the same is true for (3.3) and (3.4). However, (3.5) is not symmetrical in φ_s and φ_s^*; therefore, we shall have to consider also the conjugate complex of Eq. (3.5) as an independent condition. We obtain, therefore,

$$\begin{aligned}E_0=&-\tfrac{1}{2}\sum_{i,k=1}^{N}\lambda_{ik}\int\varphi_i^*\varphi_kdq-\sum_{ik}\frac{E_{ik}}{2}\int|\phi_{ik}|^2dq\\&-\sum_{ij}\sum_{\substack{s=1\\(s\neq ij)}}^{N}\int\lambda_{ijs}^*(2)\varphi_s^*(1)\phi_{ij}(12)dq_{12}\\&-\sum_{ji}\sum_{\substack{s=1\\(s\neq ij)}}^{N}\int\lambda_{ijs}(2)\varphi_s(1)\phi_{ij}^*(1,2)dq_{12},\end{aligned} \tag{3.26}$$

where $\lambda_{ijs}(q)$ is a Lagrangian multiplier. The symbol $\sum_{ij}$ means summation over all particle pairs.

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[16] V. Fock, M. Vesselov, and M. Petrashen, Zh. Eksperim. i Teor. Fiz. **10**, 723 (1940).

[17] See, for instance, E. M. Corson, *Perturbation Methods in the Quantum Mechanics of N-Electron Systems* (Hafner Publishing Company, New York, 1951), p. 132.

IV. THE DERIVATION OF THE EQUATIONS FOR THE ONE-PARTICLE FUNCTIONS

We proceed now to the derivation of the equations for the one-particle functions $\varphi_1, \varphi_2, \cdots, \varphi_N$. The equations will be derived from the variation principle, Eq. (2.5). Let us consider first $\delta A - E\delta B$. We obtain the equation for φ_m $(m=1, \cdots, N)$ by taking the variation with respect to $\varphi_m{}^*$. Denoting the variation with respect to $\varphi_m{}^*$ by $\delta/\delta\varphi_m{}^*$ and the variation of $\varphi_m{}^*$ itself by $\delta\varphi_m{}^*$, we obtain, on the basis of the formulas (3.20)–(3.25),

$$\frac{\delta}{\delta\varphi_m{}^*}A_1 - E\frac{\delta}{\delta\varphi_m{}^*}B_1$$

$$= \int \delta\varphi_m{}^*(1) H_0(1)\varphi_m(1) dq_1$$

$$+ \int \delta\varphi_m{}^*(1) \sum_{s=1}^{N} [V_s(1) - A_s(1)]\varphi_m(1) dq_1, \quad (4.1)$$

$$\frac{\delta}{\delta\varphi_m{}^*}A_2 - E\frac{\delta}{\delta\varphi_m{}^*}B_2$$

$$= \sum_{j\neq m} \int [\delta\varphi_m{}^*(1)]\varphi_j{}^*(2)\bar{H}_{mj}(12)\phi_{ij}(12) dq_{12}$$

$$+ \sum_{ij} \tfrac{1}{2} \int \mu_{ij}{}^*(12)\left[\frac{\delta}{\delta\varphi_m{}^*}\bar{H}_{ij}(12)\right]\phi_{ij}(12) dq_{12}. \quad (4.2)$$

In order to obtain the second term of the above expression we rewrite the whole integral in the following way:

$$\tfrac{1}{2} \int \mu_{ij}{}^*(12)\bar{H}_{ij}(12)\phi_{ij}(12) dq_{12}$$

$$= \int \mu_{ij}{}^*(12)\Big[H_0(1) + \sum_{\substack{s=1\\(s\neq ij)}}^{N} \{V_s(1) - A_s(1)\}$$

$$+ \tfrac{1}{2}v(12) + \tfrac{1}{2}\epsilon_{ij} - \tfrac{1}{2}E\Big]\phi_{ij}(12) dq_{12}. \quad (4.3)$$

We observe that in the square bracket only the sum over s and the ϵ_{ij} depend on $\varphi_m{}^*$. Taking into account (3.12), (3.13), (3.17), (3.18), and (3.19), we obtain

$$\sum_{ij} \tfrac{1}{2} \int u_{ij}{}^*(1,2)\left[\frac{\delta}{\delta\varphi_m{}^*}\bar{H}_{ij}(1,2)\right]\phi_{ij}(1,2) dq$$

$$= \sum_{ij\neq m} \int \mu_{ij}{}^*(12)\frac{\delta}{\delta\varphi_m{}^*}[V_m(1) - A_m(1)]\phi_{ij}(12) dq + \left(\sum_{ij\neq m} \tfrac{1}{2} \int u_{ij}{}^*\phi_{ij} dq\right)\frac{\delta}{\delta\varphi_m{}^*}T_{mm}$$

$$+ \sum_{s=1}^{N} \left(\sum_{ij\neq s,m} \tfrac{1}{2} \int \mu_{ij}{}^*\phi_{ij} dq\right)\frac{\delta}{\delta\varphi_m{}^*}U_{ms}$$

$$= \sum_{ij\neq m} \int \mu_{ij}{}^*(12)v(1,3)[\delta\varphi_m{}^*(3)\varphi_m(3)\phi_{ij}(12) - \delta\varphi_m{}^*(3)\varphi_m(1)\phi_{ij}(32)] dq + \left(\sum_{ij\neq m} \tfrac{1}{2} \int u_{ij}{}^*\phi_{ij} dq\right)$$

$$\times \int \delta\varphi_m{}^*(1)H_0(1)\varphi_m(1) dq_1 + \sum_{s=1}^{N} \left(\sum_{ij\neq s,m} \tfrac{1}{2} \int u^*{}_{ij}\phi_{ij} dq\right) \int \delta\varphi_m{}^*(1)[V_s(1) - A_s(1)]\varphi_m(1) dq_1. \quad (4.4)$$

We obtain similarly

$$\frac{\delta}{\delta\varphi_m{}^*}A_3 - E\frac{\delta}{\delta\varphi_m{}^*}B_3$$

$$= \sum_{ij} \tfrac{1}{2} \int \phi_{ij}{}^*(1,2)\left[\frac{\delta}{\delta\varphi_m{}^*}\bar{H}_{ij}(12)\right]\mu_{ij}(12) dq$$

$$= \sum_{ij\neq m} \int \phi_{ij}{}^*(12)v(13)[\delta\varphi_m{}^*(3)\varphi_m(3)\mu_{ij}(12) - \delta\varphi_m{}^*(3)\varphi_m(1)\mu_{ij}(32)] dq_{123} + \left(\sum_{ij\neq m} \tfrac{1}{2} \int \phi_{ij}{}^*\mu_{ij} dq\right)$$

$$\times \int \delta\varphi_m{}^*(1)H_0(1)\varphi_m(1) dq_1 + \sum_{s=1}^{N} \left(\sum_{ij\neq s,m} \tfrac{1}{2} \int \phi_{ij}\mu^*{}_{ij} dq\right) \int \delta\varphi_m{}^*(1)[V_s(1) - A_s(1)]\varphi_m(1) dq_1, \quad (4.5)$$

$$\frac{\delta}{\delta\varphi_m{}^*}A_4-E\frac{\delta}{\delta\varphi_m{}^*}B_4$$

$$=\sum_{ij}\tfrac{1}{2}\int\phi_{ij}{}^*(12)\left[\frac{\delta}{\delta\varphi_m{}^*}H_{ij}(12)\right]\phi_{ij}(1,2)dq_{12}+\frac{\delta}{\delta\varphi_m{}^*}\sum_{ij}\tfrac{1}{2}\epsilon_{ij}$$

$$=\sum_{ij\neq m}\int\phi_{ij}{}^*(12)v(13)[\delta\varphi_m{}^*(3)\varphi_m(3)\phi_{ij}(1,2)-\delta\varphi_m{}^*(3)\varphi_m(1)\phi_{ij}(32)]dq_{123}+\left(\sum_{ij\neq m}\tfrac{1}{2}\int|\phi_{ij}|^2dq\right)$$

$$\times\int\delta\varphi_m{}^*(1)H_0(1)\varphi_m(1)dq_1+\sum_{s=1}^{N}\left(\sum_{ij\neq s,m}\tfrac{1}{2}\int|\phi_{ij}|^2dq\right)\int\delta\varphi_m{}^*(1)[V_s(1)-A_s(1)]\varphi_m(1)dq_1,\quad(4.6)$$

$$\frac{\delta}{\delta\varphi_m{}^*}A_5-E\frac{\delta}{\delta\varphi_m{}^*}B_5$$

$$=\sum_{ij\neq m}\tfrac{1}{2}\int\phi_{ij}{}^*(12)\delta\varphi_m{}^*(3)\bar{H}_{ijm}(123)\tilde{\phi}_{ijm}(123)dq+\sum_{ijl}\tfrac{1}{2}\int\phi_{ij}{}^*(12)\varphi_l{}^*(3)\left[\frac{\delta}{\delta\varphi_m{}^*}\bar{H}_{ijl}(123)\right]\tilde{\phi}_{ijl}(123)dq_{123}.\quad(4.7)$$

In order to calculate the quantity in the square bracket of (4.7) we recall the definition of $\bar{H}_{ijl}$ given by (3.14)–(3.16). Taking into account that $\bar{H}_{ijl}$ depends on $\varphi_m{}^*$ only through the Hartree-Fock potentials and exchange operators and through ϵ_{ijl}, we obtain

$$\sum_{ijl}\tfrac{1}{2}\int\phi_{ij}{}^*(12)\varphi_l{}^*(3)\left[\frac{\delta}{\delta\varphi_m{}^*}\bar{H}_{ijl}(123)\right]\tilde{\phi}_{ijl}(123)dq$$

$$=\sum_{ijl}\tfrac{1}{2}\int\phi_{ijl}{}^*(123)\frac{\delta}{\delta\varphi_m{}^*}[H_0(1)+\sum_{\substack{s=1\\(s\neq ijl)}}^{N}\{V_s(1)-A_s(1)\}+v(12)]\tilde{\phi}_{ijl}(123)dq_{123}+\sum_{ijl}\frac{1}{3!}\int\phi_{ijl}{}^*\tilde{\phi}_{ijl}dq\frac{\delta}{\delta\varphi_m{}^*}(\epsilon_{ijl}-E)$$

$$=\sum_{ijl\neq m}\tfrac{1}{2}\int\phi_{ijl}{}^*(123)v(14)[\delta\varphi_m{}^*(4)\varphi_m(4)\tilde{\phi}_{ijl}(123)-\delta\varphi_m{}^*(4)\varphi_m(1)\tilde{\phi}_{ijl}(432)]dq+\left(\sum_{ijl\neq m}\frac{1}{3!}\int\phi_{ijl}{}^*\tilde{\phi}_{ijl}dq\right)$$

$$\times\int\delta\varphi_m{}^*(1)H_0(1)\varphi_m(1)dq_1+\sum_{s=1}^{N}\left(\sum_{ijl\neq s,m}\frac{1}{3!}\int\phi_{ijl}{}^*\tilde{\phi}_{ijl}dq\right)\int\delta\varphi_m{}^*(1)[V_s(1)-A_s(1)]\varphi_m(1)dq_1.\quad(4.8)$$

It is evident that we can calculate the variation of A_6-EB_6 in a similar fashion. We obtain with simple manipulations

$$\frac{\delta}{\delta\varphi_m{}^*}A_6-E\frac{\delta}{\delta\varphi_m{}^*}B_6$$

$$=\sum_{ijk\neq m}\tfrac{1}{2}\int\phi_{ij}{}^*(12)\varphi_K{}^*(3)\delta\varphi_m{}^*(4)\bar{H}_{ijkm}(1234)\tilde{\phi}_{ijkm}(1234)dq+\sum_{ijkl\neq m}\tfrac{1}{6}\int\phi_{ijkl}{}^*(1234)v(15)$$

$$\times[\delta\varphi_m{}^*(5)\varphi_m(5)\tilde{\phi}_{ijkl}(1234)-\delta\varphi_m{}^*(5)\varphi_m(1)\tilde{\phi}_{ijkl}(5234)]dq+\left(\sum_{ijkl\neq m}\frac{1}{4!}\int\phi_{ijkl}{}^*\tilde{\phi}_{ijkl}dq\right)$$

$$\times\int\delta\varphi_m{}^*(1)H_0(1)\varphi_m(1)dq_1+\sum_{s=1}^{N}\left(\sum_{ijkl\neq s,m}\frac{1}{4!}\int\phi_{ijkl}{}^*\tilde{\phi}_{ijkl}dq\right)\int\delta\varphi_m{}^*(1)[V_s(1)-A_s(1)]\varphi_m(1)dq_1.\quad(4.9)$$

Having calculated $\delta A-E\delta B$ the quantity which we need for the equation (2.5) is $B\delta E_0$. E_0 is given by (3.26). By forming the quantity $B\delta E_0$ we realize that B is a constant at every stage of the calculations. Therefore, we can incorporate B into the Lagrangian multipliers λ_{ik}, E_{ik}, and $\lambda_{iks}(q)$. In other words, we could eliminate B by defining a new set of Lagrangian multipliers defined as $B\lambda_{ik}$, BE_{ik}, and $B\lambda_{iks}(q)$. In order to keep the notations as simple as possible, we do not introduce new symbols, but simply consider B being incorporated into the Lagrangian multipliers. We obtain this way

$$B\delta E_0=B\frac{\delta}{\delta\varphi_m^*}E_0=-\sum_{k=1}^{N}\frac{\lambda_{mk}}{2}\int\delta\varphi_m^*(1)\varphi_k(1)dq_1-\sum_{ij\neq m}\int\lambda_{ijm}^*(2)\delta\varphi_m^*(1)\phi_{ij}(1,2)dq_{12}. \tag{4.10}$$

We are ready now to write down the equation for the one-particle orbital φ_m. From (4.1), (4.2), (4.5), (4.6), (4.7), (4.9), and (4.10) we obtain, by introducing the notations $E_m\equiv\lambda_{mm}/2$ and $\bar{\lambda}_{mk}\equiv\lambda_{mk}/2$,

$$\frac{\delta}{\delta\varphi_m^*}A-E\frac{\delta}{\delta\varphi_m^*}B+B\frac{\delta}{\delta\varphi_m^*}E_0$$

$$=\int\delta\varphi_m^*(1)\Big[H_m(1)\varphi_m(1)+Z_m(1)-E_m\varphi_m(1)-\sum_{\substack{k=1\\k\neq m}}^{N}\bar{\lambda}_{mk}\varphi_k(1)-\sum_{ij\neq m}\int\lambda_{ijm}^*(2)\phi_{ij}(12)dq_2\Big]dq_1=0, \tag{4.11}$$

where the operators H_m and Z_m will be given below. In the equation above, $\delta\varphi_m^*$ is a completely arbitrary function. Since the integral must be zero for all $\delta\varphi_m^*$, the quantity in the square bracket must be zero. From this we obtain the equation for the one-particle function φ_m,

$$H_m(1)\varphi_m(1)+Z_m(1)=E_m\varphi_m(1)+\sum_{\substack{k=1\\k\neq m}}^{N}\bar{\lambda}_{mk}\varphi_k(1)+\sum_{ij\neq m}\int\lambda_{ijm}^*(2)\phi_{ij}(12)dq_2, \tag{4.12}$$

and, of course, we obtain such an equation for $m=1, 2, \cdots, N$. We can easily verify that the operator H_m may be written in the following form:

$$H_m(1)=S_mH_0(1)+\bar{V}_m(1)-\bar{A}_m(1), \tag{4.13}$$

where S_m will be defined below, $\bar{V}_m(1)$ is a potential, and $\bar{A}_m(1)$ is an exchange operator. They are defined in the following way:

$$\bar{V}_m(1)\equiv\sum_{u=1}^{N}S_{um}V_u(1)+\sum_{ij\neq m}\left\{\int v(13)[\phi_{ij}^*(32)\mu_{ij}(32)+\mu_{ij}^*(32)\phi_{ij}(32)+|\phi_{ij}(32)|^2]dq_{32}\right\}$$
$$+\sum_{ijl\neq m}\tfrac{1}{2}\int v(14)\phi_{ijl}^*(423)\tilde{\phi}_{ijl}(423)dq_{234}+\sum_{ijkl\neq m}\tfrac{1}{6}\int\phi_{ijkl}^*(5234)\tilde{\phi}_{ijkl}(5234)v(15)dq_{2345}, \tag{4.14}$$

and

$$\bar{A}_m(1)f(1)=\sum_{u=1}^{N}S_{um}A_u(1)f(1)+\sum_{ij\neq m}\left\{\int v(13)[\mu_{ij}(12)\phi_{ij}^*(32)+\phi_{ij}(12)\mu_{ij}^*(32)+\phi_{ij}(12)\phi_{ij}^*(32)]f(3)dq_{32}\right\}$$
$$+\sum_{ijl\neq m}\tfrac{1}{2}\int\tilde{\phi}_{ijl}(123)\phi_{ijl}^*(423)v(14)f(4)dq_{234}+\sum_{ijkl\neq m}\tfrac{1}{6}\int\tilde{\phi}_{ijkl}(1234)\phi_{ijkl}^*(5234)v(1.5)f(5)dq_{2345}, \tag{4.15}$$

where V_u and A_u are the Hartree-Fock potential function and exchange operator, respectively [defined by Eqs. (3.12) and (3.13)]. The constants S_m and S_{um} which appear in (4.13), (4.14), and (4.15) are defined by the relationship

$$S_{\alpha\beta\gamma\cdots\rho}\equiv1+\sum_{ij(\neq\alpha,\beta,\cdots,\rho)}\left\{\tfrac{1}{2}\int\phi_{ij}^*\mu_{ij}dq+\tfrac{1}{2}\int\mu_{ij}^*\phi_{ij}dq+\tfrac{1}{2}\int|\phi_{ij}|^2dq\right\}$$
$$+\sum_{ijl(\neq\alpha,\beta,\gamma,\cdots,\rho)}\frac{1}{3!}\int\phi_{ijl}^*\tilde{\phi}_{ijl}dq+\sum_{ijkl(\neq\alpha,\beta,\gamma,\cdots,\rho)}\frac{1}{4!}\int\phi_{ijkl}^*\tilde{\phi}_{ijkl}dq. \tag{4.16}$$

Finally, the function Z_m is given by the formula

$$Z_m(1)=\sum_{j\neq m}\int\varphi_j^*(2)\bar{H}_{mj}(1,2)\phi_{mj}(12)dq_2+\sum_{ij\neq m}\tfrac{1}{2}\int\phi_{ij}^*(32)\bar{H}_{ijm}(321)\tilde{\phi}_{ijm}(321)dq_{23}$$
$$+\sum_{ijk\neq m}\tfrac{1}{2}\int\phi_{ij}^*(42)\varphi_k^*(3)\bar{H}_{ijkm}(4231)\tilde{\phi}_{ijkm}(4231)dq_{234}. \tag{4.17}$$

Having defined all operators in Eq. (4.12), a few remarks are in order about the limits of the summations which appear in the expression above. Double summations like $\sum_{ij}$ are to be taken for all orbital pairs. The triple summation $\sum_{ijl}$ which appears in (4.14) as well as in (4.15), should be carried out as follows. The $\sum_{ij}$ includes all orbital pairs. For each (ij) pair, the summation over l means

$$\sum_{l}=\sum_{l=1}^{N}\ (l\neq ij). \tag{4.18}$$

Finally, $\sum_{ijkl}$ means summation for all (ij) pairs; for each (ij) pair the summation over k and l means summation over all pairs except (ij). If certain indices are excluded from a summation, this is indicated explicitly.

Besides the quantities discussed above, Eq. (4.12) contains also the unknown Lagrangian multipliers $\bar{\lambda}_{mk}$ and $\lambda_{ijm}(q)$. It will be shown below that these can be expressed in terms of the one- and two-particle functions.

V. THE DERIVATION OF THE EQUATIONS FOR THE TWO-PARTICLE FUNCTIONS

Our next task will be the derivation of the equations for the two-particle functions ϕ_{ij}. In the derivation we shall use Eq. (2.5) again, this time taking the variations with respect to the two-particle functions. We obtain the equation for ϕ_{ij} by varying with respect to ϕ_{ij}^*. We denote the variation of a quantity with respect to ϕ_{ij}^* by $\delta/\delta\phi_{ij}^*$ and the variation of ϕ_{ij}^* itself by $\delta\phi_{ij}^*$. From the formulas (3.20)–(3.25), we obtain

$$\frac{\delta}{\delta\phi_{ij}^*}A_1-E\frac{\delta}{\delta\phi_{ij}^*}B_1=\frac{\delta}{\delta\phi_{ij}^*}A_2-E\frac{\delta}{\delta\phi_{ij}^*}B_2=0, \tag{5.1}$$

$$\frac{\delta}{\delta\phi_{ij}^*}A_3-E\frac{\delta}{\delta\phi_{ij}^*}B_3=\tfrac{1}{2}\int\delta\phi_{ij}^*(12)\bar{H}_{ij}(12)\mu_{ij}(12)dq, \tag{5.2}$$

$$\frac{\delta}{\delta\phi_{ij}^*}A_4-E\frac{\delta}{\delta\phi_{ij}^*}B_4=\tfrac{1}{2}\int\delta\phi_{ij}^*(12)H_{ij}(12)\phi_{ij}(12)dq, \tag{5.3}$$

$$\frac{\delta}{\delta\phi_{ij}^*}A_5-E\frac{\delta}{\delta\phi_{ij}^*}B_5=\sum_{l\neq ij}\tfrac{1}{2}\int\delta\phi_{ij}^*(12)\varphi_l^*(3)\bar{H}_{ijl}(123)\tilde{\phi}_{ijl}(123)dq, \tag{5.4}$$

$$\frac{\delta}{\delta\phi_{ij}^*}A_6-E\frac{\delta}{\delta\phi_{ij}^*}B_6=\sum_{kl\neq ij}\tfrac{1}{4}\int\delta\phi_{ij}^*(12)\mu_{kl}^*(34)\bar{H}_{ijkl}(1234)\tilde{\phi}_{ijkl}(1234)dq. \tag{5.5}$$

Next we calculate $B\delta E_0$. Here we treat B again in such a way as we have done in the derivation of the one-particle equations, i.e., we incorporate the constant B into the Lagrangian multipliers. We obtain, by taking the variation with respect to ϕ_{ij}^*,

$$B\frac{\delta}{\delta\phi_{ij}^*}E_0=-\frac{E_{ij}}{2}\int(\delta\phi_{ij}^*)\phi_{ij}dq-\sum_{\substack{s=1\\ s\neq ij}}^{N}\int\lambda_{ijs}(2)\varphi_s(1)\delta\phi_{ij}^*(12)dq. \tag{5.6}$$

As was mentioned above, in the derivation of the expressions (3.21)–(3.25) we have assumed that the two-particle functions are antisymmetric. We can take into account this fact by writing the variation of ϕ_{ij}^* in the form

$$\delta\phi_{ij}^*(12)=\delta\varphi_{ij}^*(12)-\delta\varphi_{ij}^*(21), \tag{5.7}$$

where $\delta\varphi_{ij}^*$ is completely arbitrary. On putting (5.7) into the expressions (5.2)–(5.8), we obtain, for the variation principle (2.5),

$$\frac{\delta}{\delta\phi_{ij}^*}A-E\frac{\delta}{\delta\phi_{ij}^*}B+B\frac{\delta}{\delta\phi_{ij}^*}E_0=\int\delta\varphi_{ij}^*(12)[H_{ij}(12)\phi_{ij}(12)+Z_{ij}(12)-E_{ij}\phi_{ij}(12)$$
$$-\sum_{\substack{s=1\\ (s\neq ij)}}^{N}\{\lambda_{ijs}(2)\varphi_s(1)-\lambda_{ijs}(1)\varphi_s(2)\}]dq_{12}=0, \tag{5.8}$$

where H_{ij} and Z_{ij} are given below. Since $\delta\varphi_{ij}^*$ is an arbitrary function, it follows from the above equation that the quantity in the square bracket must be zero. From this we obtain the equation for ϕ_{ij}

$$H_{ij}(12)\phi_{ij}(12)+Z_{ij}(12)=E_{ij}\phi_{ij}(12)+\sum_{\substack{s=1\\(s\neq ij)}}^{N}[\lambda_{ijs}(2)\varphi_s(1)-\lambda_{ijs}(1)\varphi_s(2)]. \tag{5.9}$$

The operator H_{ij} and the function Z_{ij} are defined as follows:

$$H_{ij}(12)=H_{ij}(1)+H_{ij}(2)+v(12), \tag{5.10}$$

where $H_{ij}(1)$ was given by (3.14); and

$$Z_{ij}(12)=\bar{H}_{ij}(12)\mu_{ij}(12)+\sum_{l\neq ij}\int\varphi_l^*(3)\bar{H}_{ijl}(123)\tilde{\phi}_{ijl}(123)dq_3+\sum_{kl\neq ij}\tfrac{1}{2}\int u_{kl}^*(34)\bar{H}_{ijkl}(1234)\tilde{\phi}_{ijkl}(1234)dq_{34}. \tag{5.11}$$

Similarly to the equation for the one-particle functions, Eq. (5.9) also contains the unknown Lagrangian multipliers $\lambda_{ijs}(q)$. In the next section we shall show how these multipliers can be expressed in terms of the one-particle and two-particle functions.

VI. THE ELIMINATION OF THE LAGRANGIAN MULTIPLIERS

The equation system given by (4.12) and (5.9) contains, besides the one- and two-particle functions, also the unknown Lagrangian multipliers $\bar{\lambda}_{mk}$ and $\lambda_{ijs}(q)$. In this section our goal is to express these multipliers in terms of the one- and two-particle functions. We start with Eq. (5.9). Let us introduce the notation

$$X_{ij}(12)\equiv H_{ij}(12)\phi_{ij}(12)+Z_{ij}(12). \tag{6.1}$$

Let us introduce this quantity into (5.9), multiply the equation from the left by $\varphi_t^*(1)$,[18] and integrate over q_1. Taking into account that φ_t is orthogonal to ϕ_{ij}, we obtain, for $t=s$,

$$\lambda_{ijs}(2)=\int\varphi_s^*(1)X_{ij}(12)dq_1+\sum_{\substack{t=1\\(t\neq ij)}}^{N}\int\lambda_{ijt}(1)\varphi_t(2)\varphi_s^*(1)dq_1. \tag{6.2}$$

Introducing $\Omega_{ij}(1)$ with the definition (3.7) we obtain, by putting (6.2) back into Eq. (5.9),

$$X_{ij}(12)=E_{ij}\phi_{ij}(12)+\Omega_{ij}(1)X_{ij}(12)+\sum_{\substack{t=1\\(t\neq ij)}}^{N}\varphi_t(2)\Omega_{ij}(1)\lambda_{ijt}(1)-\sum_{\substack{s=1\\(s\neq ij)}}^{N}\lambda_{ijs}(1)\varphi_s(2). \tag{6.3}$$

Let us multiply now this equation from the left by $\varphi_u^*(2)$ and integrate over q_2. We obtain, for $u=s$,

$$-\lambda_{ijs}(1)=\int\varphi_s^*(2)X_{ij}(12)dq_2-\int\Omega_{ij}(1)X_{ij}(12)\varphi_s^*(2)dq_2-\Omega_{ij}(1)\lambda_{ijs}(1), \tag{6.4}$$

and putting $-\lambda_{ijs}(1)$, given above, into the last term of Eq. (6.3), we obtain

$$X_{ij}(12)=E_{ij}\phi_{ij}(12)+[\Omega_{ij}(1)+\Omega_{ij}(2)-\Omega_{ij}(1)\Omega_{ij}(2)]X_{ij}(12)=E_{ij}\phi_{ij}(12)+\Omega_{ij}(12)X_{ij}(12), \tag{6.5}$$

where we have used the condensed notation (3.6). The Lagrangian multipliers are eliminated thereby from Eq. (5.9). Instead of (5.9) now we have for the two-electron function the equation (6.5).

We proceed now to eliminate the Lagrangian multipliers from the one-particle equation (4.12). Introducing the notation

$$X_m(1)\equiv H_m(1)\varphi_m(1)+Z_m(1), \tag{6.6}$$

(4.12) takes the form:

$$X_m(1)=E_m\varphi_m(1)+\sum_{k\neq m}\bar{\lambda}_{mk}\varphi_k(1)+\sum_{ij\neq m}\int\lambda_{ijm}^*(2)\phi_{ij}(12)dq_2. \tag{6.7}$$

For $\lambda_{ijm}^*(2)$ we have already derived an expression above. Comparing Eqs. (5.9) and (6.5) we see that

$$\lambda_{ijs}(2)=\int\varphi_s^*(3)X_{ij}(32)dq_3-\tfrac{1}{2}\sum_{\substack{t=1\\(t\neq ij)}}^{N}\varphi_t(2)\int\varphi_s^*(3)\varphi_t^*(4)X_{ij}(34)dq_{34}. \tag{6.8}$$

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[18] $t=1, \cdots, N$, $t\neq ij$.

Putting the complex conjugate of (6.8) into (6.7), we get

$$X_m(1)=E_m\varphi_m(1)+\sum_{k\neq m}\bar{\lambda}_{mk}\varphi_k(1)+\sum_{ij\neq m}\int\phi_{ij}(12)X_{ij}^*(32)\varphi_m(3)dq_{23}. \tag{6.9}$$

Multiplying this equation from the left by $\varphi_t^*(1)$ $(t\neq m)$ and integrating over q_1, we get

$$\bar{\lambda}_{mk}=\int\varphi_k^*(1)X_m(1)dq_1-\sum_{j\neq m,k}\int\varphi_k^*(1)\phi_{ij}(12)X_{ij}^*(32)\varphi_m(3)dq, \tag{6.10}$$

and by putting (6.10) back into (6.9) we obtain

$$X_m(1)=E_m\varphi_m(1)+\sum_{k\neq m}\varphi_k(1)\int\varphi_k^*(3)X_m(3)dq_3-\sum_{k\neq m}\sum_{j\neq m,k}\varphi_k(1)\int\varphi_k^*(3)\phi_{kj}(32)X_{kj}^*(42)\varphi_m(4)dq_{234}$$
$$+\sum_{ij\neq m}\int\phi_{ij}(12)X_{ij}^*(32)\varphi_m(3)dq_{23}. \tag{6.11}$$

Let us introduce the following operators:

$$\omega_s(1)f(1)\equiv\varphi_s(1)\int\varphi_s^*(2)f(2)dq_2, \tag{6.12}$$

$$\bar{\omega}_{st}(1)f(1)\equiv\int\phi_{st}(12)X_{st}^*(32)f(3)dq_{23}. \tag{6.13}$$

Using these notations, (6.11) can be written in the form

$$X_m(1)=E_m\varphi_m(1)+\sum_{K\neq m}\omega_k(1)X_m(1)-\sum_{k\neq m}\sum_{j\neq m,k}\omega_k(1)\bar{\omega}_{kj}(1)\varphi_m(1)+\sum_{ij\neq m}\bar{\omega}_{ij}(1)\varphi_m(1). \tag{6.14}$$

Since this equation contains only the one- and two-particle functions, the elimination of the Lagrangian multipliers is thereby completed.

VII. DISCUSSION

A. Summary of the Results

We have considered an N-particle system with the Hamiltonian (2.1). We have written the approximate wave function of the system in the form

$$\Psi=\Psi_0+\sum_{ij}f^{(2)}(ij), \tag{7.1}$$

which we have called the two-particle approximation because it contains all two-particle correlations. We have investigated how the best two-particle approximation can be obtained. In order to obtain the equations which determine the best two-particle approximation, we have applied the variation principle. By varying the total energy [the expectation value of the Hamiltonian with respect to (7.1)] with respect to the one- and two-particle wave functions, and taking into account the subsidiary conditions we have obtained the following equation system:

$$X_m(1)=E_m\varphi_m(1)+\sum_{\substack{k=1\\(k\neq m)}}^{N}\omega_k(1)X_m(1)$$
$$-\sum_{k\neq m}\sum_{j\neq m,k}\omega_k(1)\bar{\omega}_{kj}(1)\varphi_m(1)$$
$$+\sum_{ij\neq m}\bar{\omega}_{ij}(1)\varphi_m(1),\quad (m=1,2,\cdots N), \tag{7.2}$$

and

$$X_{ij}(12)=E_{ij}\phi_{ij}(1,2)+\Omega_{ij}(12)X_{ij}(12),$$
$$[\text{for all } (ij) \text{ pairs}, i, j=1,2,\cdots,N]. \tag{7.3}$$

We have N equations (7.2) for the one-particle orbitals and the orbital parameters E_1, E_2, $\cdots$, E_N; and we have $\frac{1}{2}N(N-1)$ two-particle equations (7.3) for the two-particle functions ϕ_{12}, ϕ_{13}, $\cdots$, $\phi_{N-1,N}$ and the orbital parameters E_{12}, E_{13}, $\cdots$, $E_{N-1,N}$. Both the one- and two-particle equations contain [in the operators $X_m(1)$ and $X_{ij}(1,2)$] also the total energy E; this is connected with the solutions of the equations through the relationship $E=A/B$ [Eq. (2.3)].

B. Self-Consistent Solution of the Equations

Let us introduce the operators $\tilde{H}_m(1)$, $\tilde{Z}_m(1)$ and $\tilde{H}_{ij}(1,2)$, $\tilde{Z}_{ij}(1,2)$ with the following definitions:

$$\tilde{H}_m\equiv[1-\sum_{\substack{k=1\\(k\neq m)}}^{N}\omega_k]H_m+\sum_{k\neq m}\sum_{j\neq m,k}\omega_k\bar{\omega}_{kj}-\sum_{ij\neq m}\bar{\omega}_{ij}, \tag{7.4}$$

$$\tilde{Z}_m\equiv-[1-\sum_{\substack{k=1\\(k\neq m)}}^{N}\omega_k]Z_m, \tag{7.5}$$

$$\tilde{H}_{ij}\equiv[1-\Omega_{ij}]H_{ij}, \tag{7.6}$$

$$\tilde{Z}_{ij}=-[1-\Omega_{ij}]Z_{ij}. \tag{7.7}$$

Using these notations, the equations (7.2) and (7.3) may be written in the following form:

$$\tilde{H}_m(1)\varphi_m(1)=E_m\varphi_m(1)+\tilde{Z}_m(1),\quad (m=1,2,\cdots N), \tag{7.8}$$

$$\tilde{H}_{ij}(12)\phi_{ij}(12)=E_{ij}\phi_{ij}(12)+\tilde{Z}_{ij}(12),\quad [\text{for all } (ij) \text{ pairs, } i,j=1,2,\cdots,N]. \tag{7.9}$$

This equation system may be solved in the following way. We may start with an orthogonal set of one-particle functions which is chosen on the basis of plausible physical arguments.[19] Let us denote this set by $\boldsymbol{\varphi}_{(1)}$. Then, using $\boldsymbol{\varphi}_{(1)}$ we may calculate two-particle functions ϕ_{ij} *one at a time* for each pair. This is possible, since if we consider only one pair function at a time, (7.9) reduces to

$$\tilde{H}_{ij}(12)\phi_{ij}(12)=E_{ij}\phi_{ij}(12)-\bar{H}_{ij}(12)\mu_{ij}(12)+\Omega_{ij}(12)\bar{H}_{ij}(12)\mu_{ij}(12), \tag{7.10}$$

where the operators depend only on the set $\boldsymbol{\varphi}_{(1)}$. After that, we calculate the set of two-particle functions taking into account *all of them* simultaneously. In other words, we solve the equations (7.9). Let us denote the set of solutions by $\boldsymbol{\Phi}_{(1)}$. Our first approximation is therefore the combined set

$$\boldsymbol{\Psi}_{(1)}\rightarrow(\boldsymbol{\varphi}_{(1)},\boldsymbol{\Phi}_{(1)}). \tag{7.11}$$

Next we form the operators $\tilde{H}_m(1)$ and $\tilde{Z}_m(1)$ with the sets $\boldsymbol{\varphi}_{(1)}$, $\boldsymbol{\Phi}_{(1)}$ and compute from the equations (7.8) a new set of one-particle functions which we denote by $\boldsymbol{\varphi}_{(2)}$. Using these we calculate from the equations (7.9) a new set of two-particle functions, exactly in the same way as we have calculated $\boldsymbol{\Phi}_{(1)}$. We denote the new set of two-particle functions by $\boldsymbol{\Phi}_{(2)}$. At the end of this cycle we shall have the second approximation given by the combined set

$$\boldsymbol{\Psi}_{(2)}\rightarrow(\boldsymbol{\varphi}_{(2)},\boldsymbol{\Phi}_{(2)}). \tag{7.12}$$

We continue this procedure until we find that

$$\boldsymbol{\varphi}_{(n-1)}=\boldsymbol{\varphi}_{(n)},\quad \boldsymbol{\Phi}_{(n-1)}=\boldsymbol{\Phi}_{(n)}, \tag{7.13}$$

in which case our system is self-consistent. By putting $\boldsymbol{\varphi}_{(n)}$ and $\boldsymbol{\Phi}_{(n)}$ into the trial function (7.1), we obtain the wave function of the system including all two-particle correlations. All properties of the system, including the total energy may be computed easily by using the wave function (7.1).

C. General Discussion of the Structure of the Equations

As is well known, the independent-particle (Hartree-Fock) approximation is characterized by the fact that the problem of calculating the wave function for an N-particle system is reducible to the solution of N one-particle equations (the Hartree-Fock equations). In the two-particle approximation, in which we have the wave function (7.1), we must calculate, besides the one-particle functions also two-particle functions; therefore, our task is to solve a set of one-particle equations *and* a set of two-particle equations. The interesting point is, however, that even in this approximation, in which correlation is taken into account, the one-particle aspect of the problem does not disappear; on the contrary, even after we introduced correlation, a part of the problem is still the solution of a set of one-particle equations. *In other words the concept of one-particle orbitals and one-particle orbital energies is not exclusively connected with the independent-particle approximation.* After introducing correlation, we still have the one-particle orbitals and one-particle orbital energies to calculate, but these are not the solutions of the Hartree-Fock equations any more, but the solutions of the more complicated equations (7.8). [It is easy to show that if we neglect the correlation, i.e., if we put all two-particle functions equal to zero, then (7.8) reduces to the Hartree-Fock equations.] The difference between the independent-particle model and the two-particle approximation is that in the two-particle approximation we have to solve, in addition to the set of one-particle equations, also a set of two-particle equations for the functions which represent the correlation.

Another interesting feature of the equations (7.8) is that all terms which occur in the operator H_m except the term containing H_0 may be described as *potentials* and *exchange operators*. In other words, whereas, in the Hartree-Fock approximation, the equations for the one-particle functions are characterized by the presence of the Hartree-Fock potentials (and exchange operators), in the two-particle approximation the equations for the one-particle orbitals are characterized by the presence of the generalized potentials (4.14) and of the generalized exchange operators (4.15). As we see from (4.14) the first term in the generalized potential $\bar{V}_m$ is the Hartree-Fock potential (multiplied by the constant S_{um} which is equal to 1 if there is no correlation). The fact that the other terms are also potentials can be seen easily by replacing the two-particle functions everywhere by the corresponding Slater determinants. For instance, if ϕ_{ij} and ϕ_{jl} are replaced by μ_{ij} and μ_{jl}, respectively, then

$$\tfrac{1}{2}\int\phi_{ijl}{}^{*}(423)\tilde{\phi}_{ijl}(423)v(14)dq_{234}\rightarrow V_i(1)+V_j(1)+V_l(1), \tag{7.14}$$

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[19] It is, in general, a mistake to start with the solutions of the Hartree-Fock equations. This can be seen from the fact that the operators which occur in the equations for the one-particle functions [Eq. (7.8)] are, in general, very different from the Hartree-Fock Hamiltonian operator. We have arrived at this conclusion by investigating the electronic correlation in the Be atom using the approximation presented here [L. Szasz, Phys. Letters **3**, 263 (1963), and to be published]. In other words, the best one-particle functions in the two-particle approximation are, in general, different from the Hartree-Fock one-particle functions to such an extent that it is an extremely poor approximation to start calculations with these.

where the V_i's are the Hartree-Fock potentials defined by (3.12). Also, it is interesting to note that besides the term

$$\int v(13)|\phi_{ij}(32)|^2 dq_{32}, \tag{7.15}$$

which occurs in (4.14) and which may be interpreted as the potential arising from the two-particle functions, the two-particle functions are responsible also for other potential terms which cannot be interpreted in a simple way. In other words if we would like to write down the potential for the one-particle equations intuitively, taking into account the presence of the two-particle functions, we would certainly include (7.15); however, as we see from (4.14) there are also other terms in the potential in which the two-particle and one-particle functions occur in a nonsymmetrical way[20] and which cannot be derived from simple considerations.

D. Concluding Remarks

As was mentioned in the introduction and as it is evident from the derivations, the results presented in this paper can be applied—in principle—to any system of fermions. However, the successful application of the model will depend on whether the equations (7.8) and (7.9) can be solved for a given, particular type of interaction. The practicality of the method has been established for Coulomb interactions, by using the method for the investigation of electronic correlation in the Be atom. Using Hylleraas type functions for the two-particle functions representing the correlation between the two 1s and between the two 2s electrons of the Be atom we have shown that 80% of the correlation can be taken into account by a 10-parameter variational wave function. It is important to note however, that this application is not completely satisfactory, since we have not solved the two-particle equations (7.9) *exactly*. In the case of atoms, the two-particle equation (7.9) is a six-dimensional equation which can be reduced to a three-dimensional equation by separating out the angular part of the two-particle wave functions. However, at the present time, there is no possibility for the exact solution of a three-dimensional equation. In the calculations mentioned above we have written the two-particle functions as simple analytical expressions, containing variational parameters, and calculated these parameters from the energy minimum principle. This procedure however is only a slowly converging approximation to the exact solution of the equations (7.9).

Whether the method can be applied in nuclear physics will depend on whether the equations (7.8) and (7.9) can be solved for the short-range, "hard-core" type interactions. The main problem probably will be the solution of the one-particle equations (7.8). In this case the solution of the two-particle equations (7.9) perhaps may be carried out by introducing as new coordinates the center-of-mass of the two-particles and their relative distance. This way the equations would be reduced to one-dimensional equations. Application of the model to various problems is now being carried out by this writer and the results will be presented in later publications.

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[20] For instance, in the potential containing ϕ_{ijl}^* and $\tilde{\phi}_{ijl}$.