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Atomic Many-Body Problem. I. General Theory of Correlated Wave Functions*

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The purpose of the paper is to present the general theory of atomic wave functions which explicitly depend on the distances between the electrons. The total wave function for the atom will be written as a composition of one-electron spin-orbitals, and 2-electron, 3-electron, $\cdots N$-electron functions, respectively. The wave function has the following properties: (1) It becomes identical with the exact solution of the many-body problem if one expands the many-electron functions in terms of a complete set of Slater determinants; (2) it represents superposition of configurations if one writes the many-electron functions in the form of linear combination of a finite set of determinants; (3) one obtains the generalization of the Hylleraas r_{12}-method introducing the interelectronic distances explicitly into the many-electron functions.

It will be shown that the many-electron functions can be orthogonalized with respect to the one-electron spin-orbitals, without restricting the generality of the total wave function. General formulas for the matrix components of the Hamiltonian with respect to correlated functions will be derived. The approximation containing only 2-electron correlations will be discussed, and it will be pointed out that in this approximation all matrix components can be reduced to 2-electron and 3-electron integrals, respectively; and the calculation of the 3-electron integrals may be simplified by introducing two interelectronic distances as integration variables.

I. INTRODUCTION

It is well known that in the Russell-Saunders approximation the atomic many-body problem may be formulated as follows: We are looking for the solutions of the Schrödinger equation,

$$\mathbf{H}\Psi = E\Psi, \tag{1.1}$$

where $\mathbf{H}$ is the nonrelativistic many-body Hamiltonian,

$$\mathbf{H}=\sum_{i=1}^{N}\left\{-\tfrac{1}{2}\Delta_i-\frac{Z}{r_i}\right\}+\tfrac{1}{2}\sum_{\substack{i=1\\ i\neq j}}^{N}\sum_{j=1}^{N}\frac{1}{r_{ij}}. \tag{1.2}$$

Since the exact solutions of Eq. (1.1) for atoms with more than one electron are not known at the present time, the only way to obtain theoretical information on the properties of complex atoms is to calculate approximate solutions of Eq. (1.1). The most frequently used approximation is the Hartree-Fock method[1] (H-F method). The basic idea of this approximation is to set up the approximate solution as a determinant built from one-electron spin-orbitals (Slater determinant). The application of the energy minimum principle yields the set of H-F equations; the solutions of these equations are the best one-electron spin orbitals.

It is obvious that the H-F wave function is only a modestly good approximation of the actual solution of Eq. (1.1). Because of the presence of the second sum in the Hamiltonian (1.2), the actual solution must depend to a certain degree on the relative position of the electrons and cannot be represented very accurately by a single determinant. A much more powerful approximation than the H-F method is the method of superposition of configurations (S-C method).[2] The basic idea of this method is the following: It is known that the exact solution of Eq. (1.1) can be written as an expansion in terms of a complete set of Slater determinants. This fact in itself does not enable us to calculate the exact solution, because the mathematical treatment of infinite secular problems has not been worked out up to the present time. We can calculate, however, an approximate solution as follows: We choose as our trial function a finite expansion of Slater determinants, chosen from the members of a complete set, and determine the coefficients of the expansion by the energy minimum principle. Our task is then to solve a secular problem of finite order. This procedure will give us a much better approximation of the solutions of Eq. (1.1) than the H-F method, and has the property, that—in principle—the accuracy of the approximation could be improved to any desired extent by adding more and more Slater determinants to the expansion.

Let us consider now the simplest many-body problem, the He atom. The best approximation of the energy eigenvalue computed up to the present time with the S-C method is[3] $E_{\mathrm{SC}}=-2.90343$ au while the exact eigenvalue is[4] $E=-2.90372$ au and the H-F method yields $E_{\mathrm{HF}}=-2.861680$ au.[5] Thus, it is evident that although the S-C method produces a much better energy value than the H-F procedure, if we would rely

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[1] D. R. Hartree, Proc. Cambridge Phil. Soc. **24**, 89, 111 (1928); V. Fock, Z. Physik **61**, 126 (1930); **62**, 795 (1930); J. C. Slater, Phys. Rev. **35**, 210 (1930).

[2] See, for instance, P. O. Löwdin, Phys. Rev. **97**, 1474 (1955), or the article of P. O. Löwdin, in the *Advances in Chemical Physics* (Interscience Publishers Inc., New York, 1959), p. 207.

[3] D. H. Tycho, L. H. Thomas, and K. M. King, Phys. Rev. **109**, 369 (1958).

[4] We suppose, that the energy value computed by Pekeris is equal to the exact eigenvalue. C. L. Pekeris, Phys. Rev. **115**, 1216 (1959).

[5] C. C. J. Roothaan, L. M. Sachs, and A. W. Weiss, Revs. Modern Phys. **32**, 191 (1960).

only upon this method, the capability of the quantum mechanics, to produce an energy value which agrees with the experiment, would not be established even with the simplest many-body problem.

The slow convergence of the S-C approximation was early recognized by Hylleraas.[6] He investigated the He problem and suggested that the wave function should depend explicitly on the distance between the two electrons. This approximation which he suggested (Hy method) has been very successful in the explanation of the properties of two-electron systems; in particular, the computed energy value for the ground state of the He atom agrees completely with the experiment.[4]

If we want to calculate approximate solutions of Eq. (1.1) for atoms with a larger number of electrons, naturally, we should choose that approximation which has been most successful in the case of the He atom. Although that is obviously the Hy method, up to the present time only the H-F and S-C methods have been developed for atoms with arbitrary number of electrons.[7] It is the purpose of the present paper to develop a method for the calculation of approximate solutions of Eq. (1.1) with wave functions of Hylleraas type, for atoms with any number of electrons (the method of correlated wave functions).

The necessity of applying the Hy method for the calculation of wave functions for larger atoms was early recognized by James and Coolidge.[8] James and Coolidge computed a wave function of Hylleraas type for the ground state of the Li atom. Later Fock, Vesselov, and Petrashen investigated how the correlation between the two valence electrons of a larger atom can be taken into account.[9] Jucys extended the theory of Fock *et al.* by discussing atoms with more than two valence electrons.[10] Lennard-Jones, Hurley, and Pople suggested a wave function[11] in which the correlation, between electrons in the same space-orbital but with antiparallel spins could be taken into account. The above theories have this in common: that (1) none of them suggested a wave function with which the correlation between all electrons of the atom could be taken into account; (2) the relationship between the suggested wave functions and the exact solution of Eq. (1.1) was not investigated; and (3) the problem of the calculation of integrals containing more than one interelectronic distances remained open. In addition, Lennard-Jones *et al.* introduced an orthogonality condition, which prevents the use of functions of Hylleraas type.

In a recent paper, a new method for the calculation of Hylleraas-type wave functions has been suggested by the present author.[12] The problem of the calculation of integrals which occur if we use Hylleraas-type wave functions has also been discussed.[13] The theory presented in this paper is a generalization of the approximation suggested in reference 12.

In the next section we begin the discussion by writing the exact solution of Eq. (1.1) as a composition of the H-F function and of single-, double-, $\cdots$, N-fold substituted configurations. On the basis of these considerations we shall suggest a new trial function which consists of one-electron spin orbitals and 2-electron, 3-electron, $\cdots$, N-electron functions, respectively. It will be shown that the new trial function becomes identical with the exact solution of the Schrödinger equation if we expand the 2-electron, 3-electron, $\cdots$, N-electron functions in terms of complete sets of (2×2), (3×3), $\cdots$, $(N\times N)$ Slater determinants, respectively. The generalization of the Hylleraas method will be obtained by introducing the interelectronic distances explicitly into the total wave function. In Sec. 3 we shall discuss orthogonality properties of the correlated wave functions, which are important for the calculation of the matrix components of the Hamiltonian with respect to these functions. In Sec. 4 we shall derive general formulas for the matrix components of the Hamiltonian with respect to arbitrary correlated wave functions. Finally, in Sec. 5 we shall discuss the approximation which we obtain if we include in the total wave function all 2-electron correlations but neglect all correlations of higher order.

2. FORMULATION OF THE METHOD OF CORRELATED WAVE FUNCTIONS

Let us consider an atom with N electrons, and suppose that its wave function may be approximated by a single Slater determinant. We introduce the complete, orthonormal set of one-electron spin orbitals $\varphi_i(q)$ $(i=1, 2, 3, \cdots)$, where q means the space and spin coordinates (x,y,z,σ).[14] We shall call the first N orbitals of the complete set the "basic set." In the H-F approxi-

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[6] E. A. Hylleraas, Z. Physik **48**, 469 (1928); **54**, 347 (1929); **60**, 624 (1930); **63**, 291 (1930); **65**, 209 (1930).

[7] For an extensive review of the H-F method, see J. C. Slater, *Quantum Theory of Atomic Structures*, I-II (McGraw-Hill Book Company, Inc., New York, 1961), particularly Chaps. 9 and 17; also D. R. Hartree, *The Calculation of Atomic Structures* (John Wiley & Sons, Inc., New York, 1957). A list of the publications on the S-C method is given by J. C. Slater, *ibid.*, Appendix 16; see particularly the papers of S. F. Boys *et al.* and A. P. Jucys *et al.*

[8] H. M. James and A. S. Coolidge, Phys. Rev. **49**, 676 (1936).

[9] V. Fock, M. Vesselov, and M. Petrashen, J. Exptl. Theoret. Phys. (U.S.S.R.), **10**, 723 (1940).

[10] A. P. Jucys, J. Exptl. Theoret. Phys. (U.S.S.R.), **23**, 371 (1952).

[11] J. Lennard-Jones, A. C. Hurley, J. A. Pople, Proc. Roy. Soc. (London) **A320**, 446 (1953). See also P. G. Lykos and R. G. Parr, J. Chem. Phys. **24**, 1166 (1956); J. M. Parks and R. G. Parr, J. Chem. Phys. **28**, 335 (1958); R. McWeeny, Proc. Roy. Soc. (London) **A253**, 242 (1959).

[12] L. Szász, Z. Naturforsch. **15a**, 909 (1960).

[13] L. Szász, J. Chem. Phys. **35**, 1072 (1961).

[14] Here and throughout the present paper the single subscript attached to the symbol of the spin-orbital means a set of quantum numbers which characterize the spin-orbital in the H-F approximation. Instead of $\varphi_i(q)$ we shall also use $\varphi_i(q)\equiv\varphi(i|q)$ if the subscript is a complicated symbol. In the argument of φ_i we shall use the condensed notation $\varphi_i(q_k)\equiv\varphi_i(k)$, and also $\varphi(i|q_k)\equiv\varphi(i|k)$.

mation the wave function for the atom may be written as

$$\Psi_F=\frac{1}{(N!)^{\frac{1}{2}}}\begin{vmatrix}\varphi_1(1) & \varphi_1(2) & \cdots & \varphi_1(N)\\ \varphi_2(1) & \varphi_2(2) & \cdots & \varphi_2(N)\\ \vdots & & & \vdots\\ \varphi_N(1) & \varphi_N(2) & \cdots & \varphi_N(N)\end{vmatrix}. \qquad (2.1)$$

The exact solution of the Schrödinger Eq. (1.1) may be written as the expansion[15]

$$\Psi_{\text{exact}}=\sum_{k_1k_2\cdots k_N=1}^{\infty} c(k_1k_2\cdots k_N)\times[\varphi(k_1|1)\varphi(k_2|2)\cdots\varphi(k_N|N)], \qquad (2.2)$$

where the $c(k_1k_2\cdots k_N)$ are expansion coefficients. We rewrite (2.2) as a composition of the H-F function, and single-, double-, $\cdots$ N-fold substituted configurations. By n-fold substituted configuration ($1\leqq n\leqq N$) we refer to a determinant, which may be obtained from (2.1) by replacing the set of n orbitals $\varphi(i|q)$, $\varphi(j|q)\cdots\varphi(m|q)$, by the orbitals $\varphi(k_i|q)$, $\varphi(k_j|q)$, $\cdots$ $\varphi(k_m|q)$, where the latter are chosen from the complete set excluding the basic set. It may be written as

$$\begin{aligned}\mathfrak{F}^{(n)}(k_ik_j\cdots k_m)&=\frac{1}{(N!)^{\frac{1}{2}}}\det[\varphi(1|q_1)\varphi(2|q_2)\cdots\\ &\quad\times\varphi(i-1|q_{i-1})\varphi(k_i|q_i)\varphi(i+1|q_{i+1})\cdots\\ &\quad\times\varphi(j-1|q_{j-1})\varphi(k_j|q_j)\varphi(j+1|q_{j+1})\cdots\\ &\quad\times\varphi(k_m|q_m)\cdots\varphi(N|q_N)],\end{aligned} \qquad (2.3)$$

and (2.2) may be written in the following form:

$$\begin{aligned}\Psi_{\text{exact}}=\Psi_F&+\sum_{i=1}^{N}\sum_{k_i=N+1}^{\infty}c(k_i)\mathfrak{F}^{(1)}(k_i)\\ &+\sum_{i=1}^{N}\sum_{j=i+1}^{N}\frac{1}{2!}\sum_{k_ik_j=N+1}^{\infty}c(k_ik_j)\mathfrak{F}^{(2)}(k_ik_j)+\cdots\\ &+\frac{1}{N!}\sum_{k_1k_2\cdots k_N=N+1}^{\infty}c(k_1k_2\cdots k_N)\\ &\qquad\times\mathfrak{F}^{(N)}(k_1k_2\cdots k_N).\end{aligned} \qquad (2.4)$$

Let us rewrite (2.4) as follows. Consider the Laplace expansion of the determinant (2.3) in terms of the functions $\varphi(k_i|q)$, $\varphi(k_j|q)\cdots\varphi(k_m|q)$, i.e., in terms of the rows of the determinant which contain these functions:

$$\begin{aligned}\mathfrak{F}^{(n)}&(k_ik_j\cdots k_m)\\ &=\frac{1}{(N!)^{\frac{1}{2}}}\sum_{t_1=1}^{N}\sum_{t_2=t_1+1}^{N}\cdots\sum_{t_n=t_{n-1}+1}^{N}\\ &\quad\times(-1)^{i+j+\cdots+m+t_1+t_2+\cdots+t_n}\mu^{(n)}(k_ik_j\cdots k_m|t_1t_2\cdots t_n)\\ &\quad\times D^{(N-n)}(ij\cdots m|t_1t_2\cdots t_n),\end{aligned} \qquad (2.3a)$$

where $\mu^{(n)}$ is given by

$$\mu^{(n)}(k_ik_j\cdots k_m|1,2,\cdots n)\equiv\det[\varphi(k_i|1)\varphi(k_j|2)\cdots\varphi(k_m|n)], \qquad (2.5)$$

and $D^{(N-n)}(ij\cdots m|1,2,\cdots n)$ is an $(N-n)\times(N-n)$ determinant which may be obtained from (2.1) by omitting the rows containing the n functions $(\varphi_i\varphi_j\cdots\varphi_m)$ and the columns containing the n coordinates q_1, $q_2\cdots q_n$. Then (2.4) may be written

$$\begin{aligned}\Psi_{\text{exact}}=\Psi_F&+\frac{1}{(N!)^{\frac{1}{2}}}\sum_{i=1}^{N}\sum_{k_i=N+1}^{\infty}c(k_i)\sum_{t_1=1}^{N}(-1)^{i+t_1}\varphi(k_i|t_1)D^{(N-1)}(i|t_1)\\ &\times\frac{1}{(N!)^{\frac{1}{2}}}\sum_{i=1}^{N}\sum_{j=i+1}^{N}\frac{1}{2!}\sum_{k_ik_j=N+1}^{\infty}c(k_ik_j)\sum_{t_1=1}^{N}\sum_{t_2=t_1+1}^{N}(-1)^{i+j+t_1+t_2}\mu^{(2)}(k_ik_j|t_1t_2)D^{(N-2)}(ij|t_1t_2)+\cdots\\ &+\frac{1}{(N!)^{\frac{1}{2}}}\frac{1}{N!}\sum_{k_1k_2\cdots k_N=N+1}^{\infty}c(k_1k_2\cdots k_N)\mu^{(N)}(k_1k_2\cdots k_N|1,2,\cdots N).\end{aligned} \qquad (2.6)$$

Let us introduce now a new trial function as follows. Let

$$\Phi^{(2)}(ij|q_1q_2),\quad\Phi^{(3)}(ijl|q_1q_2q_3),\quad\cdots\Phi^{(n)}(ijl\cdots m|q_1q_2\cdots q_n)$$

be antisymmetric but otherwise completely arbitrary 2-electron, 3-electron, $\cdots$ n-electron functions ($n\leqq N$). We shall call these functions "correlation functions." In the symbol $\Phi^{(n)}(ijl\cdots m|q_1q_2\cdots q_n)$, the letters $ijl\cdots m$ refer to n sets of quantum numbers which characterize the n-electron function similarly as the single symbol i characterized the one-electron spin-orbital φ_i. The symbols $q_1q_2\cdots q_n$ indicate that the $\Phi^{(n)}$ depends on n set of coordinates $(x_1y_1\cdots z_n\sigma_n)$. Instead of $\Phi^{(n)}(ijl\cdots m|q_1q_2\cdots q_n)$ we shall use also the condensed notation $\Phi^{(n)}(ijl\cdots m|1,2,\cdots n)$. As the basis of the theory of correlated wave functions we suggest the

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[15] See P. O. Löwdin, reference 2.

function

$$\Psi=\Psi_F+\frac{1}{(N!)^{\frac{1}{2}}}\sum_{i=1}^{N}\sum_{j=i+1}^{N}\sum_{t_1=1}^{N}\sum_{t_2=t_1+1}^{N}(-1)^{i+j+t_1+t_2}\Phi^{(2)}(ij\,|\,t_1t_2)D^{(N-2)}(ij\,|\,t_1t_2)$$

$$+\frac{1}{(N!)^{\frac{1}{2}}}\sum_{i=1}^{N}\sum_{j=i+1}^{N}\sum_{l=j+1}^{N}\sum_{t_1=1}^{N}\sum_{t_2=t_1+1}^{N}\sum_{t_3=t_2+1}^{N}(-1)^{i+j+l+t_1+t_2+t_3}\Phi^{(3)}(ijl\,|\,t_1t_2t_3)D^{(N-3)}(ijl\,|\,t_1t_2t_3)+\cdots$$

$$+\frac{1}{(N!)^{\frac{1}{2}}}\Phi^{(N)}(1,2,\cdots N\,|\,1,2,\cdots N), \quad (2.7)$$

where the $D^{(N-2)}$, $D^{(N-3)}$, $\cdots$ have the same meaning as in formula (2.6). Introducing the notation

$$f^{(n)}(ijl\cdots m)$$

$$\equiv\frac{1}{(N!)^{\frac{1}{2}}}\sum_{t_1=1}^{N}\sum_{t_2=t_1+1}^{N}\cdots\sum_{t_n=t_{n-1}+1}^{N}(-1)^{i+j+\cdots+m+t_1+t_2+\cdots+t_n}$$

$$\times\Phi^{(n)}(ijl\cdots m\,|\,t_1t_2\cdots t_n)$$

$$\times D^{(N-n)}(ijl\cdots m\,|\,t_1t_2\cdots t_n), \quad (2.8)$$

the function (2.7) may be written as[16]

$$\Psi=\Psi_F+\sum_{ij}f^{(2)}(ij)+\sum_{ijl}f^{(3)}(ijl)+\cdots$$

$$+f^{(N)}(1,2,\cdots N). \quad (2.9)$$

It is obvious that the function (2.7) becomes identical with the exact solution (2.6) if we expand the correlation functions in terms of determinants built from the complete set φ_i $(i=1, 2, \cdots)$, i.e., if we put[17]

$$\Phi^{(n)}(ij\cdots m\,|\,1,2,\cdots n)$$

$$=\frac{1}{n!}\sum_{k_ik_j\cdots k_m=1}^{\infty}c(k_ik_j\cdots k_m)\mu^{(n)}(k_ik_j\cdots k_m\,|\,1,2,\cdots n),$$

$$(2\leqq n\leqq N). \quad (2.10)$$

We shall call the approximation 1-electron, 2-electron, $\cdots$ n-electron approximation if we consider the functions

$$\Psi^{(1)}\equiv\Psi_F,$$

$$\Psi^{(2)}\equiv\Psi_F+\sum\nolimits_{(ij)}f^{(2)}(ij),$$

$$\cdots \quad (2.11)$$

$$\Psi^{(n)}\equiv\Psi_F+\sum\nolimits_{(ij)}f^{(2)}(ij)+\sum\nolimits_{(ijl)}f^{(3)}(ijl)+\cdots$$

$$+\sum\nolimits_{(ijl\cdots m)}f^{(n)}(ijl\cdots m),$$

where the various approximations may be characterized by saying that in the 1-electron approximation we neglect the correlation between the electrons, while in the 2-electron, 3-electron, $\cdots$ N-electron approximations we can take into account 2-electron, 3-electron, $\cdots$ N-electron correlations, respectively.

Our next task will be to write the trial function (2.7) in a form which will be the generalization of the Hy method. For this purpose we introduce 2-electron, 3-electron, $\cdots$ N-electron correlation factors[18] and we denote the n-electron correlation factor $(2\leqq n\leqq N)$ with respect to the orbitals $(\varphi_i,\varphi_j\cdots\varphi_m)$ by

$$w(ij\cdots m\,|\,\mathbf{r}_1\mathbf{r}_2\cdots\mathbf{r}_n).$$

We introduce these functions into (2.7) putting

$$\Phi^{(n)}(ij\cdots m\,|\,1,2,\cdots n)=\tilde{A}\{\varphi_i(1)\varphi_j(2)\cdots$$

$$\varphi_m(n)[w(ij\cdots m\,|\,\mathbf{r}_1\mathbf{r}_2\cdots\mathbf{r}_n)]\}, \quad (2.12)$$

where $\tilde{A}$ is the total antisymmetrizer operator with respect to the n coordinates. We obtain the direct generalization of the Hy method if we put

$$w(ij\,|\,\mathbf{r}_1\mathbf{r}_2)=w(ij\,|\,r_1,r_2,r_{12}),$$

$$\cdots \quad (2.13)$$

$$w(ij\cdots m\,|\,\mathbf{r}_1\mathbf{r}_2\cdots\mathbf{r}_n)$$

$$=w(ij\cdots m\,|\,r_1,r_2\cdots r_n,r_{12},r_{13},\cdots r_{n-1,\,n}),$$

where r_{12}, $r_{13}\cdots r_{n-1,\,n}$ are the interelectronic distances.

It is easy to see that (2.7) with (2.12) and (2.13) reduces to the Hylleraas function in the case of the ground-state of He atom. Denoting the two spin-orbitals in the ground state of the He by φ_1 and φ_2 we obtain from (2.7) and (2.12):

$$\Psi_{\mathrm{He}}=\frac{1}{(2!)^{\frac{1}{2}}}\tilde{A}\{\varphi_1(q_1)\varphi_2(q_2)[1+w(1,2\,|\,\mathbf{r}_1\mathbf{r}_2)]\}, \quad (2.14)$$

and putting $\varphi_1(q)=e^{-\lambda r}\alpha(\sigma)$, $\varphi_2(q)=e^{-\lambda r}\beta(\sigma)$, where α

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[16] We would like to point out that the function (2.7) is *not* derived from the function (2.6). The considerations which lead to (2.6) were necessary only because we want to show, that if we expand the correlation functions in terms of complete sets of Slater determinants, we obtain the function (2.6) which is identical with the exact solution of the Schrödinger equation (1.1).

[17] The single substituted configurations are included in the expansion of $\Phi^{(2)}(ij\,|\,1,2)$ since, from the limits of the summation over k_i in (2.10), we see that *one* of the orbitals of the determinants $\mu^{(2)}(k_ik_j\,|\,1,2)$ in the expansion may be identical with an orbital of the basic set, i.e., those cases in which $k_i\leqq N$ are included in the expansion.

[18] This is a generalization of the correlation factor suggested by Löwdin [see the papers in reference 2, and also Revs. Modern Phys. **32**, 328 (1960)]. The correlation factor presented here is more general than that suggested by Löwdin in two important respects: (1) It refers to two, three, $\cdots$ N spin-orbitals instead of referring to *all* spin-orbitals simultaneously; and (2) It does not need to be symmetrical in the variables. In other words we introduce different correlation factors for every spin-orbital pair, and not an *average* factor for the whole atom.

and β are the two spin functions, and putting

$$w(1,2|\mathbf{r}_1\mathbf{r}_2)=\sum_{m,n,l} c(m,n,l)(r_1-r_2)^{2m}(r_1+r_2)^n r_{12}{}^l, \qquad (2.15)$$

we get

$$\Psi_{\mathrm{He}}=e^{-\lambda(r_1+r_2)}\{1+\sum_{m,n,l} c(m,n,l)(r_1-r_2)^{2m}(r_1+r_2)^n r_{12}{}^l \times[\alpha(\sigma_1)\beta(\sigma_2)-\alpha(\sigma_2)\beta(\sigma_1)]\}. \qquad (2.16)$$

The wave function (2.7) may be generated also from the Hylleraas He wave function. Let us start with (2.16) and let us write it in the form given by (2.14). If we want to generalize (2.14) for an atom with N electrons, the simplest generalization is to introduce 2-electron correlations, i.e., to put[19]

$$\Psi=\frac{1}{(N!)^{\frac{1}{2}}}\tilde{A}\{\varphi_1(1)\varphi_2(2)\cdots\varphi_N(N) \times[1+\sum_{ij} w(ij|\mathbf{r}_i\mathbf{r}_j)]\}, \qquad (2.17)$$

and if we introduce 3-electron, $\cdots$ N-electron correlations we put

$$\Psi=\frac{1}{(N!)^{\frac{1}{2}}}\tilde{A}\{\varphi_1(1)\varphi_2(2)\cdots\varphi_N(N) \times[1+\sum_{ij} w(ij|\mathbf{r}_i\mathbf{r}_j)+\sum_{ijl} w(ijl|\mathbf{r}_i\mathbf{r}_j\mathbf{r}_l)+\cdots +w(1,2,\cdots N|\mathbf{r}_1\mathbf{r}_2\cdots\mathbf{r}_N)]\}. \qquad (2.18)$$

Reading the Eq. (2.12) from the right to the left, i.e., *defining* $\Phi^{(n)},(2\leqq n\leqq N)$ by this equation, we obtain immediately from (2.18) the function (2.9) or the function (2.7) with

$$\frac{1}{(N!)^{\frac{1}{2}}}\tilde{A}\{\varphi_1(1)\varphi_2(2)\cdots\varphi_N(N)\}=\Psi_F,$$

$$\cdots$$

$$\frac{1}{(N!)^{\frac{1}{2}}}\tilde{A}\{\varphi_1(1)\varphi_2(2)\cdots\varphi_N(N)w(ijl\cdots m|\mathbf{r}_i\mathbf{r}_j\mathbf{r}_l\cdots\mathbf{r}_m)\} =f^{(n)}(ijl\cdots m), \quad (2\leqq n\leqq N). \qquad (2.19)$$

We may formulate now the method of correlated wave functions. As an approximate solution of Eq. (1.1) we suggest the wave function (2.7). This function has the following properties: (1) It becomes identical with the exact solution if we expand the correlation functions in terms of *complete* sets of Slater determinants [formula (2.10)]; (2) It is identical with the S-C expansion if we write the correlation functions as *finite* expansions; and (3) The distances between the electrons may be introduced explicitly by writing the correlation functions in the form given by (2.12) and (2.13). The actual calculations for a particular atom may be carried out as follows: We choose as the basis for the calculations a set of N one-electron orbitals $(\varphi_1\cdots\varphi_N)$ which may be for instance the results of previous H-F calculations. Then we build up correlation functions according to formulas (2.12), (2.13) or we can write some of the correlation functions as the superposition of configurations also. Finally the trial wave function will appear as the linear combination of functions with unknown coefficients. Application of the energy minimum principle with respect to the coefficients yields us the secular equation from which we obtain the approximate energy value of the atom. Having computed the energy value, we obtain easily the approximate solution of the Schrödinger equation (1.1).

Finally we would like to point out that by introducing correlation into the wave function we introduce correlation between the spin-orbitals, rather than between the electrons. Since the total wave function is fully antisymmetric, it does not make sense to say that some particular electron is associated with some particular spin-orbital. The introduction of the correlation function $\Phi^{(2)}(ij|1,2)$ means that we can take into account the correlation between the orbitals φ_i and φ_j but we cannot associate some particular electron pair with the two-electron function $\Phi^{(2)}$.

3. ORTHOGONALITY PROPERTIES

In the H-F approximation it is usual to demand, that the one-electron spin-orbitals should be orthogonal. Although this is not essential from the physical point of view, it makes the form of the energy expression simple. In this section we shall show, that it is possible to introduce for the correlation functions orthogonality conditions, without restricting the generality of the total wave function.

First let us consider the H-F wave function (2.1) and let us assume, that the first $M=N-n$ orbitals are orthonormal but the last n orbitals are normalized but not orthogonal to the first $(N-n)$ orbitals, and they are also nonorthogonal to each other. Let us denote the first $M=N-n$ orbitals by φ_1, φ_2, $\cdots\varphi_M$, and the nonorthogonal orbitals by $\varphi_1{}^0$, $\varphi_2{}^0\cdots\varphi_n{}^0$. Then the H-F function may be written as

$$\Psi_F=\frac{1}{(N!)^{\frac{1}{2}}}\det[\varphi_1(1)\varphi_2(2)\cdots\varphi_M(M)\varphi_1{}^0(M+1) \times\varphi_2{}^0(M+2)\cdots\varphi_n{}^0(N)]. \qquad (3.1)$$

The Laplace expansion in terms of the last n rows, which contain the nonorthogonal orbitals, gives

$$\Psi_F=\frac{1}{(N!)^{\frac{1}{2}}}\sum_{t_1=1}^{N}\sum_{t_2=t_1+1}^{N}\cdots\sum_{t_n=t_{n-1}+1}^{N} \times(-1)^{t_1+t_2+\cdots+t_n+(N-n+1)+\cdots+N} \times\mu^{(n)}(\varphi_1{}^0\varphi_2{}^0\cdots\varphi_n{}^0|t_1t_2\cdots t_n) \times D^{(N-n)}(\varphi_1{}^0\varphi_2{}^0\cdots\varphi_n{}^0|t_1t_2\cdots t_n), \qquad (3.2)$$

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[19] This function was suggested by the author in his thesis [Ludwig-Maximilians University, Munich, 1959 (unpublished)] and the corresponding theory was developed in reference 12.

where $\mu^{(n)}$ is defined by (2.5) and $D^{(N-n)}$ is an $(N-n)\times(N-n)$ determinant built from the orthonormal orbitals $\varphi_1, \varphi_2, \cdots\varphi_M$. Let us now orthogonalize the orbitals $\varphi_1{}^0, \varphi_2{}^0\cdots\varphi_n{}^0$ with respect to $\varphi_1, \varphi_2\cdots\varphi_M$ with Schmidt's procedure. We obtain for the orthogonalized orbitals

$$\bar{\varphi}_k{}^0(q)=\varphi_k{}^0(q)-\sum_{i=1}^{M} c_{ki}\varphi_i(q),$$
$$c_{ki}=\int\varphi_i{}^*(q)\varphi_k{}^0(q)dq, \quad (k=1, 2, \cdots n). \tag{3.3}$$

Equation (3.3) may be written as

$$\bar{\varphi}_k{}^0(q)=[1-\sum_{i=1}^{M}\mathbf{\Omega}_i(q)]\varphi_k{}^0(q), \tag{3.4}$$

where the symbol $\mathbf{\Omega}_i(q)$ means the operator

$$\mathbf{\Omega}_i(q)F(q)=\varphi_i(q)\int\varphi_i{}^*(q')F(q')dq'. \tag{3.5}$$

[$F(q)$ is an arbitrary function.] The substitution $\varphi_k{}^0\rightarrow\bar{\varphi}_k{}^0$ does not change the Slater determinant (3.1), and therefore it is irrelevant as far as the physical situation is concerned. It is useful, however, for the calculation of the energy expression. Let us now substitute the functions $\bar{\varphi}_k{}^0$ into (3.2), i.e., into the determinant $\mu^{(n)}$. Then we obtain

$$\begin{aligned}\bar{\mu}^{(n)}(\bar{\varphi}_1{}^0\bar{\varphi}_2{}^0\cdots\bar{\varphi}_n{}^0|1,2,\cdots n)&\\ \equiv\det[\bar{\varphi}_1{}^0(1)\bar{\varphi}_2{}^0(2)\cdots\bar{\varphi}_n{}^0(n)]&\\ =(\prod_{k=1}^{n}[1-\sum_{i=1}^{M}\mathbf{\Omega}_i(k)])\mu^{(n)}(\varphi_1{}^0\varphi_2{}^0\cdots\varphi_n{}^0|1,2,\cdots n).&\end{aligned} \tag{3.6}$$

We may formulate the meaning of Eq. (3.6) as follows:

Theorem 1. The orthogonalization of the spin-orbitals $\varphi_k{}^0$ $(k=1, \cdots n)$ (occurring in the determinant $\mu^{(n)}$) with respect to the $M=(N-n)$ orbitals $\varphi_1\cdots\varphi_M$ (occurring in the determinant Ψ_F) may be carried out by multiplying the determinant with the operator

$$[1-\mathbf{O}(q_1q_2\cdots q_n)]\equiv\prod_{k=1}^{n}[1-\sum_{i=1}^{M}\mathbf{\Omega}_i(q_k)]. \tag{3.6a}$$

Because the H-F function does not change, if we replace the functions $\varphi_k{}^0$ by $\bar{\varphi}_k{}^0$ we may state:

Theorem 2. The H-F function (3.1) does not change, if we replace $\mu^{(n)}$ by $\bar{\mu}^{(n)}$ where

$$\bar{\mu}^{(n)}=[1-\mathbf{O}]\mu^{(n)}.$$

It is easy to prove the following theorem:

Theorem 3. After the orthogonalization of the one-electron orbitals $\varphi_k{}^0$ $(k=1, 2, \cdots n)$ with respect to the orbitals φ_s $(s=1, 2, \cdots M)$, the determinant $\bar{\mu}^{(n)}$ fulfills the orthogonality condition:

$$\int\bar{\mu}^{(n)}(\bar{\varphi}_1{}^0\bar{\varphi}_2{}^0\cdots\bar{\varphi}_n{}^0|1,2,\cdots n)\varphi_s{}^*(1)dq_1\equiv0, \quad (s=1, 2, \cdots M). \tag{3.7}$$

Proof. Let us consider the Laplace expansion of $\bar{\mu}^{(n)}$ in terms of the members of the first column of the determinant:

$$\bar{\mu}^{(n)}=\sum_{k=1}^{n}(-1)^{1+k}\bar{\varphi}_k{}^0(q_1)\times\bar{\mu}^{(n-1)}(\bar{\varphi}_1{}^0\cdots\bar{\varphi}_{k-1}{}^0\bar{\varphi}_{k+1}{}^0\cdots\bar{\varphi}_n{}^0|q_2q_3\cdots q_n), \tag{3.8}$$

and put this expression into the left side of Eq. (3.7):

$$\int\bar{\mu}^{(n)}\varphi_s{}^*(1)dq_1=\sum_{k=1}^{n}(-1)^{1+k}\int\bar{\varphi}_k{}^0(1)\varphi_s{}^*(1)dq_1\times\bar{\mu}^{(n-1)}(\bar{\varphi}_1{}^0\cdots\bar{\varphi}_n{}^0|2,3,\cdots n), \quad (s=1, 2, \cdots M). \tag{3.9}$$

Because the one-electron orbitals $\bar{\varphi}_k{}^0$ are orthogonal to the orbitals φ_s, we obtain that the expression (3.9) is equal to zero, which proves Theorem 3.

Let us consider now the correlated wave function (2.9):

$$\Psi=\Psi_F+\sum_{ij}f^{(2)}(ij)+\sum_{ijl}f^{(3)}(ijl)+\cdots+f^{(N)}(1,2,\cdots N), \tag{3.10}$$

where the functions $f^{(2)}(ij)$, $f^{(3)}(ijl)\cdots$ are defined by Eq. (2.8), and consider the function

$$f^{(n)}(ij\cdots m)\equiv\frac{1}{(N!)^{\frac{1}{2}}}\sum_{t_1=1}^{N}\sum_{t_2=t_1+1}^{N}\cdots\sum_{t_n=t_{n-1}+1}^{N}(-1)^{i+j+\cdots+m+t_1+\cdots+t_n}\times\Phi^{(n)}(ij\cdots m|t_1t_2\cdots t_n)\times D^{(N-n)}(ij\cdots m|t_1t_2\cdots t_n). \tag{3.11}$$

This function may be generated from (2.1) by taking the Laplace expansion in terms of the rows containing the spin orbitals $\varphi_i, \varphi_j, \cdots\varphi_m$ and replacing in the expansion the $(n\times n)$ determinant built from the orbitals $(\varphi_i, \varphi_j, \cdots\varphi_m)$ by the correlation function $\Phi^{(n)}$. We have seen that the $(n\times n)$ determinants in such an expansion fulfill the condition (3.7). We demand therefore, that after expanding Ψ_F in terms of the rows containing $\varphi_i, \varphi_j, \cdots\varphi_m$, the $(n\times n)$ determinants in the expansion which contain the spin orbitals $\varphi_i\cdots\varphi_m$, should be replaced by a correlation function which fulfills the orthogonality condition:

$$\int \bar{\Phi}^{(n)}(ij\cdots m|1,2,\cdots n)\varphi_s^*(1)dq_1 \equiv 0,$$
$$(s=1,2,\cdots N;\, s\neq ijl\cdots m). \quad (3.12)$$

It is obvious that, in general, the correlation functions will not satisfy the condition (3.12). We shall show, however, that it is always possible to build from an arbitrary correlation function a function which satisfies (3.12). Let $\Phi^{(n)}$ be an arbitrary correlation function which does not fulfill the condition (3.12). Then we can prove easily the following theorem:

Theorem 4. The function

$$\bar{\Phi}^{(n)}(ij\cdots m|1,2,\cdots n)$$
$$=(\prod_{k=1}^{n}[1-\sum_{t=1}^{N}\mathbf{\Omega}_t(k)])\Phi^{(n)}(ij\cdots m|1,2,\cdots n),$$
$$(t\neq ij\cdots m), \quad (3.13)$$

fulfills the condition (3.12) regardless of the form of $\Phi^{(n)}$.

Proof. Put (3.13) into the left side of (3.12); then we obtain

$$\int \bar{\Phi}^{(n)}\varphi_s^*(1)dq_1=\int \varphi_s^*(1)\{[1-\sum_{t=1}^{N}\mathbf{\Omega}_t(1)]$$
$$\times(\prod_{k=2}^{n}[1-\sum_{t=1}^{N}\mathbf{\Omega}_t(k)])\Phi^{(n)}(ij\cdots m|1,2,\cdots n)\}dq_1$$
$$=\int \varphi_s^*(1)[1-\sum_{t=1}^{N}\mathbf{\Omega}_t(1)]\Lambda(1,2,\cdots n)dq_1,$$
$$(s,\, t\neq i,\, j,\, \cdots m), \quad (3.14)$$

where

$$\Lambda\equiv(\prod_{k=2}^{n}[1-\sum_{t=1}^{N}\mathbf{\Omega}_t(k)])\Phi^{(n)}(ij\cdots m|1,2,\cdots n). \quad (3.14a)$$

Taking into account the definition of $\mathbf{\Omega}_t(1)$ [Eq. (3.5)] and the orthonormality of the φ_i, we obtain

$$\int \Phi^{(n)}\varphi_s^*(1)dq_1$$
$$=\int \varphi_s^*(1)\Lambda(1,2,\cdots n)dq_1-\sum_{t=1}^{N}\int \varphi_t(1)\varphi_s^*(1)dq_1$$
$$\times\int \varphi_t^*(q)\Lambda(q,2,\cdots n)dq\equiv 0,$$
$$(s=1,2,\cdots N;\, s,\, t\neq i,\, j,\, \cdots m), \quad (3.15)$$

regardless of the form of Λ, i.e., regardless of the form of $\Phi^{(n)}$. Theorem 4 is therefore proved.

We have seen above that the orthogonalization of the determinant $\mu^{(n)}$ with the aid of the operator $[1-\mathbf{O}]$ has not changed Ψ_F (Theorem 2). We would like to show that a similar theorem holds in the case of the orthogonalization of the function $\Phi^{(n)}$. Let $\Phi^{(n)}$ be an arbitrary correlation function and $\bar{\Phi}^{(n)}$ the orthogonalized function defined by (3.13). Let $f^{(n)}$ be the correlated function containing $\Phi^{(n)}$, and let $\bar{f}^{(n)}$ be the function containing $\bar{\Phi}^{(n)}$, i.e.,

$$f^{(n)}(ij\cdots m)$$
$$\equiv\frac{1}{(N!)^{\frac{1}{2}}}\sum_{t_1<t_2<\cdots<t_n}(-1)^{i+j+\cdots+m+t_1+t_2+\cdots+t_n}$$
$$\times\Phi^{(n)}(ij\cdots m|t_1t_2\cdots t_n)D^{(N-n)}$$
$$\times(ij\cdots m|t_1t_2\cdots t_n), \quad (3.16)$$

$$f^{(n)}(ij\cdots m)$$
$$\equiv\frac{1}{(N!)^{\frac{1}{2}}}\sum_{t_1<t_2<\cdots<t_n}(-1)^{i+j+\cdots+m+t_1+t_2\cdots t_n}$$
$$\times\bar{\Phi}^{(n)}(ij\cdots m|t_1t_2\cdots t_n)D^{(N-n)}$$
$$\times(ij\cdots m|t_1t_2\cdots t_n). \quad (3.17)$$

Theorem 5. $\bar{f}^{(n)}=f^{(n)}$. In other words, the wave function does not change if we replace the arbitrary correlation function $\Phi^{(n)}$ by the function $\bar{\Phi}^{(n)}$, where $\bar{\Phi}^{(n)}=[1-\mathbf{O}]\Phi^{(n)}$.

Proof. For the sake of simplicity let us identify the indices $(i,j,\cdots m)$ with the indices of the last n orbitals in the H-F determinant and let us denote the first $M=(N-n)$ orbitals again by φ_1, φ_2, $\cdots \varphi_M$. The operator $[1-\mathbf{O}]$ may be written in the form of a sum:

$$[1-\mathbf{O}(q_1q_2\cdots q_n)]$$
$$\equiv\prod_{k=1}^{n}[1-\sum_{i=1}^{M}\mathbf{\Omega}_i(k)]=1-\sum_{k=1}^{n}\sum_{i=1}^{M}\mathbf{\Omega}_i(k)$$
$$+\sum_{k=1}^{n}\sum_{l=k+1}^{n}\sum_{i=1}^{M}\sum_{j=1}^{M}\mathbf{\Omega}_i(k)\mathbf{\Omega}_j(l)-\cdots+\cdots. \quad (3.18)$$

In order to prove Theorem 5 we have to show that

$$\sum_{t_1<t_2<\cdots<t_n}(-1)^{A}\mathbf{O}(t_1t_2\cdots t_n)\Phi^{(n)}(t_1t_2\cdots t_n)$$
$$\times D^{(N-n)}(t_1t_2\cdots t_n)\equiv 0, \quad (3.19)$$

where we have dropped in the argument of $\Phi^{(n)}$ and $D^{(N-n)}$ the symbols characterizing the last n orbitals, and $A=t_1+t_2+\cdots+t_n+(N-n+1)+\cdots+N$.

It is obvious that it is enough to show that the contribution from the first sum in (3.18) to the left side of Eq. (3.19) gives zero. In order to show this, let us expand $\Phi^{(n)}$ in terms of the products built up from the complete set φ_i $(i=1,2,\cdots)$:

$$\Phi^{(n)}=\sum_{k_1k_2\cdots k_n=1}^{\infty}c(k_1k_2\cdots k_n)$$
$$\times[\varphi(k_1|1)\varphi(k_2|2)\cdots\varphi(k_n|n)]. \quad (3.20)$$

Multiplying from the left with the operator

$$\sum_{s=1}^{n}\sum_{i=1}^{M}\boldsymbol{\Omega}_i(s),$$

we obtain

$$\sum_{s=1}^{n}\sum_{i=1}^{M}\boldsymbol{\Omega}_i(s)\Phi^{(n)}=\sum_{s=1}^{n}\sum_{k_s=1}^{M}\times\sum_{k_1\cdots k_n=1}^{\infty}{}^{(k_s)}$$

$$\times c(k_1\cdots k_n)[\varphi(k_1|1)\varphi(k_2|2)\cdots\varphi(k_n|n)], \qquad (3.21)$$

where the superscript k_s on the summation sign indicates that the summation over k_s is *excluded.* Multiplication of both sides with the antisymmetry projection operator $[1/(n!)]\sum_P(-1)^pP$, where the summation has to be extended over all permutations of the n coordinates, converts the expression (3.21) into a sum of determinants

$$\sum_{s=1}^{n}\sum_{i=1}^{M}\boldsymbol{\Omega}_i(s)\Phi^{(n)}=\frac{1}{n!}\sum_{s=1}^{n}\sum_{k_s=1}^{M}\times\sum_{k_1\cdots k_n=1}^{\infty}{}^{(k_s)}\;c(k_1k_2\cdots k_n)$$

$$\times\det[\varphi(k_1|1)\varphi(k_2|2)\cdots\varphi(k_s|s)\cdots\varphi(k_n|n)]. \qquad (3.22)$$

With this expression we obtain for the contribution from the first sum in (3.18) to the left side of Eq. (3.19):

$$\sum_{t_1<t_2<\cdots<t_n}(-1)^A\frac{1}{n!}\sum_{s=1}^{n}\sum_{k_s=1}^{M}\times\sum_{k_1k_2\cdots k_n=1}^{\infty}{}^{(k_s)}\;c(k_1k_2\cdots k_n)$$

$$\times\det[\varphi(k_1|t_1)\varphi(k_2|t_2)\cdots\varphi(k_s|t_s)\cdots$$

$$\times\varphi(k_n|t_n)]D^{(N-n)}(t_1t_2\cdots t_n)$$

$$=\frac{1}{n!}\sum_{s=1}^{n}\sum_{k_s=1}^{M}\times\sum_{k_1\cdots k_n=1}^{\infty}{}^{(k_s)}\;c(k_1k_2\cdots k_n)$$

$$\times\det[\varphi(1|1)\varphi(2|2)\cdots\varphi(M|M)$$

$$\times\varphi(k_1|M+1)\varphi(k_2|M+2)\cdots\varphi(k_s|M+s)\cdots$$

$$\times\varphi(k_n|N)]. \qquad (3.23)$$

But this expression is equal to zero, because the orbital $\varphi(k_s|q)$ has to be selected from the orbitals $\varphi_1\cdots\varphi_M$, i.e., two rows of the determinant will become identical. Thus we obtain that the left side of Eq. (3.19) is actually equal to zero, which proves theorem 5.

In their paper Lennard-Jones *et al.*[11] introduced 2-electron functions demanding that they should satisfy the orthogonality condition:

$$\int\psi_\alpha^*(1,2)\psi_\beta(2,3)dq_2\equiv 0. \qquad \text{(a)}$$

Let us suppose that we would like to introduce r_{12} explicitly into ψ_α and ψ_β. It is clear that in this case they will not satisfy the condition (a). From the discussion of this section it is evident, that the condition (a) could be postulated only, if there would exist a generalization of the Schmidt procedure, which would make it possible to orthogonalize 2-electron functions with respect to each other, in the sense of Eq. (a). The equation (a) can be of course satisfied if ψ_α and ψ_β are products of one-electron functions. We can characterize Eq. (a) by saying that it prevents the use of Hylleraas-type functions and so restricts the generality of the wave function seriously.

On the basis of the results of this section, we shall demand throughout this paper that in the wave function (2.7) the one-electron orbitals should be orthonormal:

$$\int\varphi_i^*(q)\varphi_k(q)dq=\delta_{ik}, \qquad (3.24)$$

and the correlation functions should satisfy the orthogonality condition:

$$\int\bar{\Phi}^{(n)}(ij\cdots m|1,2,\cdots n)\varphi_s^*(1)dq_1\equiv 0,$$

$$(s\neq i,j\cdots m). \qquad (3.25)$$

It is always possible to construct one-electron orbitals which fulfill the condition (3.24). Starting with an arbitrary correlation function $\Phi^{(n)}$, we can always build up a function $\bar{\Phi}^{(n)}$ which fulfills the condition (3.25), by means of the operator $[1-\mathbf{O}]$:

$$\bar{\Phi}^{(n)}(ij\cdots m|1,2,\cdots n)$$

$$=[1-\mathbf{O}]\Phi^{(n)}(ij\cdots m|1,2,\cdots n)$$

$$=\Big(\prod_{k=1}^{n}[1-\sum_{t=1}^{N}\boldsymbol{\Omega}_t(k)]\Big)\Phi^{(n)}(ij\cdots m|1,2,\cdots n),$$

$$(t\neq i,j,\cdots m), \qquad (3.26)$$

and it is established that the orthogonalization does not restrict the full generality of the wave function (2.7).

4. MATRIX COMPONENTS OF THE HAMILTONIAN WITH RESPECT TO CORRELATED WAVE FUNCTIONS

In this section we are interested in the formulas for the matrix components of the Hamiltonian (1.2) with respect to the correlated function (2.7). All matrix components which occur can be derived from a formula given by Jucys,[10] which we now state. Let

$$\Phi_A(k_1k_2\cdots k_n|q_1q_2\cdots q_n)\quad\text{and}\quad\Phi_B(k_1k_2\cdots k_n|q_1q_2\cdots q_n)$$

be n-electron functions, where $(k_1k_2\cdots k_n)$ is an arbitrary selection of n indices from the indices of the basic set $\varphi_1\varphi_2\cdots\varphi_N$, and we assume that Φ_A and Φ_B fulfill the following conditions:

(1) They are antisymmetric:

$$P_{ik}\Phi_A=-\Phi_A,\quad P_{ik}\Phi_B=-\Phi_B, \qquad (4.1)$$

where P_{ik} is the operator exchanging q_i and q_k, and q_i and q_k are any two coordinates of Φ_A and Φ_B.

(2) They fulfill the orthogonality conditions:

$$\begin{gathered}\int \Phi_A(k_1k_2\cdots k_n|1,2,\cdots n)\varphi_s^*(1)dq_1\equiv 0,\\ \int \Phi_B(k_1k_2\cdots k_n|1,2,\cdots n)\varphi_s^*(1)dq_1\equiv 0,\\ (s=1,\,2,\,\cdots N;\, s\neq k_1k_2\cdots k_n).\end{gathered}\tag{4.2}$$

Consider the eigenfunctions

$$f_A\equiv\frac{1}{(N!)^{\frac{1}{2}}}\sum_{t_1<t_2<\cdots<t_n}(-1)^{k_1+k_2+\cdots+k_n+t_1+t_2+\cdots+t_n}\times\Phi_A(k_1\cdots k_n|t_1\cdots t_n)\times D^{(N-n)}(k_1\cdots k_n|t_1\cdots t_n),\tag{4.3}$$

$$f_B\equiv\frac{1}{(N!)^{\frac{1}{2}}}\sum_{t_1<t_2<\cdots<t_n}(-1)^{k_1+k_2+\cdots+k_n+t_1+t_2+\cdots+t_n}\times\Phi_A(k_1\cdots k_n|t_1\cdots t_n)\times D^{(N-n)}(k_1\cdots k_n|t_1\cdots t_n).\tag{4.4}$$

Obviously f_A and f_B may be generated from the H-F function (2.1) by taking the Laplace expansion of Ψ_F in terms of the n rows which contain the n spin-orbitals $\varphi(k_1|q)\cdots\varphi(k_n|q)$ and replacing the $(n\times n)$ determinant built from these n spin-orbitals by Φ_A and Φ_B, respectively. Denoting the one-electron part of the Hamiltonian (1.2) by $\sum(i)\mathbf{H}_i$, we obtain according to Jucys[10]:

$$\int f_A^*[\sum_{i=1}^{N}\mathbf{H}_i]f_B dq_N=\frac{1}{(n-1)!}\int\Phi_A^*(k_1\cdots k_n|1,2,\cdots n)\mathbf{H}_1\Phi_B(k_1\cdots k_n|1,2,\cdots n)dq_n +\frac{1}{n!}\int\Phi_A^*\Phi_B dq_n\times\left\{\sum_{s=1}^{n}\int\varphi_s^*(1)\mathbf{H}_1\varphi_s(1)dq_1\right\},\tag{4.5}$$

$$\cdots$$

$$\begin{aligned}\int f_A^*\left[\frac{1}{2}\sum_{ij}\frac{1}{r_{ij}}\right]f_B dq_N=&\frac{1}{2(n-2)!}\int\Phi_A^*(k_1\cdots k_n|1,2,\cdots n)\frac{1}{r_{12}}\Phi_B(k_1\cdots k_n|1,2,\cdots n)dq_n\\ &+\frac{1}{(n-1)!}\int\sum_{s=1}^{N}|\varphi_s(2)|^2\frac{1}{r_{12}}\Phi_A^*(k_1\cdots k_n|1,3,\cdots n+1)\Phi_B(k_1\cdots k_n|1,3,\cdots n+1)dq_{n+1}\\ &-\frac{1}{(n-1)!}\int\sum_{s=1}^{N}\varphi_s(1)\varphi_s^*(2)\frac{1}{r_{12}}\Phi_A^*(k_1\cdots k_n|1,3,\cdots n+1)\Phi_B(k_1\cdots k_n|2,3,\cdots n+1)dq_{n+1}\\ &+\frac{1}{n!}\int\Phi_A^*\Phi_B dq_n\times\left\{\frac{1}{2}\sum_{\substack{s=1\\(s\neq t)}}^{N}\sum_{t=1}^{N}\frac{|\varphi_s(1)|^2|\varphi_t(2)|^2-\varphi_s(1)\varphi_s^*(2)\varphi_t^*(1)\varphi_t(2)}{r_{12}}dq_2\right\},\quad (s,\,t\neq k_1k_2\cdots k_n).\end{aligned}\tag{4.6}$$

$$\int f_A^*f_B dq_N=\frac{1}{n!}\int\Phi_A^*\Phi_B dq_n.\tag{4.7}$$

In the formulas above $dq_m\equiv dq_1dq_2dq_3\cdots dq_m$, and $1\leqq m\leqq N$.

4a. Diagonal Matrix Components

We want a formula for the diagonal matrix component of the Hamiltonian with respect to the correlated wave function (2.8):

$$f^{(n)}(ij\cdots m)=\frac{1}{(N!)^{\frac{1}{2}}}\sum_{t_1<t_2<\cdots<t_n}(-1)^{i+j+\cdots+m+t_1+\cdots+t_n}\times\Phi^{(n)}(ij\cdots m|t_1t_2\cdots t_n)D^{(N-n)}(ij\cdots m|t_1t_2\cdots t_n).\tag{4.8}$$

The function $\Phi^{(n)}$ may have the form given by (2.12) and (2.13), i.e., it can depend explicitly on the distances between the electrons $r_{12}, r_{13}, \cdots, r_{n-1,n}$. In order to bring (4.8) into the form of (4.3), we utilize the results of the previous section. We have seen that

$$\Phi^{(n)}(ij\cdots m|1,2,\cdots n)$$

can be orthogonalized with respect to the orbitals φ_s $(s=1,\,2,\,\cdots N;\, s\neq i,\,j,\,\cdots m)$ by means of the operator $[1-\mathbf{O}]$ and the orthogonalization does not change the function $f^{(n)}(ij\cdots m)$. We put, therefore,

$$\bar{\Phi}^{(n)}(ij\cdots m|1,2,\cdots n)=(\prod_{k=1}^{n}[1-\sum_{t=1}^{N}\mathbf{\Omega}_t(k)])\Phi^{(n)}(ij\cdots m|1,2,\cdots n),\quad (t\neq ij\cdots m),\tag{4.9}$$

and now $\bar{\Phi}^{(n)}$ fulfills the condition (4.2) which is required for the function Φ_A to satisfy, and after replacing in (4.8) $\Phi^{(n)}$ by $\bar{\Phi}^{(n)}$, $\bar{f}^{(n)}$ will have the same form as f_A in (4.3).

We obtain, therefore, the diagonal matrix component with respect to $f^{(n)}(ij\cdots m)$ *from the formulas (4.5)–(4.7) by putting*

$$\Phi_A \equiv \Phi_B = \bar{\Phi}^{(n)}(ij\cdots m|1,2,\cdots n), \qquad (4.10)$$

where $\bar{\Phi}^{(n)}(ij\cdots m|1,2,\cdots n)$ *is defined by (4.9).* The symbols $(k_1,k_2,\cdots,k_n)$ in the formulas (4.5)–(4.7) are identical with the indices of the correlation function $\bar{\Phi}^{(n)}(ij\cdots m|1,2,\cdots n)$, i.e., $k_1\equiv i$, $k_2\equiv j$, $\cdots k_n\equiv m$.

4b. Off-Diagonal Matrix Components

Matrix components of this type can occur if we want a formula for the integral with respect to correlated functions of the same order [by "the order of $f^{(n)}(ij\cdots m)$" we refer to the number n] but referring to two different sets of orbitals [e.g., $f^{(3)}(ijl)$ and $f^{(3)}(kmn)$], or if we calculate the matrix component with respect to correlated functions of different order [e.g., $f^{(2)}(ij)$ and $f^{(4)}(ijmn)$]. Both cases can be treated as follows. Suppose we want a formula for the matrix component with respect to a correlated function where the orbitals $\varphi(a_1|q)$, $\varphi(a_2|q)\cdots\varphi(a_s|q)$ are "correlated" and a function where the orbitals $\varphi(b_1|q)$, $\varphi(b_2|q)\cdots\varphi(b_t|q)$ are "correlated," i.e., we consider the matrix component with respect to the functions $f^{(s)}(a_1\cdots a_s)$ and $f^{(t)}(b_1\cdots b_t)$, where among the members of the two sets a_i and b_j some might be identical. Let us consider the combined set k_1, k_2, $\cdots k_n$ which is built from the two sets $(a_1\cdots a_s)$ and $(b_1\cdots b_t)$ in such a way that those indices which appear in both subsets appear in the combined set only once. For instance, if the first set is $(ijlm)$ and the second is (jku), the combined set is $(ijlmku)$. We suppose that the order of the indices in the two subsets, as well as in the combined set, is the same as in the function Ψ_F. Evidently $n\leqq s+t$. Let us consider the Laplace expansion of the H-F function (2.1) in terms of the rows which contain the functions of the combined set, i.e., in terms of the rows which contain the functions $\varphi(k_1|q)$, $\varphi(k_2|q)$, $\cdots\varphi(k_n|q)$:

$$\Psi_F = \frac{1}{(N!)^{\frac{1}{2}}} \sum_{t_1<t_2<\cdots<t_n} (-1)^{k_1+k_2+\cdots+k_n+t_1+t_2+\cdots+t_n} \times \mu^{(n)}(k_1\cdots k_n|t_1\cdots t_n) \times D^{(N-n)}(k_1\cdots k_n|t_1\cdots t_n). \qquad (4.11)$$

We can obtain both $f^{(s)}(a_1\cdots a_s)$ and $f^{(t)}(b_1\cdots b_t)$ from (4.11) as follows. We expand $\mu^{(n)}(k_1\cdots k_n|1,2,\cdots n)$ first in terms of the rows containing the orbitals $\varphi(a_1|q)$, $\cdots\varphi(a_s|q)$:

$$\mu^{(n)}(k_1\cdots k_n|1,2,\cdots n) = \sum_{u_1<u_2<\cdots<u_s} (-1)^{\alpha_1+\alpha_2+\cdots+\alpha_s+u_1+u_2+\cdots+u_s} \times \mu^{(s)}(a_1\cdots a_s|u_1\cdots u_s) \times d^{(n-s)}(a_1\cdots a_s|u_1\cdots u_s), \qquad (4.12)$$

where $d^{(n-s)}(a_1\cdots a_s|u_1\cdots u_s)$ is an $(n-s)\times(n-s)$ determinant which may be obtained from $\mu^{(n)}$ by dropping the rows containing $\varphi(a_1|q)$, $\varphi(a_2|q)$, $\cdots\varphi(a_s|q)$ and the columns containing q_1, q_2, $\cdots q_s$; and where α_1, α_2, $\cdots\alpha_s$ are the numbers characterizing the positions of the rows containing $\varphi(a_1|q)$, $\varphi(a_2|q)$, $\cdots\varphi(a_s|q)$ in $\mu^{(n)}$. Let us replace $\mu^{(s)}$ in (4.12) by the correlation function $\Phi^{(s)}$, and let us denote the resulting function by $\tilde{\mu}^{(n)}$, i.e.,

$$\tilde{\mu}^{(n)}(k_1\cdots k_n|1,2,\cdots n) \equiv \sum_{u_1<u_2<\cdots<u_s} (-1)^{\alpha_1+\alpha_2+\cdots+\alpha_s+u_1+u_2+\cdots+u_s} \times \Phi^{(s)}(a_1\cdots a_s|u_1\cdots u_s) \times d^{(n-s)}(a_1\cdots a_s|u_1\cdots u_s). \qquad (4.13)$$

Obviously if we replace $\mu^{(n)}$ by $\tilde{\mu}^{(n)}$ in the formula (4.11) the resulting function will be identical with $f^{(s)}(a_1\cdots a_s)$ since the $f^{(s)}$ is *defined* that way. We may write, therefore,

$$f^{(s)}(a_1\cdots a_s) = \frac{1}{(N!)^{\frac{1}{2}}} \sum_{t_1<t_2<\cdots<t_n} (-1)^{k_1+\cdots+k_n+t_1+\cdots+t_n} \times \tilde{\mu}^{(n)}(k_1\cdots k_n|t_1\cdots t_n) \times D^{(N-n)}(k_1\cdots k_n|t_1\cdots t_n). \qquad (4.14)$$

What we have done here is the following. By definition $f^{(s)}(a_1\cdots a_s)$ may be generated from Ψ_F by expanding Ψ_F in terms of the rows containing the orbitals $\varphi(a_1|q)$, $\varphi(a_2|q)$, $\cdots\varphi(a_s|q)$ and replacing the $(s\times s)$ determinant in the expansion by the correlation function $\Phi^{(s)}(a_1\cdots a_s|1,\cdots s)$. But $f^{(s)}$ can be also generated by expanding Ψ_F in terms of the larger set $\varphi(k_1|q)$, $\varphi(k_2|q)$, $\cdots\varphi(k_n|q)$ [formula (4.11)], then expanding the $(n\times n)$ determinant $\mu^{(n)}(k_1\cdots k_n|1,2,\cdots n)$ again in terms of the orbitals $\varphi(a_1|q)$, $\varphi(a_2|q)$, $\cdots\varphi(a_s|q)$, and then replacing the $(s\times s)$ subdeterminant $\mu^{(s)}(a_1\cdots a_s|1,2,\cdots s)$ by the correlation function $\Phi^{(s)}(a_1\cdots a_s|1,2,\cdots s)$.

We obtain $f^{(s)}(b_1\cdots b_t)$ similarly. We expand $\mu^{(n)}$ in (4.11) now in terms of the rows containing the orbitals $\varphi(b_1|q)$, $\varphi(b_2|q)$, $\cdots$, $\varphi(b_t|q)$:

$$\mu^{(n)}(k_1\cdots k_n|1,\cdots n) = \sum_{v_1<v_2<\cdots<v_t} (-1)^{\beta_1+\beta_2+\cdots+\beta_t+v_1+v_2+\cdots+v_t} \times\mu^{(t)}(b_1\cdots b_t|v_1\cdots v_t) \times d^{(n-t)}(b_1\cdots b_t|v_1\cdots v_t). \quad (4.15)$$

Let us replace $\mu^{(t)}$ by the correlation function $\Phi^{(t)}$ and let us denote the resulting function by $\mu'^{(n)}$:

$$\mu'^{(n)}(k_1\cdots k_n|1,\cdots n) = \sum_{v_1<v_2<\cdots<v_t} (-1)^{\beta_1+\beta_2+\cdots+\beta_t+v_1+v_2+\cdots+v_t} \times\Phi^{(t)}(b_1\cdots b_t|v_1\cdots v_t) \times d^{(n-t)}(b_1\cdots b_t|v_1\cdots v_t), \quad (4.16)$$

and we obtain $f^{(t)}(b_1\cdots b_t)$ from (4.11) replacing $\mu^{(n)}(k_1\cdots k_n|1,2,\cdots n)$ by $\mu'^{(n)}(k_1\cdots k_n|1,\cdots n)$.

With these simple manipulations we have brought the off-diagonal matrix component with respect to $f^{(s)}(a_1\cdots a_s)$ and $f^{(t)}(b_1\cdots b_t)$ into the form of a diagonal matrix component, i.e., we have brought $f^{(s)}(a_1\cdots a_s)$ and $f^{(t)}(b_1\cdots b_t)$ into the form of f_A and f_B [(4.3) and (4.4)] where $\tilde{\mu}^{(n)}$ corresponds to Φ_A and $\mu'^{(n)}$ corresponds to Φ_B. The analogy is not complete, however, because $\tilde{\mu}^{(n)}$ and $\mu'^{(n)}$ contain the arbitrary correlation functions $\Phi^{(s)}$ and $\Phi^{(t)}$, from which it follows that $\tilde{\mu}^{(n)}$ and $\mu'^{(n)}$ will not fulfill the orthogonality condition (4.2). However, we can use the Schmidt procedure again and put

$$\bar{\Phi}^{(s)}(a_1\cdots a_s|1,\cdots s) = \left(\prod_{u=1}^{s}\left[1-\sum_{v=1}^{N}\mathbf{\Omega}_v(u)\right]\right)\Phi^{(s)}(a_1\cdots a_s|1,\cdots s), \quad (v\neq a_1,\cdots a_s), \quad (4.17\text{a})$$

$$\bar{\Phi}^{(t)}(b_1\cdots b_t|1,\cdots t) = \left(\prod_{u=1}^{t}\left[1-\sum_{v=1}^{N}\mathbf{\Omega}_v(u)\right]\right)\Phi^{(t)}(b_1\cdots b_t|1,\cdots t), \quad (v\neq b_1\cdots b_t). \quad (4.17\text{b})$$

We replace $\Phi^{(s)}$ by $\bar{\Phi}^{(s)}$ in (4.13) and $\Phi^{(t)}$ by $\bar{\Phi}^{(t)}$ in (4.16). This substitution, as we have seen in Sec. 3, does not cause any change in the total wave function. Let us denote the resulting functions by $\mathcal{O}\tilde{\mu}^{(n)}$ and $\mathcal{O}\mu'^{(n)}$, i.e., let

$$\mathcal{O}\tilde{\mu}^{(n)}(k_1\cdots k_n|1,\cdots n) = \sum_{u_1<u_2<\cdots<u_s} (-1)^{\alpha_1+\alpha_2+\cdots+\alpha_s+u_1+u_2+\cdots+u_s} \times\bar{\Phi}^{(s)}(a_1\cdots a_s|u_1\cdots u_s) \times d^{(n-s)}(a_1\cdots a_s|u_1\cdots u_s), \quad (4.18\text{a})$$

$$\mathcal{O}\mu'^{(n)}(k_1\cdots k_n|1,\cdots n) = \sum_{v_1<v_2<\cdots<v_t} (-1)^{\beta_1+\beta_2+\cdots+\beta_t+v_1+v_2+\cdots+v_t} \times\bar{\Phi}^{(t)}(b_1\cdots b_t|v_1\cdots v_t) \times d^{(n-t)}(b_1\cdots b_t|v_1\cdots v_t). \quad (4.18\text{b})$$

It is easy to see that the functions (4.18) fulfill the orthogonality conditions (4.2). Let us put $\mathcal{O}\tilde{\mu}^{(n)}$ into the left side of Eq. (4.2):

$$\int \varphi_m^*(1)[\mathcal{O}\tilde{\mu}^{(n)}]dq_1 = \int \varphi_m^*(1)\Big\{ \sum_{u_1<u_2<\cdots<u_s} (-1)^{\alpha_1+\alpha_2+\cdots+\alpha_s+u_1+u_2+\cdots+u_s} \times\bar{\Phi}^{(s)}(a_1\cdots a_s|u_1\cdots u_s) \times d^{(n-s)}(a_1\cdots a_s|u_1\cdots u_s)\Big\}dq_1, \quad (m=1,2,\cdots N;\, m\neq k_1,\cdots k_n). \quad (4.19)$$

Because of the summation $\sum(u_1,\cdots u_s)$ the coordinate q_1 is either in $\bar{\Phi}^{(s)}$ or in $d^{(n-s)}$. If q_1 is in $\bar{\Phi}^{(s)}$ the integral becomes zero because, as we see from (4.17a), the function $\bar{\Phi}^{(s)}$ is orthogonal to all orbitals φ_m for which $m=1, 2, \cdots N$, $m\neq k_1\cdots k_n$. If the coordinate q_1 is in $d^{(n-s)}$, the expression (4.19) becomes zero, because $d^{(n-s)}$ is a determinant built from the orbitals $\varphi(k_1|q)$, $\varphi(k_2|q)$, $\cdots$, $\varphi(k_n|q)$ excluding $\varphi(a_1|q)\cdots\varphi(a_s|q)$, and these orbitals are orthogonal to all orbitals φ_m for which $m=1, 2, \cdots N$, $m\neq k_1\cdots k_n$. Thus it is evident that $\mathcal{O}\tilde{\mu}^{(n)}$ satisfies the orthogonality condition (4.2). Similarly, it is easy to show that also $\mathcal{O}\mu'^{(n)}$ satisfies the condition (4.2). Since both $\mathcal{O}\tilde{\mu}^{(n)}$ and $\mathcal{O}\mu'^{(n)}$ are antisymmetric, they satisfy also the condition (4.1).

On the basis of these considerations we may formulate our result with regard to the off-diagonal matrix components:

The off-diagonal matrix component with respect to $f^{(s)}(a_1\cdots a_s)$ *and* $f^{(t)}(b_1\cdots b_t)$ *may be obtained from (4.5)–(4.7) putting*

$$\Phi_A=\mathcal{O}\tilde{\mu}^{(n)}(k_1\cdots k_n|1,2,\cdots n), \quad \Phi_B=\mathcal{O}\mu'^{(n)}(k_1\cdots k_n|1,2,\cdots n), \quad (4.20)$$

where $\mathcal{O}\tilde{\mu}^{(n)}$ *and* $\mathcal{O}\mu'^{(n)}$ *are given by (4.18a) and (4.18b) and the set of n indices* $(k_1k_2\cdots k_n)$ *has to be formed from the members of the two subsets* $(a_1a_2\cdots a_s)$ *and* $(b_1b_2\cdots b_t)$ in such a way that those indices which occur in both subsets have to be taken account only once in the combined set.

5. TWO-ELECTRON APPROXIMATION

The theory of correlated wave functions developed in the previous sections enables us to introduce into the wave function correlation of any order. It is clear, however, that the matrix components of the higher approximations are expressions of formidable complexity, and the calculations become increasingly difficult if we introduce higher approximations. Fortunately there are some arguments which indicate that the major part of the correlation can be calculated with the relatively simple 2-electron approximation.

Let us consider a Hamiltonian, which contains 1-particle, 2-particle, $\cdots n$-particle interactions:

$$\mathbf{H}=\sum_i \mathbf{H}_i+\frac{1}{2!}\sum_{i,j} H_{ij}+\frac{1}{3!}\sum_{ijl} H_{ijl}+\cdots+\frac{1}{n!}\sum_{ijl\cdots m} H_{ijl\cdots m}. \tag{5.1}$$

Let $\mathbf{H}_F(i)$ be the H-F Hamiltonian operator expressed as a function of the coordinates of the ith particle, and let φ_k ($k=1, 2, \cdots$) be the complete set of the solutions of the H-F equations. Let us denote the H-F determinant by Ψ_0 and the complete set of determinants formed from the one-particle spin orbitals φ_k ($k=1, 2, \cdots$) by Ψ_M ($M=0, 1, 2, \cdots$). The Hamiltonian (5.1) may be written as

$$\mathbf{H}=\mathbf{H}_0+\mathbf{H}', \tag{5.2}$$

with

$$\mathbf{H}_0\equiv\textstyle\sum_i \mathbf{H}_F(i), \tag{5.3}$$

$$\mathbf{H}'\equiv \sum_i \mathbf{H}_i+\frac{1}{2!}\sum_{ij} H_{ij}+\cdots+\frac{1}{n!}\sum_{ij\cdots m} H_{ij\cdots m}-\sum_i \mathbf{H}_F(i). \tag{5.4}$$

Suppose we want to make a perturbation calculation starting with Ψ_0 as the unperturbed function and $\mathbf{H}'$ as the perturbation operator, and suppose we want the energy up to second order. Then we obtain

$$E_2=E_0+\int \Psi_0^*\mathbf{H}'\Psi_0 dq_N+\sum_{M=1}^{\infty}\left|\int \Psi_M^*\mathbf{H}'\Psi_0 dq_N\right|^2 \Big/ (E_0-E_M), \tag{5.5}$$

where E_M is given by the equation

$$\textstyle\sum_{(i)} \mathbf{H}_F(i)\Psi_M=E_M\Psi_M.$$

The complete set of determinants $\Psi_0, \Psi_1, \cdots\Psi_M\cdots$ includes, besides Ψ_0, all single-, double-, $\cdots$, N-fold substituted configurations. It is known, however, that if the perturbation Hamiltonian H' contains only n-particle interactions, the matrix component $\int\Psi_M^*\times\mathbf{H}'\Psi_0 dq_N$ vanishes if Ψ_M differs from Ψ_0 in more than n one-electron orbitals. Therefore, if the Hamiltonian contains n-particle interactions, the formula for the second order perturbation energy contains only those types of integrals which occur in the n-electron approximation. In the case of our actual Hamiltonian (1.2) the formula for the second order perturbation energy contains only single and double substituted configurations. There exist therefore a close correspondence between the 2-electron approximation, as it was defined in Sec. 2, and the second order perturbation theory. This fact indicates that a large part of the correlation energy may be computed with the 2-electron approximation.

In this section we note some characteristic properties of the 2-electron approximation. The wave function was given by (2.11):

$$\Psi^{(2)}=\Psi_F+\sum_{ij}\frac{1}{(N!)^{\frac{1}{2}}}\sum_{t_1=1}^{N}\sum_{t_2=t_1+1}^{N}(-1)^{i+j+t_1+t_2}\times\Phi^{(2)}(ij|t_1t_2)D^{(N-2)}(ij|t_1t_2). \tag{5.6}$$

For $\Phi^{(2)}$ we put

$$\Phi^{(2)}(ij|1,2)=[\varphi_i(1)\varphi_j(2)-\varphi_i(2)\varphi_j(1)]\times\sum_{m,n,l} c(ijmnl)(r_1-r_2)^{2m}(r_1+r_2)^n r_{12}{}^l, \tag{5.7}$$

where the $c(ijmnl)$ are variational parameters.

The calculation of a correlated wave function of the type (5.6) may be carried out as follows. After choosing a set of one-electron orbitals $\varphi_1, \varphi_2, \cdots\varphi_N$ we put the eigenfunction (5.6) into the Schrödinger energy expression and apply the energy minimum principle with respect to the parameters $c(ijmnl)$. The resulting secular equation may be solved with standard methods. The main difficulty lies in the calculation of the matrix components of the Hamiltonian which occur in the secular equation.

Formulas for these matrix components may be obtained from the general formulas of Sec. 4 and may be found also in reference (12). If the eigenfunction has the form given by (5.6) and (5.7) the matrix components, in general, will be 2-, 3-, 4-, and 5-electron integrals containing the distances between the electrons. The general analysis of integrals containing interelectronic distances is reserved for a forthcoming paper, but we note here an important result concerning the 2-electron approximation.

In the 2-electron approximation all occurring matrix components of the Hamiltonian can be reduced to the following two types of integrals:

$$I_1=\int F_1(r_1\vartheta_1\phi_1)F_2(r_2\vartheta_2\phi_2)r_{12}{}^a dv_1dv_2, \tag{5.8}$$

$$I_2=\int F_1(r_1\vartheta_1\phi_1)F_2(r_2\vartheta_2\phi_2)F(r_3\vartheta_3\phi_3)\times(r_{13}{}^a r_{23}{}^b r_{12}{}^{-1})dv_1dv_2dv_3, \tag{5.9}$$

where the $F_i(r\vartheta\phi)$ have the form

$$F_i(r,\vartheta\phi)=\mathcal{G}_i(r)Y_{l_im_i}(\vartheta\phi); \qquad (5.10)$$

$Y_{l_im_i}(\vartheta\phi)$ are the normalized spherical harmonics, and a and b are positive integers or zero. Integrals of type (5.8) have been investigated by Hylleraas,[6] Breit[18] and recently by Calais and Löwdin,[19] and it has been shown that the calculation may be simplified by introducing r_{12} as integration variable. The present writer has investigated (5.9) and has shown that the calculation of these integrals can also be simplified by introducing r_{13} and r_{23} as integration variables.[13] Thus we may characterize the 2-electron approximation by saying that the calculation of the matrix components is relatively simple, because only 2-electron and 3-electron integrals occur, and in the 3-electron integrals two of the interelectronic distances may be introduced as integration variables.

6. CONCLUDING REMARKS

By developing the method presented in this paper, our goal was to generalize the highly successful method of Hylleraas for the calculation of wave functions for atoms with any number of electrons. The mathematical technique developed in Secs. 2–4 provides the basis for calculations of Hylleraas-type wave functions. There are several basic problems, however, which still remain to be investigated. First, in general, the matrix components of the Hamiltonian will be integrals containing $\frac{1}{2}N(N-1)$ interelectronic distances. The investigation of these integrals is reserved for a forthcoming paper; some results, on integrals containing 3 interelectronic distances [Eq. (5.9)] are published already.[13] The next question concerns the symmetry properties of the correlated wave functions. Obviously even if the H-F function (2.1) was an eigenfunction of the total orbital and spin angular momentum operators, the correlated wave functions (2.8) would not necessarily possess these properties. The best method for the investigation of the questions concerning the symmetry properties of the wave functions seems to be the projection operator method developed by Löwdin.[20] Using the projection operator method we can start with an arbitrary correlated function like (2.7); application of the angular momentum projection operators will ensure that the resulting function will be an eigenfunction of the angular momentum operators. The details of this procedure will be discussed in a forthcoming paper.

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