$a/L$ is small, the steady state saturation voltage is proportional to the surface recombination velocity $\sigma$; when $a/L$ is large, the saturation voltage is independent of $\sigma$ but inversely proportional to the diffusion length $L$.

Mathematically, the key to the initial peaking of the function $V$ lies in the relation of the first two terms in each of the infinite series. In the numerator $F_2, \gg F_1$, and the $F_n$ increase progressively; hence the second term with high exponential damping dominates the series initially. Since the series is subtractive, the numerator grows quickly. In the denominator, on the other hand, $F_1, \gg F_0'$, and the first term with lower damping dominates the series, also subtractive; thus the denominator grows relatively slowly. However, in a short time, only the first term in each series remains significant and since $F_1, \gg F_1$, the denominator growth overtakes that of the numerator and brings the potential down toward a steady state value.

We have already seen in (17) the physically reasonable behavior: the Hall voltage developed is directly proportional to the current (through its proportionality to the concentration gradient) and is inversely proportional to the conductance.

While the steady state Hall voltage may be used to measure the surface recombination velocity of a sample, as observed by Moss et al., the dependence of the transient behavior on the specimen parameters appears to be too complicated to afford a method for their determination.

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P H Y S I C A L  R E V I E W  V O L U M E 9 7 ,  N U M B E R 6  M A R C H 1 5 , 1 9 5 5

Quantum Theory of Many-Particle Systems. I. Physical Interpretations by Means of Density Matrices, Natural Spin-Orbitals, and Convergence Problems in the Method of Configurational Interaction*

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In order to calculate the average value of a physical quantity containing also many-particle interactions in a system of $N$ antisymmetric particles, a set of generalized density matrices are defined. In order to permit the investigation of the same physical situation in two complementary spaces, the Hermitean density matrix of order $k$ has two sets of indices of each $k$ variables, and it is further antisymmetric in each set of these indices.

Every normalizable antisymmetric wave function may be expanded in a series of determinants of order $N$ over all ordered configurations formed from a basic complete set of one-particle functions $\psi_{nk}$, which gives a representation of the wave function and its density matrices also in the discrete $k$-space. The coefficients in an expansion of an eigenfunction to a particular operator may be determined by the variation principle, leading to the ordinary secular equation of the method of configurational interaction. It is shown that the first-order density matrix may be brought to diagonal form, which defines the "natural spin-orbitals" associated with the system. The situation is then partly characterized by the corresponding occupation numbers, which are shown to lie between 0 and 1 and to assume the value 1, only if the corresponding spin-orbital occurs in all configurations necessary for describing the situation. If the system has exactly $N$ spin-orbitals which are fully occupied, the total wave function may be reduced to a single Slater determinant. However, due to the mutual interaction between the particles, this limiting case is never physically realized, but the introduction of natural spin-orbitals leads then instead to a configurational expansion of most rapid convergence.

In case the basic set is of finite order $M$, the best choice of this set is determined by a form of extended Hartree-Fock equations. It is shown that, in this case, the natural spin-orbitals approximately fulfill some equations previously proposed by Slater.

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forms. The number of coordinates will further be doubled in order to permit us to consider the same physical situation in two complementary spaces.

1. DEFINITION OF GENERAL DENSITY MATRICES

Let us consider a system of \( N \) identical antisymmetric particles with the coordinates \( x_1, x_2 \ldots x_N \) moving under the influence of a fixed potential framework and their mutual interaction. Each coordinate \( x_i \) is a combination of a space coordinate \( r_i \) and a spin coordinate \( s_i \), and, in considering nucleons, we will include also the coordinate of the isotopic spin. The physical situation of the system is described by a wave function \( \psi \), which we assume to be normalized. It fulfills the antisymmetry condition

\[
P \psi(x_1, x_2, \ldots x_N) = (-1)^P \psi(x_{i_1}, x_{i_2}, \ldots x_{i_N}),
\]

where \( P \) is a permutation operator working on the indices of the \( N \) coordinates and \( P \) its parity. In considering the configuration space, we will let

\[
(dx) = dx_1 dx_2 \cdots dx_N
\]

indicate integration-summation over all coordinates, \( (dx_i') \) the same procedure over all coordinates except \( x_i \), \( (dx_k') \) the same over all coordinates except \( x_i \), and \( x_j \), etc.

A physical quantity \( \Omega \) associated with the system is represented in the configuration space by a Hermitean operator \( \Omega_{op} \) which is symmetrical in the indices of the particles. It may be expressed in the form

\[
\Omega_{op} = \Omega_{ij} + \sum_i \Omega_i + \frac{1}{2!} \sum_{ij} \Omega_{ij} + \frac{1}{3!} \sum_{ijk} \Omega_{ijk} + \cdots,
\]

where each term is a zero-, one-, two-, three-, \ldots, or many-particle operator, respectively; the prime on the summation signs indicates that we omit all terms having two or more indices equal. In order to evaluate the average value of this quantity in a situation characterized by the normalized wave function \( \psi \), we will now introduce a series of density matrices of various orders:

\[
\gamma(x_i|x_1) = N \int \psi^*(1'2'3'\ldots N)\psi(123\ldots N)(dx_1'),
\]

\[
\Gamma(x_1'x_2'|x_1x_2) = \binom{N}{2} \int \psi^*(1'2'3'\ldots N)\psi(123\ldots N)(dx_2'),
\]

\[
\Gamma^{(p)}(x_1'x_2'\ldots x_p'|x_1x_2\ldots x_p) = \binom{N}{p} \int \psi^*(1'2'3'\ldots p'\ldots N)\psi(123\ldots p\ldots N)(dx_1'\ldots dx_p),
\]

where, in the integrands, \( i' \) and \( i \) are abbreviations for the coordinates \( x_i' \) and \( x_i \), respectively. These density matrices are Hermitean, they are antisymmetric in each set of indices, so that

\[
\Gamma(x_1x_2|x_1'x_2') = \Gamma^*(x_1'x_2'|x_1x_2),
\]

\[
\Gamma(x_1'x_2'|x_1x_2) = -\Gamma(x_1x_2'|x_1'x_2),
\]

and they are further related by the formula,

\[
\Gamma^{(p-1)}(x_1'x_2'\ldots x_{p-1}'|x_1x_2\ldots x_{p-1}) = \frac{1}{p} \int \Gamma^{(p)}(x_1'x_2'\ldots x_{p-1}'|x_p)\psi(123\ldots N)(dx_1\ldots dx_p).
\]

Of special importance are the diagonal elements:

\[
\gamma(x_i|x_1) = \gamma(x_1|x_i),
\]

\[
\Gamma(x_1,x_2) = \Gamma(x_1|x_2),
\]

\[
\ldots \ldots ....
\]

which are all positive definite. Because of the antisymmetry of each set of indices, they are symmetric in their coordinates. The diagonal elements have the following physical interpretations: \( \gamma(x_i|dx_i) \) = number of particles \( X \) the probability for finding a particle within the volume \( dx_i \) around the point \( r_i \) having the spin \( s_i \), etc., when all the other particles have arbitrary positions and spins; \( \Gamma(x_1x_2|dx_1dx_2) = \) number of pairs \( X \) the probability for finding one particle within the volume \( dx_1 \) around the point \( r_1 \) with the spin \( s_1 \), etc., and another within the volume \( dx_2 \) around the point \( r_2 \) with the spin \( s_2 \), all others having arbitrary positions and spins; etc. According to (3), we obtain for the total integrals

\[
\int \gamma(x_i|dx_i) = N, \quad \int \Gamma(x_1,x_2|dx_1dx_2) = N(N-1)/2,
\]

\[
\int \Gamma^{(p)}(x_1\ldots x_p|dx_1\ldots dx_p) = \binom{N}{p}.
\]

Since the matrices (3) are antisymmetric in each set of their indices, they will vanish identically if two (or more) indices of a set are equal. For the diagonal elements, we obtain in particular:

\[
\Gamma(x_i,x_i) = 0, \quad \Gamma^{(3)}(x_i,x_j,x_k) = 0, \quad \ldots
\]

which shows that, for small distances, the antisymmetry requirement leads to a correlation effect which will strongly keep particles with parallel spins apart. This general phenomenon, which is an important consequence of the Pauli principle, was first noticed for free electrons as the "Fermi hole."\(^2\)

Let us illustrate the calculation of average values of physical quantities by considering the two-particle systems.\(^2\) See, for instance, E. Wigner and F. Seitz, Phys. Rev. 43, 804 (1933); and J. C. Slater, Phys. Rev. 81, 385 (1951).
By changing names of the integration variables and using the symmetry properties, we obtain

\[ \int \Psi^* \left( \frac{1}{2} \sum_{ij} \Omega_{ij} \right) \Psi \, dx \]

\[ = \frac{1}{2} N (N - 1) \int \Psi^* \Omega_{12} \Psi \, dx \]

\[ = \left( \begin{array}{c} N \\ 2 \end{array} \right) \int \left\{ \Psi^*(1'23 \cdots N) \Omega_{12} \times \Psi(123 \cdots N) \right\} \delta(x_1' - x_1, x_2' - x_2, \ldots, x_N' - x_N) \, dx_1 \ldots dx_N \]

In treating the density matrices, we will introduce the convention that the operators \( \Omega_{ij} \) will work only on the unprimed coordinates \( x_i, x_j, \ldots \), but not on \( x_i', x_j', \ldots \), etc., and that, after the operations have been carried out, we have to put \( x_i' = x_i, x_j' = x_j, \ldots \). We note that the diagonal elements of (3) are sufficient for describing the physical situation in the ordinary \( x \)-space, but that we need the nondiagonal elements for characterizing the situation also in complementary spaces, as the momentum space. For the operator (2), we obtain in this way

\[ \langle \Omega_{op} \rangle = \int \Psi^* \Omega_{op} \Psi \, dx \]

\[ = \Omega_{(0)} + \int \Omega_{12} \gamma(x_1|x_1) \, dx_1 + \int \Omega_{12} \Gamma(x_1|x_2) \, dx_1 \ldots dx_N \]

In order to illustrate the use of this fundamental formula by a few examples, let us first consider an electronic system (atom, molecule, or crystal) without external field at absolute zero. The system has the following basic Hamiltonian:

\[ \langle \mathcal{H} \rangle = \frac{\hbar^2}{2m} \sum_{\alpha, \beta} Z_{\alpha} \Gamma/\Gamma_{\alpha} + \left\{ \frac{p^2}{2m} - \epsilon^2 \sum_{\alpha} Z_{\alpha}/r_{\alpha} \right\} \]

\[ + \frac{1}{2} \sum_{ij} \epsilon^2/r_{ij}, \]

where \( Z_{\alpha} \) is the atomic number of the nucleus \( g \). Here we have neglected relativistic effects (including all spin couplings) and the zero-points vibrations of the nuclei. According to (10), the average energy is now given by the expression.

\[ \langle \mathcal{H} \rangle = \frac{\hbar^2}{2m} \sum_{\alpha, \beta} Z_{\alpha} \Gamma/\Gamma_{\alpha} + \left\{ \frac{p^2}{2m} - \epsilon^2 \sum_{\alpha} Z_{\alpha}/r_{\alpha} \right\} \]

\[ - \epsilon^2 \sum_{\alpha} Z_{\alpha} \int \gamma(x_{\alpha}) \, dx_{\alpha} + \epsilon^2 \int \Gamma(x_{\alpha}, x_{\beta}) \, dx_{\alpha} \ldots dx_{\beta}, \]

where the first term is the repulsive Coulomb potential between the nuclei, the second the kinetic energy of the electrons, the third the attractive Coulomb potential between the nuclei and the electrons, and the last term the repulsive Coulomb potential between the electrons. For the description of the energy of such a system, it is therefore sufficient to know the second-order density matrix \( \Gamma(x', x' | x, x) \), from which the first-order density matrix may be calculated according to (5).

Let us then consider the total spin \( S^2 \) measured in units \( h \) of a system of \( N \) antisymmetric particles. According to Dirac,\(^a\) we have

\[ S^2 = \sum_{ij} S_i \cdot S_j \]

\[ = -N(N-4)/4 + \frac{1}{2} \sum_{ij} P_{ij} \]

\[ = -N(N-4)/4 + \frac{1}{2} \sum_{ij} P_{ij}, \]

where \( P_{ij} \) is the operator for permuting the spin coordinates \( s_i \) and \( s_j \) of the particles \( i \) and \( j \). Applying formula (10), we obtain

\[ \langle S^2 \rangle = -N(N-4)/4 \]

\[ + \int \Gamma(r_{1s1}, r_{2s2} | r_{1s2}, r_{2s1}) \, dx_1 \ldots dx_N, \]

which expression may be evaluated from the knowledge of the second order density matrix.

As a last example, we will consider the operator for the electric moment \( \mathbf{D} \),

\[ \langle \mathbf{D} \rangle = \epsilon \sum_i r_i \]

\[ = \epsilon \sum_i r_i \gamma(x_i) \, dx_1. \]

In this connection we observe that we shall sometimes need quantities which are related to the transition of the system between two orthogonal states, \( \Psi_1 \) and \( \Psi_2 \), which are characterized by the normalized wave functions \( \Psi_1 = \Psi_1 \) and \( \Psi_2 \). In analogy to (3), we will for this

Quantum Theory of Many-Particle Systems. I

1. Purpose

Define the transition matrices:

\[ \gamma_{11}(x'_1|x_1) = N \int \Psi_{1}^*(123\cdots N)\Psi_{11}(123\cdots N)(dx'_1), \]

\[ \Gamma_{11}(x'_1|x'_2|x_1|x_2) = \binom{N}{2} \int \Psi_{1}^*(1'2'3\cdots N)\Psi_{11}(123\cdots N)(dx'_1), \]

and, in the same way as before, we can derive the formula

\[ (\Omega_{op}|\Pi) = \int \Psi_{1}^*\Omega_{op}\Psi_{11}(dx) \]

\[ = \int \Omega_{11}(x'_1|x_1)dx_1 \]

\[ + \int \Omega_{12}\Gamma_{11}(x'_1|x'_2|x_1|x_2)dx_1dx_2 + \cdots \]  

For the transition moment, we obtain, in particular,

\[ (\Pi|D|\Pi) = \epsilon \int \Gamma_{11}(x_1)dx_1. \]

We observe the simplification of the physical picture of the system provided by the use of the density matrices (3). In considering a physical quantity (2), containing many-particle operators up to the order \( k \), the average value of this quantity is determined by (10) and the density matrix of order \( k \), from which all density matrices of lower orders may be evaluated successively by using (5). For \( k=2 \), we obtain for instance

\[ \langle \Omega_{op} \rangle = \int \left[ \Omega_{11} + N\Omega_{12} \right] \Gamma(x'_1|x'_2|x_1|x_2)dx_1dx_2 \]

\[ = \frac{\int \Gamma(x_1|x_2)dx_1dx_2}{\int \Gamma(x_1|x_2)dx_1dx_2}, \]  

where, in agreement with the convention introduced in connection with (9), we have to put \( x'_1 = x_1 \) and \( x'_2 = x_2 \) after the operations in the integrand in the numerator have been carried out; the denominator is introduced in order to take care automatically of the normalization.

The density matrices (3) may be derived from the wave function \( \Psi \) or from the matrix of highest order \( k=N \). It would also be of some interest to investigate the reverse problem and to see how much the knowledge of a lower-order density matrix \( k<N \) would determine the wave function, i.e., the physical situation of the system. From (10) it is clear that the average values of all physical quantities (2) containing only many-particle operators up to the order \( k \) are entirely fixed. The eigenfunctions of such an operator fulfill the relation,

\[ \Omega_{op}\Psi = \lambda \Psi, \]

and may also be derived from the variation principle,

\[ \delta(\Omega_{op}) = 0, \]

which leads to a variation condition for the density matrix of order \( k \); compare (20). In this and following papers we will discuss these problems in some detail, and we will show that these preliminary results are quickly changed if we impose also additional restrictions on the form of the wave function. It will, for instance, be shown, in the Hartree-Fock scheme where the total wave function is approximated by a single Slater determinant, the first-order density matrix \( \gamma(x'_1|x_1) \) alone determines all the higher-order matrices, the wave function, and consequently the entire physical situation. In the part of our present electronic theory of atoms, molecules, and crystals, which is based on the Hartree-Fock approximation, the first-order density matrix is therefore an appropriate tool for giving a simple physical picture of the system. In the following, we will largely concentrate our interest on the properties of the general first-order density matrix, and we will investigate its behavior also in the higher approximations.

2. Analysis of the Properties of the Density Matrices

(a) Expansion Theorem

In order to investigate the properties of the density matrices in greater detail, we will introduce an orthonormal and complete set of discrete\(^4\) one-particle functions \( \phi_k(x) \) \((k=1, 2, 3, \ldots)\) of such a type that every normalizable function \( \psi(x) \) of a single coordinate \( x \) may be expanded in the form

\[ \psi(x) = \sum \phi_k(x)c_k, \]

\[ c_k = \int \psi(x)\phi_k^*(x)dx, \]

Following Slater,\(^5\) we will here include all spin properties explicitly in the wave functions, and the one-particle functions \( \phi_k(r,s) \) are therefore spin-orbitals, obtained by multiplying two complete orthonormal sets of orbitals (being functions only of \( r \)) by the spin functions \( \alpha(s) \) and \( \beta(s) \), respectively. In considering nucleons, we include the isotopic spin functions in the same way. From the very beginning, we are going to make ourselves free from the idea of “doubly filled orbitals,” and the two sets of basic orbitals associated

\(^4\) For the sake of simplicity, the set is here chosen discrete, but there are no major difficulties in extending the treatment to include also continuous sets.

\(^5\) J. C. Slater, Phys. Rev. 34, 1293 (1929).
with the ordinary spin must therefore not necessarily be the same, but the orbitals in one set may, of course, be expanded in the orbitals of the other set. These distinctions will later be of value in treating correlation properties.

By introducing a set of spin orbitals $\psi_i(x_i)$ for each coordinate $x_i$ (i = 1, 2, ..., N) and by successively applying (23), we may now expand every normalizable function $\Psi$ in configuration space in the following form:

$$\Psi(x_1, x_2, \ldots x_N) = \sum_{k_1k_2\ldots k_N} \psi_{k_1}(x_1)\psi_{k_2}(x_2)\cdots \times \psi_{k_N}(x_N) C(k_1, k_2, \ldots k_N),$$

(25)

$$C(k_1, k_2, \ldots k_N) = \int \Psi(12\cdots N)\psi_{k_1}^*(1)\times \psi_{k_2}^*(2)\times \psi_{k_N}^*(N) (dx).$$

For antisymmetric functions fulfilling (1), it follows from (25) that also the coefficients $C$ are antisymmetric in their indices:

$$PC(k_1, k_2, \ldots k_N) = (-1)^r C(k_1, k_2, \ldots k_N).$$

(26)

A selection of $N$ indices $k_1, k_2, \ldots k_N$ will in the following be called a configuration, and the space described by all values of these indices will simply be called the $k$-space. In the terminology of the transformation theory, the antisymmetric quantity $C(k_1, k_2, \ldots k_N)$ may be considered as the representation of the wave function in the $k$-space, and we note that it fulfills the normalization condition

$$\sum_{k_1k_2\ldots k_N} |C(k_1, k_2, \ldots k_N)|^2 = \int |\Psi|^2(dx).$$

(27)

Because of the property (26), the number of independent coefficients $C$ in expansion (24) may be essentially reduced, for instance by referring the indices to a specific order. If a selection of $N$ indices $k_1, k_2, \ldots k_N$ fulfills the condition $k_1 < k_2 < \cdots < k_N$, it will in the following be called an ordered configuration and will be denoted by the abbreviated symbol $K$. In this connection, it is also convenient to introduce the symbol

$$C_K = (N!)^{-1} C(k_1, k_2, \ldots k_N),$$

(28)

for then the normalization condition (27) takes the form

$$\sum_K |C_K|^2 = \int |\Psi|^2(dx),$$

(29)

where we have to sum only over the ordered configurations $K$.

The quantities $C_K$ represent all independent coefficients in expansion (24). By permuting the dummy indices $k_1, k_2, \ldots k_N$ and by using (26) and (28), we may now rearrange this expansion in the following way:

$$\Psi(x_1, x_2, \ldots x_N) = (N!)^{-1} \sum_P P \sum_{k_1k_2\ldots k_N} \psi_{k_1}(x_1)\psi_{k_2}(x_2)\cdots \times \psi_{k_N}(x_N) C(k_1, k_2, \ldots k_N)$$

$$= (N!)^{-1} \sum_{k_1k_2\ldots k_N} C(k_1, k_2, \ldots k_N) \sum_P (-1)^r P \times \psi_{k_1}(x_1)\psi_{k_2}(x_2)\cdots \psi_{k_N}(x_N)$$

$$= \sum_{k_1k_2\ldots k_N} C(k_1, k_2, \ldots k_N) \det{\psi_{k_1}, \psi_{k_2}, \ldots \psi_{k_N}}$$

$$= \sum_K C_K \Psi_K(x_1, x_2, \ldots x_N),$$

(30)

where

$$\Psi_K(x_1, x_2, \ldots x_N) = (N!)^{-1} \det{\psi_{k_1}, \psi_{k_2}, \ldots \psi_{k_N}}$$

(31)

is the normalized Slater determinant belonging to the ordered configuration $K$. Hence it is possible to expand an antisymmetric wave function in configuration space in a series of Slater determinants over all ordered configurations $K$.

Two ordered configurations $K = (k_1, k_2, \ldots k_N)$ and $L = (l_1, l_2, \ldots l_N)$ are said to be the same if they are identical in all their indices, and they are said to be different if they differ in at least one index. It is easily shown that two Slater determinants $\Psi_K$ and $\Psi_L$ belonging to two different ordered configurations $K$ and $L$ are orthogonal, and hence we have

$$\int \Psi_K^*\Psi_L(dx) = \delta_{KL}.$$  

(32)

The Slater determinants associated with all ordered configurations form therefore an orthonormal set, which is complete with respect to normalizable, antisymmetric functions in configuration space. The coefficients $C_K$ may be derived from (30) and (32) or from (25) and (28), which gives the two expressions

$$C_K = \int \Psi(12\cdots N)\psi_K^*(dx)$$

$$= (N!)^1 \int \Psi(12\cdots N)\psi_1^*(1)\psi_2^*(2)\cdots \times \psi_N^*(N) (dx).$$

(33)

The connection between them is discussed in greater detail in Appendix I.

We may now also expand the density matrices (3) in a similar way. For the first-order matrix, we obtain

$$\gamma(x' | x_i) = \sum_{j} \psi_j^*(x') \psi_j(x_i) \gamma(l | k),$$

(34)

where, according to (4) the coefficients form an Hermitian matrix: $\gamma(k | l) = \gamma^*(l | k)$. For a density matrix of order $p$, which is Hermitian and antisymmetric in each

\[\text{See Eq. (39).}\]
set of its indices, we obtain in general:

\[
\Gamma^{(p)}(x_1'x_2' \cdots x_p'|x_1x_2 \cdots x_p) = \sum_{i_1 \cdots i_p} \psi_{i_1}^*(x_1') \cdots \psi_{i_p}^*(x_p') \psi_{i_1}(x_1) \cdots \psi_{i_p}(x_p) \Gamma^{(p)}(l_1l_2 \cdots l_p|k_1k_2 \cdots k_p)
\]

The expansion coefficients \(\Gamma^{(p)}(l_1l_2 \cdots l_p|k_1k_2 \cdots k_p)\), which are Hermitian and antisymmetric in each set of their indices, may be considered as the representations of the density matrices in the \(k\)-space, and now it remains to investigate how these densities depend on the wave function \(C(k_1k_2 \cdots k_N)\), i.e., to derive the relations in \(k\)-space corresponding to the definitions (3).

(b) Density and Transition Matrices for Slater Determinants

In order to derive the general expressions for the density matrices in \(k\)-space, we will first consider the transition matrices associated with two Slater determinants \(U\) and \(V\):

\[
U = (N!)^{-1} \sum \delta_{u_1u_2} \cdots \delta_{u_N} u_1(x_1) \cdots u_N(x_N)
\]

\[
V = (N!)^{-1} \sum \delta_{v_1v_2} \cdots \delta_{v_N} v_1(x_1) \cdots v_N(x_N)
\]

which are built up from two basic sets of spin-orbitals \(u_1, u_2, \cdots u_N\), and \(v_1, v_2, \cdots v_N\). For the sake of completeness, we will not impose any orthogonality condition on the sets \(u_k\) and \(v_i\), and we will further assume that they have mutual "nonorthogonality" integrals

\[
d_{uv}(kl) = \int u_k^*(x_1) v_i(x_1) dx_1,
\]

which may be different from zero for \(k \neq l\). If there is no risk for confusion, we will often in the symbol \(d_{uv}\) omit the indices \(u\) and \(v\).

By using formula (109) in Appendix I, we obtain

\[
\int U^* V(dx) = \int u_1^*(x_1) \cdots u_N^*(x_N) v_1(x_1) \cdots v_N(x_N) \times \text{det}_{(v_1, v_2, \cdots v_N)}(dx_1)
\]

\[
= \sum (-1)^p p! d(1_1) d(2_2) \cdots d(N_1_N) = \text{det}(d(kl))
\]

which shows that the "nonorthogonality" integral of two Slater determinants \(U\) and \(V\) equals the determinant \(D_{UV}\) of all the "nonorthogonality" integrals \(d_{uv}(kl)\) associated with the two sets of one-particle functions involved:

\[
\int U^* V(dx) = D_{UV} = \text{det}(d_{uv}(kl)).
\]

The determinant \(D_{UV}\) is of basic importance for the following discussion, and we need it as well as its minors of various orders:

\[
D_{UV}(k|l), D_{UV}(k_1k_2|l_1l_2), D_{UV}(k_1k_2k_3|l_1l_2l_3), \cdots.
\]

These minors are originally defined only for ordered sets \(k_1 < k_2 < \cdots < k_N\) and \(l_1 < l_2 < \cdots < l_N\), but they are easily generalized to the total \((k,l)\)-space by assuming that they are antisymmetric functions in each sets of their indices.

In the following we need also the minors of the determinants in (36), which will be denoted by symbols of the type

\[
\det_u(12 \cdots p | k_1k_2 \cdots k_p), \quad \det_v(12 \cdots p | l_1l_2 \cdots l_p).
\]

The minors of order \(p\) are determinants of order \((N-p)\), and we note that, according to (39), they fulfill the relation

\[
\prod (N-p)! \int \det_u(12 \cdots p | k_1k_2 \cdots k_p) \times \det_v(12 \cdots p | l_1l_2 \cdots l_p) (dx_1 \cdots dx_p) = D_{UV}(k_1k_2 \cdots k_p | l_1l_2 \cdots l_p).
\]

In order to derive the first-order transition matrix associated with \(U\) and \(V\) and defined by (17), we will expand the determinants (36) in terms of their first rows:

\[
U(x_1x_2 \cdots x_N) = (N!)^{-1} \sum \delta_{u_1u_2} \cdots \delta_{u_N} u_1(x_1) \cdots u_N(x_N)
\]

\[
V(x_1x_2 \cdots x_N) = (N!)^{-1} \sum \delta_{v_1v_2} \cdots \delta_{v_N} v_1(x_1) \cdots v_N(x_N)
\]

By using (42), we then obtain

\[
\int U^* V(dx) = D_{UV} = \det(d(kl)).
\]

The determinant \(D_{UV}\) is of basic importance for the following discussion, and we need it as well as its minors of various orders:

\[
D_{UV}(k|l), D_{UV}(k_1k_2|l_1l_2), D_{UV}(k_1k_2k_3|l_1l_2l_3), \cdots.
\]

Taking the normalization of \(U\) and \(V\) into account, we finally get

\[
\gamma_{UV}(x_1'|x_1) = (D_{UV} D_{VV})^{-1} \sum \delta_{u_1^*u_1} v_1(x_1) D_{UV}(k|l).
\]

\[
\times v_1(x_1) D_{UV}(k|l).
\]
In order to derive the transition matrix of order $p$, we will use Laplace's theorem\(^7\) and expand the determinants (36) in terms of their first rows:

$$U(x_1 x_2 \cdots x_N) = (N!)^{-1} \sum_{k_1 < k_2 < \cdots < k_p} \begin{vmatrix} u_{k_1}(x_1) & \cdots & u_{k_p}(x_1) \\ \vdots & \ddots & \vdots \\ u_{k_1}(x_p) & \cdots & u_{k_p}(x_p) \end{vmatrix} \det_s(12 \cdots p | k_1 k_2 \cdots k_p),$$

$$V(x_1 x_2 \cdots x_N) = (N!)^{-1} \sum_{k_1 < k_2 < \cdots < k_p} \begin{vmatrix} v_{k_1}(x_1) & \cdots & v_{k_p}(x_1) \\ \vdots & \ddots & \vdots \\ v_{k_1}(x_p) & \cdots & v_{k_p}(x_p) \end{vmatrix} \det_s(12 \cdots p | l_1 l_2 \cdots l_p).$$

(46)

According to (17) and (42), we then obtain

$$\left( \begin{array}{c} \sum_{k_1 < k_2 < \cdots < k_p} \frac{u_{k_1}(x_1)}{u_{k_1}(x_p)} \cdots \frac{u_{k_p}(x_1)}{u_{k_p}(x_p)} \end{array} \right) = \left( \begin{array}{c} (N!)^{-1} \sum_{k_1 < k_2 < \cdots < k_p} \frac{u_{k_1}(x_1)}{u_{k_1}(x_p)} \cdots \frac{u_{k_p}(x_1)}{u_{k_p}(x_p)} \end{array} \right) \left( \begin{array}{c} \det \left( \begin{array}{cccc} 1 & \cdots & 1 \\ 2 & \cdots & 2 \\ \vdots & \ddots & \vdots \\ p & \cdots & p \end{array} \right) \end{array} \right)^{-1}$$

$$\times \int \det_s(12 \cdots p | k_1 k_2 \cdots k_p) \det_s(12 \cdots p | l_1 l_2 \cdots l_p) dx_1 x_2 \cdots x_p$$

(47)

where, in the last form, we are using the generalized minors defined in the entire $(k,l)$-space by the antisymmetry requirement. Observing the normalization of $U$ and $V$, we get therefore for the transition matrix of order $p$ in the $(k,l)$-space:

$$\Gamma^{(p)}(l_1 l_2 \cdots l_p | k_1 k_2 \cdots k_p) = (p!)^{-1} \int \det_s(12 \cdots p | k_1 k_2 \cdots k_p | l_1 l_2 \cdots l_p) D_{UV}(k_1 k_2 \cdots k_p l_1 l_2 \cdots l_p).$$

(48)

According to (18), we are now able to find the matrix element of an operator $\Omega$ with respect to two Slater determinants:

$$\int U^* \Omega V (dx) = \Omega_{(0)} D_{UV} + \sum_{k \Omega} \left\{ \frac{u_{k}(x_1)}{u_{k}(x_p)} \cdots \frac{u_{k}(x_1)}{u_{k}(x_p)} \right\} D_{UV}(k | l)$$

$$+ \frac{1}{2!} \sum_{k_2 k_2} \left\{ \frac{u_{k_1 k_2}(x_1)}{u_{k_1 k_2}(x_p)} \right\} \frac{u_{k_2 k_1}(x_2)}{u_{k_2 k_1}(x_p)} D_{UV}(k_1 k_2 | l_1 l_2)$$

$$+ \frac{1}{3!} \sum_{k_3 k_3 k_3} \left\{ \frac{u_{k_1 k_2 k_3}(x_1)}{u_{k_1 k_2 k_3}(x_p)} \right\} \frac{u_{k_2 k_3 k_1}(x_2)}{u_{k_2 k_3 k_1}(x_p)} \frac{u_{k_3 k_1 k_2}(x_3)}{u_{k_3 k_1 k_2}(x_p)} D_{UV}(k_1 k_2 k_3 | l_1 l_2 l_3) + \cdots.$$  

(49)

where we have used the matrix notations

$$\{ k | \Omega_1 | l \} = \int u_{k}(x_1) \Omega_1 v_{l}(x_1) dx_1,$$

(50)

$$\{ k | \Omega_{12} | l_1 l_2 \} = \int u_{k}(x_1) \Omega_{12} v_{l_1}(x_1) v_{l_2}(x_2) dx_1 dx_2,$$

(51)

This is the general formula\(^8\) for nonorthogonal basic sets $u_\alpha$ and $v_\beta$. The corresponding formula for the orthogonal case was first derived by Slater\(^9\), and the nonorthogonal case has then been discussed rather extensively in the literature.\(^10\) We note that the formula for the diagonal

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\(^7\) See, for instance, G. Kowalewski, *Determinantentheorie* (Veit & Company, Leipzig, 1909).

\(^8\) A preliminary report of this result was given in P. O. Löwdin, Quarterly Progress Report of the Solid-State and Molecular Theory Group at Massachusetts Institute of Technology, January 15, 1952 (unpublished), p. 10. For some simplifications in the present derivation, the author is indebted to discussions with Dr. A. Meckler, Massachusetts Institute of Technology.

\(^9\) J. C. Slater, Phys. Rev. 34, 1293 (1929); 38, 1109 (1931); see also E. U. Condon, Phys. Rev. 36, 1121 (1930).

elements \((U = V)\) in the nonorthogonal case, previously given by the author,\(^{11}\) was derived in an entirely different way.

In the special case when \(D_{UV} \neq 0\), a considerable simplification may be introduced in (49), for, according to a well-known theorem in the theory of determinants,\(^7\) we then have

\[
D_{UV}(k_1 k_2 \cdots k_p | l_1 l_2 \cdots l_p)
= D_{UV}^{\text{-1}}(k_1 l_1) \cdots \left( D_{UV}^{\text{-1}}(k_p l_p) \right)
\]

\[
= D_{UV}^{\text{-1}}(l_1 k_1) \cdots \left( D_{UV}^{\text{-1}}(l_p k_p) \right)
\]

where \(D_{UV}^{\text{-1}}(k l)\) is the inverse matrix to the matrix \(D_{kl}\), defined by (37). It may be shown that, in this case, all transition matrices may be expressed in the fundamental invariant

\[
\sum_n \text{det}(x_1 \cdots x_n) d^{-1}(l k)
\]

and that, except for a factor, all higher-order matrices may be expressed as determinants of the first-order matrix. This case will be discussed in greater detail in a following paper.

(c) General Properties of the Density Matrices

We are now ready to discuss the general properties of the density matrices (3) and their representations in the \(k\)-space. If we let the symbol \((k)\) denote all ordered configurations \(K\) containing a specific index \(k\), the symbol \((k_1 k_2)\) denotes all ordered configurations \(K\) containing a specific pair of indices \(k_1\) and \(k_2\), etc., then we may rearrange our summations by the formulas

\[
\sum_k \sum_{k_1} \cdots \sum_{k_p} \gamma(k_1 k_2 \cdots k_p | l_1 l_2 \cdots l_p)
\]

\[
\sum_{k_1} \sum_{k_2} \cdots \sum_{k_p} \gamma(k_1 k_2 \cdots k_p | l_1 l_2 \cdots l_p)
\]

We will assume that our normalizable wave function \(\Psi\) may be expanded in a series of Slater determinants \(\Psi_K\) over all ordered configurations \(K\):

\[
\Psi = \sum_K \Psi_K C_K
\]

according to (30). Applying (45) and (53), we obtain for the first-order density:

\[
\gamma(x_1 | x_1) = \sum_{KL} C^*_K \gamma_{KL}(x_1 | x_1) C_L / \sum_K |C_K|^2
\]

or, for the first-order density in the \(k\)-space:

\[
\gamma(l | k) = \sum_{KL} C^*_K \gamma_{KL}(l | k) C_L / \sum_K |C_K|^2
\]

Similarly, by using (48) and (53), we obtain for the density of order \(p\):

\[
\Gamma^{(p)}(x_1 \cdots x_p | x_1 \cdots x_p) = \sum_{KL} C^*_K \Gamma^{(p)}(x_1 \cdots x_p | x_1 \cdots x_p) C_L / \sum_K |C_K|^2
\]

This formula gives the density matrices in \(k\)-space expressed in the wave function \(C(k_1 k_2 \cdots k_p)\) or its independent elements \(C_K\), and it corresponds therefore to the definitions (3).

We note that the density matrices in \(k\)-space are Hermitian and antisymmetric in each set of their indices. By using (7) and (57), we find for their total values

\[
\sum_k \gamma(k | k) = N,
\]

\[
\sum_{k_1 k_2 \cdots k_p} \Gamma^{(p)}(k_1 k_2 \cdots k_p | k_1 k_2 \cdots k_p) = \binom{N}{p}
\]

chemistry developed by Coulson and Longuet-Higgins,\textsuperscript{12} we will call $\gamma(k|k)$ the charge order of the spin-orbital $k$ and the coefficient $Y(l|k)$ for $k \neq l$ the bond order of the two spin-orbitals $k$ and $l$, hence associating the product of two spin-orbitals in (55) with a "bond" between them. The first-order density matrix $Y(k|l)$ in $k$-space is therefore also called the charge- and bond-order matrix. Similar concepts may be introduced also for the higher-order densities in $k$-space, and we note that the second-order density $\Gamma(k_1k_2|k_3k_4)$ correlates the charge and bond orders of two particles and maximum four spin-orbitals.

Due to the antisymmetry of each set of indices in the density matrices, we can conclude that, if two indices in the same set are equal, then the corresponding elements vanish. For the diagonal elements, we obtain in particular

$$\Gamma(k_1k_1) = 0, \quad \Gamma(k_3k_3) = 0, \ldots$$

(61)

showing that the probability for two particles to be in the same spin-orbital vanishes identically. This consequence of the antisymmetry requirement is an expression for Pauli's exclusion principle in $k$-space.

Let us now discuss the properties of the diagonal elements (60) in greater detail. Since our basic set $\psi_i(x)$ of one-particle functions is assumed to be orthonormal ($d_{ii} = \delta_{ii}$), the only nonvanishing elements in the basic determinant $D_{KL}$ defined by (39), appear for pairs $(k,l)$ referring to the same spin-orbital occurring in both ordered configurations $K$ and $L$ ($d_{ii} = 1$). Due to the ordering of the indices, these elements 1 may occur anywhere in the determinant, but, by interchanging rows and columns in a suitable way, they may be brought to the diagonal, which procedure changes the value of the original determinant and its minors only by a sign factor $+$ or $-$. If $K$ and $L$ are different ordered configurations, the diagonal contains also one or more elements which are zero, and in general, we therefore obtain the relation

$$D_{KL}(k_1k_2\cdots k_m|k_1k_2\cdots k_p) = \delta_{KL}.$$  

(62)

Substituting this expression into (56) and (58), we get finally for the diagonal elements (60):

$$\gamma(k) = \sum_{K} \frac{|C_K|^2}{\sum_{K} |C_K|^2},$$

(63)

$$\Gamma(k_1k_2\cdots k_m|k_1k_2\cdots k_p) = \sum_{K} \frac{|C_K|^2}{\sum_{K} |C_K|^2} \delta_{KL},$$

(66)

in agreement with the interpretation of $C$ as a "wave function" given before. However, we note that, since the quantities $|C_K|^2$ are all positive definite, (63) and (66) lead to the inequalities

$$0 \leq \gamma(k) \leq 1, \quad 0 \leq \Gamma(k_1k_2\cdots k_p) \leq 1,$$

(64)

showing that the charge order of a specific spin-orbital $k$ lies always between 0 and 1, and that it can assume the value 1, only if the spin-orbital $k$ occurs in all ordered configurations $K$, which are necessary in (54) for describing the total wave function characteristic for the physical situation under consideration. Similarly, the "combined charge order" for the group $(k_1,k_2,\cdots k_p)$ is always between 0 and 1, and it can assume the value 1, only if the group $(k_1,k_2,\cdots k_p)$ occurs in all ordered configurations $K$ necessary for describing the situation.

The charge order $\gamma(k)$ may be interpreted as the average number of particles in the spin-orbital $k$ in the physical situation under consideration; see also (59). Since the inequalities (64) are essentially depending on the antisymmetry requirement (1), this condition has here deeper consequences than the Pauli principle in its "naive" formulation, which considers only the occupation numbers 0 or 1. This problem will be further discussed in a following section.

3. METHOD OF CONFIGURATIONAL INTERACTION

In quantum mechanics we are particularly interested in finding the eigenvalues of the Hermitian operators $\Omega_{kk}$ corresponding to physical quantities, i.e., in solving the equation

$$\Omega_{kk}\Psi = \Psi.$$  

(65)

In order to discuss this problem, we will assume that the eigenfunction $\Psi$ exists and is normalizable. We will further introduce a complete orthonormal basic set of one-particle functions or spin-orbitals $\psi_i (k = 1, 2, \ldots)$. According to (30), the solution may now be expanded in a series of Slater determinants $\psi_i$ over all ordered configurations $K = (k_1,k_2,\cdots k_N)$ with $k_1<k_2<\cdots<k_N$:

$$\Psi = \sum_K \Psi_K C_K,$$

(66)

$$\Psi_K = (N!)^{-1} \det \{\psi_{i_1}\psi_{i_2}\cdots\psi_{i_N}\}.$$  

According to (28), the coefficients $C_K$ are the independent elements of an antisymmetric wave function $C(k_1,k_2,\cdots k_N)$ in $k$-space.

Every normalizable wave function $\Psi$ may be expanded in the same way, and, for the average value of $\Omega_{kk}$ with respect to such a wave function, we find therefore

$$\langle \Omega_{kk} \rangle_{\Psi} = \int \Psi^* \Omega_{kk} \Psi \; dx / \int \Psi^* \Psi \; dx = \sum_{KL} C_K^* \langle K | \Omega_{kk} | L \rangle C_L / \sum_{KL} C_K^* \delta_{KL} C_L,$$

(67)
where, according to (2) and (49), we have

\[ \langle K | \Omega_\alpha | L \rangle = \int \psi^*_\alpha(x_1) \Omega \psi(x_1) dx_1, \]

with the matrix notations

\[ \{ k | \Omega_\alpha | l \rangle = \int \psi^*_\alpha(x_1) \Omega \psi(x_1) dx_1, \]

\[ \{ k, l \} = \int \psi^*_\alpha(x_1) \psi(x_2) \Omega \psi(x_2) dx_1 dx_2, \]

\[ \{ k, l \} = \int \psi^*_\alpha(x_1) \psi(x_2) \Omega \psi(x_3) dx_1 dx_2 dx_3, \]

In order to determine the coefficients \( C_K \), i.e., the wave function in \( k \)-space, we will now apply the variation principle (22) to expression (68). This leads to a system of linear equations

\[ \sum_k \{ k | \Omega_\alpha | l \} = \Omega_{\alpha l}, \]

The condition for solubility is given by the secular equation

\[ \text{det} \{ K | \Omega_\alpha | L \} = 0, \]

which determines the eigenvalues \( \Omega \). The values of \( C_K \) may then be determined from the system (70), which may be considered as the representation of the eigenvalue problem (65) in \( k \)-space.

The many-body problem (65) is in this way reduced to a form which is essentially the same as in the one-particle problem; the Eqs. (70) and (71) are in both cases infinite. The method of "configurational interaction" is therefore in principle simple, but the analytical or numerical work necessary for evaluating the matrix elements (68) and for solving the Eqs. (70) and (71) is certainly still formidable. However, during the last few years, the work in several research groups has shown that it is practically possible to tackle the numerical problem of solving secular equations (70) of comparatively high orders by means of the modern electronic computers, and one can expect a steady development of the methods of programming, etc.

In this connection there are also two principal problems which have been put in the foreground, namely, firstly, how to determine the basic set of one-particle functions in such a way that the series (66) obtains as rapid convergence as possible, and, secondly, how to get simple physical interpretations of the complicated total wave functions derived in this way. In the next section, we will show that the theory of density matrices is useful for treating both these problems.

4. NATURAL SPIN-ORBITALS AND THE CONVERGENCE PROBLEM IN THE METHOD OF CONFIGURATIONAL INTERACTION

The many-particle problems, which have been solved with the greatest accuracy up till now, are connected with the theory of electronic structure of atoms, molecules, and crystals. In their treatments of atoms and molecules, Boys and Meckler and others have used the method of configurational interaction in an approximate form, and they have overcome the numerical difficulties by aid of electronic computers. However, their preliminary results are then rather complicated wave functions in configuration space, and one is still looking for simple physical interpretations. In this connection, we would like to point out the importance of the first, second, and higher order density matrices (3).

Let us start by considering only the first-order density matrix \( \gamma_{\alpha \beta} \), derived from the wave function according to (3) or (55). The corresponding matrix \( \gamma(l | k) \) in the \( k \)-space, i.e., the charge- and bond-order matrix, is Hermitean, and it is therefore possible to find a unitary matrix \( U \) which transforms this matrix to diagonal form with the eigenvalues \( n_{kl} = \hat{n}_k \):
According to (64) and (59), the occupation numbers fulfill the two conditions

\[ 0 \leq n_k \leq 1, \quad \sum_k n_k = N, \quad (75) \]

and we can therefore conclude that the particles must be distributed over more than \( N \) natural spin-orbitals with a limiting case, when they are occupying exactly \( N \) spin-orbitals. The condition for the limiting case may be expressed in the form

\[ \gamma^2 = \gamma, \quad \text{Tr}(\gamma) = N, \quad (76) \]

where \( \text{Tr}(\gamma) \) means the formation of the diagonal sum, for \( \gamma(l|k) \) has then exactly \( N \) eigenvalues equal to 1 and the remaining zero. If, in such a case, we would choose the natural spin-orbitals as our basic set, all configurations in expansion (66) must contain the fully occupied spin-orbitals, i.e., this expansion is reduced to a single Slater determinant. This would mean that, provided the necessary existence and convergence theorems for the solution \( \Psi \) are fulfilled, the relation \( \gamma^2 = \gamma \) in k- or \( x \)-space would form a sufficient condition for the possibility of reducing the total wave function to a single determinant, i.e., for the strict validity of the Hartree-Fock approximation. Our conclusion, which is based on Eqs. (63) and (64), is the reverse to a theorem previously shown by Dirac.\(^1\)

It is well known that, in a system where the particles show mutual interaction, the Hartree-Fock approximation is usually not strictly valid, and this means that, by the effect of this interaction, the occupation numbers are depressed below 1: \( 0 \leq n_k < 1 \). The corresponding Cayley-Hamilton equation for the matrix \( \gamma \) is then more complicated than the first relation (76).

We note that the antisymmetry requirement (1), which leads to the first condition (75), is here more general than Pauli's exclusion principle in its original form, which considers only the occupation numbers 0 or 1 and therefore explicitly must refer to the Hartree-Fock approximation. We note that part of the importance of the Hartree-Fock scheme depends on its physical simplicity and visuality connected with the fact that some changes of the system, as ionization and excitation, may be described as resulting from entire particles jumping from occupied to unoccupied spin-orbitals or to infinity. In this scheme, the natural spin-orbitals are identical with the ordinary Hartree-Fock functions, being undetermined on unitary transformations of the two groups of orbitals, associated with different spin types. Already at this stage, the numerical computations involved are extremely laborious, but, by aid of the modern electronic computers, it seems now possible to reach beyond this approximation. In a more exact theory, the circumstances are certainly more complicated,\(^16\) since the occupation numbers may lie between 0 and 1, and ionizations and excitations of the system are then accompanied by changes of the numbers \( n_k \) by fractions of 1 with possible changes also of the nondiagonal elements \( n_{kl} \). However, in a following paper, we will show that it is possible to preserve some of the simplicity and visuality of the Hartree-Fock scheme even in more exact treatments using the method of configurational interaction.

Let us now turn to the convergence problem connected with the expansion (66) after ordered configurations \( K \). It could happen that the arbitrarily chosen basic set \( \psi_b \) is inconvenient for its purpose, and the convergence of (66) is then correspondingly slow. In order to investigate the effect of introducing natural spin-orbitals \( \chi_b \), we will now carry out the matrix transformation \( \Psi = \chi U \), or

\[ \psi_b = \sum \chi_a U_{ab}. \quad (77) \]

By using a theorem\(^3\) for expanding a determinant of a matrix being a product of two rectangular matrices, we obtain the following transformation for the basic Slater determinants \( \Psi_K \) and \( \chi_L \):

\[ \Psi_K = \sum \chi_L A_{LK}, \quad \chi_L = (\xi^l)^{-1} \text{det}(\chi_1\chi_2\cdots\chi_N), \quad (78) \]

where

\[ A_{LK} = \begin{bmatrix}
U^t(\chi_{k1}) & \cdots & U^t(\chi_{kN}) \\
\cdots & \cdots & \cdots & \cdots \\
U^t(\chi_{nP}) & \cdots & U^t(\chi_{NP})
\end{bmatrix}. \quad (79) \]

By putting this formula into (66), the total wave function may instead be expanded in determinants \( \chi_L \) over all ordered configurations \( L \) of the natural spin-orbitals \( \chi_l \):

\[ \Psi = \sum \chi_L \left( \sum_K A_{LK} C_K \right). \quad (80) \]

In contrast to (66), we could call (80) the natural expansion of the total wave function.

Its convergence properties may now be understood from the relations (63), (64), and (74). In the limiting case, when exactly \( N \) natural spin-orbitals are fully occupied and the relation \( \gamma^2 = \gamma \) is fulfilled, the natural expansion (80) is reduced to a single Slater determinant. In considering the convergence, this is of course the most favorable case. However, if only a finite number of the occupation numbers \( n_L \) in (74) are essentially different from zero, the natural expansion (80) will be reduced to a sum of determinants over all ordered configurations associated with these essentially occurring spin-orbitals, i.e., to a sum of comparatively few terms. The introduction of natural spin-orbitals seems therefore to provide a simple solution of the convergence problem, previously discussed by Slater.\(^17\)

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15 T. Koopmans, Physica 1, 104 (1933).
16 The same complications will also occur, for instance, in an exact electron-positron theory, which is based on Dirac's original idea of a fully-occupied vacuum.
Quantum theory of many-particle systems.

Note added in proof.—It is desirable to have also a more exact mathematical measure for the rapidity of convergence of the two configurational interaction series (66) and (80). We note that, according to (60) and (63), the charge order \( \gamma(k) \) gives the probability for the ordinary spin-orbital \( \psi \) to occur in the expansion of the total wave function \( \Psi \). If only \( M \) of the numbers \( \gamma(k) \), \( k = 1, 2, 3, \cdots \), are essentially different from zero, then the number of essential terms in (66) is given by the corresponding number of possible configurations: \( M! / (M-N)! \). In using this procedure, however, it is necessary to evaluate the individual quantities \( \gamma(k) \) and to distinguish between essential and unessential charge orders.

A still simpler measure of convergence may be constructed by observing that the charge orders always lie between 0 and 1 and that, in the limiting cases \( \gamma(k) = 0 \) and \( \gamma(k) = 1 \), the corresponding spin-orbital \( \psi \) occurs in none or in all of the terms in (66), respectively, without contributing to the slowing down of the convergence of the series. The eventual slowness of the convergence of (66) depends instead on the possibility for an electron to be distributed over two or more spin-orbitals, giving charge orders of an intermediate order of magnitude, \( 0 < \gamma(k) < 1 \). The rapidity of convergence of (66) may therefore be measured by the smallness of an quantity \( \phi = (1/N) \sum (1-\gamma(k)) \gamma(k) = 1 - (1/N) \sum \gamma(k) \), which fulfills the inequality of 0 \( \leq \phi \leq 1 \). In considering different basic sets \( \psi_1, \psi_2, \psi_3, \cdots \) for the description of the same total wave function \( \Psi \), it is clear that the natural spin-orbitals \( \chi \) are characterized by having the smallest \( \phi \) value possible. According to (72), we have \( \gamma = \text{Un} \psi \) and \( \gamma = \text{Un} \psi \), leading to \( \text{Tr}(\gamma') = \text{Tr}(\psi') \). The necessity follows from Dirac's theorem (see reference 1) which proves our theorem. This means that the natural spin-orbitals \( \chi \) are distinguished not only by having vanishing bond densities may now be expressed in the natural spin-orbitals. The deviation from zero of the single number \( \phi \), \( \gamma(k) = \text{Un} \psi(Xl')XZ(Xl)Xl(Xl)Xl'(Xl)) \), which, for \( k \neq l \), lead to the existence of the well-known exchange effects associated with each pair of natural spin-orbitals \( \chi \). Higher-order densities may be treated analogously. The corresponding expansions in the general case (74) are slightly more complicated, but there are no principal difficulties in deriving them.

We note finally that the diagonal elements of the second-order matrix have previously been used successfully by, among others, Lennard-Jones in discussing correlation properties between electrons in atoms and molecules. In case of symmetric wave functions \( \Psi \), they have also been used by London in investigating the distance correlation in a Bose-Einstein gas.

5. Limited Configurational Interaction. Extended Hartree-Fock Equations

In the last three sections, we have assumed that the basic set \( \psi_k \) of one-particle functions is infinite and complete. An arbitrary normalizable function \( F(x_l' \mid x_l) \) may then be expressed by the expansion

\[
F(x_l' \mid x_l) = \sum \psi_k^*(x_l') \psi_k(x_l) F_{kl}.
\]

However, it is immediately clear that, in applications to particular problems, we must usually replace this set by a set of finite order \( M \). Since the basic set is then no longer complete, we meet the problem how to determine this set in order to obtain a solution (66) to (65), which is as accurate as possible. In the case \( M = N \), this leads to the ordinary Hartree-Fock problem, but, if \( M > N \), it leads to an extension of this scheme recently proposed by Slater.

Let us assume that \( M \geq N \) and that our basic set \( \{k = 1, 2, \cdots M\} \) is orthonormal,

\[
\int \psi_k^* \psi_l \, dx = \delta_{kl},
\]

which imposes an orthogonality condition on the

\[ ^{18} \text{J. Lennard-Jones, J. Chem. Phys. 29, 1024 (1952); J. Len­nard-Jones and J. A. Pople, Phil. Mag. 43, 581 (1952).} \]
\[ ^{19} \text{F. London, J. Chem. Phys. 11, 203 (1943).} \]
\[ ^{20} \text{J. C. Slater, see reference 17. Compare also J. Frenkel, Wave Mechanics, Advanced General Theory Clarendon Press, Oxford, (1934), pp. 460-462, who has treated the same problem by the method of second quantization.} \]
orbitals belonging to the same spin type. We will further characterize our basic set by a projection matrix \( \varrho \) defined by
\[
\rho(x_1, x_2) = \sum_{k=1}^{M} \psi_k^*(x_1) \psi_k(x_2). \tag{84}
\]
We observe that, since \( \varrho \) fulfills the relations
\[
\int \rho(x_1, x_2) \rho(x_1, x_3) dx_1 = \rho(x_1, x_2), \quad \int \rho(x_1, x_3) dx_2 = M,
\]
or
\[
\varrho^2 = \varrho, \quad \text{Tr}(\varrho) = M, \tag{85}
\]
it has really the character of a projection operator. In the case \( M = N \), it is identical with Dirac's density matrix, but it must not be confused with this matrix for \( M > N \). It is now no longer possible to obtain an exact expansion (82) of an arbitrary function \( F(x'_1| x_i) \), we have to be satisfied with the approximate form
\[
f(x'| x_i) = \sum_{k=1}^{M} \psi_k^*(x_1) \psi_k(x_i) F_{k}. \tag{86}
\]
The function \( f(x'| x_i) \), defined by this interrupted expansion, is said to represent the orthogonal projection of the function \( F(x'_1| x_i) \) on the subspace of the general Hilbert space, defined by the basic set \( \psi_k (k = 1, 2, \cdots M) \).

We note the validity of the matrix relation
\[
\varrho = \varrho F \varrho, \tag{87}
\]
which shows the use of the projection operator \( \varrho \). For every function \( f(x'| x_i) \) which is expandable in the basic set \( \psi_k \), i.e., which belongs to the subspace defined by this set, we have further
\[
f = \varrho f = f_0 = \varrho f_0. \tag{88}
\]
Let us now again study the eigenvalue problem (65). In expansion (66) of the solution \( \psi \), both the coefficients \( C_k \) and the basic spin-orbitals \( \psi_k (k = 1, 2, \cdots M) \) are undetermined, and, in order to derive the best approximation of the solution, we will apply the variation principle (22). According to (10), (57), and (58), we have
\[
\langle \Omega_{\text{opt}} \rangle = \Omega_{(0)} + \sum_{k, l} \langle k | \Omega_1 | l \rangle \gamma (l | k)
\]
\[
+ \sum_{k, l, m} \langle k | \Omega_2 | l \rangle \Gamma (l | m) \langle m | k \rangle
\]
\[
+ \sum_{k, l, m} \langle k | \Omega_3 | l \rangle \Omega_2 (l | m) \langle m | k \rangle
\]
\[
\times \Gamma (3) (l | m) \langle m | k \rangle \langle k | l \rangle + \cdots, \tag{89}
\]
where the matrix elements are defined by (69). Variation of the coefficients \( C_k \) leads to Eqs. (70) and (71), and variation of the basic set \( \psi_k \) leads to extended Hartree-Fock equations of the form
\[
\sum_l \Omega_{\psi} (x_l) \gamma (l | k)
\]

\[
+ 2 \sum_{l} \sum_{k, l} \langle \psi_k^* (2) \Omega_1 \psi_l (2) \rangle dx_2 \psi_l (x_1) \Gamma (l | k) dx_2
\]

\[
+ 3 \sum_{l} \sum_{l, m} \langle \psi_k^* (2) \psi_m^* (3) \Omega_2 \psi_l (2) \psi_l (3) \rangle dx_2 dx_3
\]

\[
\times \psi_l (x_1) \Gamma (3) (l | m) \langle m | k \rangle + \cdots = \sum_l \psi_l (x_l) \lambda (l | k). \tag{90}
\]
The quantities \( \lambda (l | k) \) are here the Lagrangian multipliers associated with the orthonormality condition (83). Since spin-orbitals with different spins are automatically orthogonal, the multipliers \( \lambda (l | k) \) may be different from zero only for spin-orbitals \( k \) and \( l \) associated with the same spin type. Since further the quantity
\[
\sum_{kl} \lambda (l | k) \delta \int \psi_k^* \psi dx
\]

\[
\int \Omega_{\psi} (x_l) \gamma (l | k)
\]

\[
+ 2 \sum_{l} \sum_{k, l} \langle \psi_k^* (2) \Omega_1 \psi_l (2) \rangle dx_2 \psi_l (x_1) \Gamma (l | k) dx_2
\]

\[
+ 3 \sum_{l} \sum_{l, m} \langle \psi_k^* (2) \psi_m^* (3) \Omega_2 \psi_l (2) \psi_l (3) \rangle dx_2 dx_3
\]

\[
\times \psi_l (x_1) \Gamma (3) (l | m) \langle m | k \rangle + \cdots = \sum_l \psi_l (x_l) \lambda (l | k) \tag{91}
\]

must be real, we can conclude that the multipliers \( \lambda (l | k) \) form an Hermitean matrix: \( \lambda (k | l) = \lambda^* (l | k) \).

By multiplying Eqs. (90) for each \( k \) by \( \psi_k^* (\xi'_1) \) and by summing \( k \) from 1 to \( M \), we may express the extended Hartree-Fock equations in the more condensed form
\[
\Omega_{\psi} (\xi'_1| x_i) = \sum_{l} \Omega_{\psi} (\xi'_1| x_i) \psi_l (x_l) dx_2
\]

\[
+ 2 \sum_{l} \sum_{k, l} \langle \psi_k^* (2) \Omega_1 \psi_l (2) \rangle dx_2 \psi_l (x_1) \Gamma (l | k) dx_2
\]

\[
+ 3 \sum_{l} \sum_{l, m} \langle \psi_k^* (2) \psi_m^* (3) \Omega_2 \psi_l (2) \psi_l (3) \rangle dx_2 dx_3
\]

\[
\times \psi_l (x_1) \Gamma (3) (l | m) \langle m | k \rangle + \cdots = \sum_l \psi_l (x_l) \lambda (l | k). \tag{92}
\]

where we have assumed that the operators \( \Omega_1, \Omega_2, \Omega_3, \cdots \) etc. do not work on the variables \( \xi'_1, x'_1, x'_2, \cdots \). After the operations in the integrands have been carried out, we shall as before put all \( x'_1 = x_0 \), whereas \( \xi'_1 \) may have an arbitrary value. The function \( \lambda (\xi'_1| x_i) \) in the right-hand member is here given by the Lagrangian multipliers:
\[
\lambda (\xi'_1| x_i) = \sum_{k, l} \langle k | \psi_l (x_l) \rangle \lambda (l | k). \tag{93}
\]
We note that, in Eq. (92), the left-hand member is entirely independent of \( M \), and this form is therefore convenient for discussing the transition from \( M = N \) to \( M = \infty \). The function (93) may be considered as the "projection" of an arbitrary Hermitean function \( \lambda (\xi'_1| x_i) \) on the subspace defined by the basic set of order \( M \):
\[
\lambda = \varrho \lambda. \tag{94}
\]
It is apparently this relation which gives the essential condition for determining the best set of a finite order.
However, in the limiting case when $M \to \infty$ and the set tends to be complete, we have

$$\lim_{M \to \infty} \rho(x_1, x_2) = \delta(x_1 - x_2),$$

(95)

and relation (94) is then changed into the identity $A = A$. This means that, in the limiting case, the extended Hartree-Fock equations (92) lose their meaning as a restraining condition on the basic set $\psi_\alpha$, which may then be chosen arbitrarily, in agreement with our previous assumptions.

Let us now turn back to the case of a finite order $M$. The quantities $\gamma(\xi'_1 | x_1)$ and $\lambda(\xi'_1 | x_1)$ in (92) are quadratic forms with Hermitian coefficients, and the question is whether we can bring them to diagonal forms. In the case when $M = N$, the first-order density $\gamma(\xi'_1 | x_1)$ is from the very beginning on diagonal form, and it is then possible to determine a unitary transformation of the basic set which brings also the matrix $\lambda(\xi'_1 | x_1)$ to diagonal form. This is a conventional procedure in the ordinary Hartree-Fock scheme, and the eigenvalues of the matrix $\lambda(\xi'_1 | x_1)$ are called the orbital energies of the basic spin-orbitals $\phi_k$.

However, if $M > N$, the first order density matrix $\gamma(\xi'_1 | x_1)$ may be brought to diagonal form (74) first by introducing the natural spin-orbitals $\chi_k$, and, only if several occupation numbers $n_k$ are the same with a corresponding degeneracy in the spin-orbitals $\phi_k$, we have any additional transformations free for changing the form of $\lambda(\xi'_1 | x_1)$, too. In general, we cannot therefore expect that it should always be possible to bring $\gamma(\xi'_1 | x_1)$ and $\lambda(\xi'_1 | x_1)$ simultaneously to diagonal form.

In order to consider the natural spin-orbitals in greater detail, we will start from (92) and rewrite the extended Hartree-Fock equations (90) in the form

$$\int \psi_k(\xi'_1) \Omega \gamma(\xi'_1 | x_1) d\xi'_1$$

$$+ 2 \int \psi_k(\xi'_1) \Omega \lambda(\xi'_1 | x_2 | x_1 x_2) d\xi'_1 dx_2$$

$$+ 3 \int \psi_k(\xi'_1) \Omega \lambda(\xi'_1 | x_3 | x_1 x_2 x_3) d\xi'_1 dx_2 dx_3 + \cdots$$

$$= \int \psi_k(\xi'_1) \lambda(\xi'_1 | x_1) d\xi'_1.$$  

(96)

Carrying out the transformation (77) to natural spin-orbitals $\chi_k$ and dividing by $n_k \neq 0$, we obtain

$$\Omega \chi_k(x_1) + 2n_k^{-1} \int \chi_k(\xi'_1) \Omega \lambda(\xi'_1 | x_2 | x_1 x_2) d\xi'_1 dx_2$$

$$+ 3n_k^{-1} \int \chi_k(\xi'_1) \Omega \lambda(\xi'_1 | x_3 | x_1 x_2 x_3)$$

$$\times d\xi'_1 dx_2 dx_3 + \cdots = \sum_{l=1}^M \chi_l(x_1) \lambda(l | k) n_k^{-1},$$  

(97)

where $\lambda' = U' \lambda U$. This is the exact integro-differential equation satisfied by the natural spin-orbitals, which previously are shown to lead to the most rapid convergence of the expansion (66).

**Connection with Slater's Extension of the Hartree-Fock Equations**

In some recent work, which has appeared only in preprints, Slater has investigated the convergence problem in the method of configurational interaction, and he has intuitively proposed that the basic set of one-particle functions, which would lead to the most rapid convergence, should satisfy an extended form of the Hartree-Fock equations. Since we have here shown that this set satisfies (97), it is of interest to investigate the connection with Slater's equation.

Equation (97) may also be written in the form

$$\{ \Omega + V_{op}(1) \} \chi_k(1) = \sum_{l=1}^M \chi_l(1) \lambda'(l | k) n_k^{-1},$$  

(98)

where $V_{op}$ is a rather complicated operator containing ordinary potentials as well as exchange operators. Since $V_{op}$ does not commute with the coordinate $x$, these two quantities are usually not compatible. However, in order to obtain the connection with Slater's approach, we will now replace $V_{op}$ by its "best approximation" in $x$-space:

$$V_{op} \chi_k(x_1) = V(x_1) \chi_k(x_1), \quad k = 1, 2, \ldots, M$$  

(99)

which may be defined by the condition that the sum

$$\sum_{k=1}^M | V_{op} \chi_k(x_1) - V(x_1) \chi_k(x_1) |^2,$$

(100)

should be as small as possible. The quantities $n_k$ are here appropriate weights, and, for the natural spin-orbitals, it seems natural to choose them as being just the occupation numbers: $n_k = n_k$. In this way, using the minimum condition, we obtain

$$V(x_1) = \frac{\sum_{k=1}^M n_k \chi_k^*(x_1) V_{op} \chi_k(x_1)}{\sum_{k=1}^M n_k \chi_k^*(x_1) \chi_k(x_1)}.$$  

(101)

According to (74), the quantity in the denominator is just the first-order density $\gamma(x_1 | x_1)$. Using (97) and (98), and observing the validity of the relations

$$\int \rho(x_1, \xi'_1) \Gamma(\xi'_1 \xi'_2 | x_1 x_2) d\xi'_1 = \Gamma(x_1 x_2 | x_1 x_2),$$

(102)

$$\int \rho(x_1, \xi'_1) \Gamma(\xi'_1 \xi'_2 | x_1 x_2 x_3) d\xi'_1 = \Gamma(x_1 x_2 x_3 | x_1 x_2 x_3),$$

the quantity in the numerator is

$$\sum_{l=1}^M \chi_l(x_1) \lambda'(l | k) n_k^{-1},$$

(100)
we get finally for the "average potential" \( V(\mathbf{x}_i) \):

\[
V(\mathbf{x}_i) = 2 \int \Omega_{12} \Gamma(x'_1 x'_2 | x_1 x_2) dx_2 / \gamma(x_1) + 3 \int \Omega_{123} \Gamma(x'_1 x'_2 x'_3 | x_1 x_2 x_3) dx_2 dx_3 / \gamma(x_1) + \cdots
\]

Equation (97) may therefore be replaced by the approximate form

\[
\{ \Omega_i + V(\mathbf{x}_i) \} \chi_i(\mathbf{x}_i) = \sum_{l=1}^{M} \chi_l(\mathbf{x}_i) \lambda'(l \mid k)n_k^{-1}.
\]

Since the operator \( (H_1 + V_1) \) is Hermitian, the same must hold also for the matrix \( \lambda'(l \mid k)n_k^{-1} \) in the right-hand member, which implies that, in this approximation, there can be \( \lambda' \)-couplings only between natural spin-orbitals having the same occupation number. However, each such group is degenerate and, by carrying out a suitable unitary transformation, we may then also bring the matrix \( \lambda'(l \mid k)n_k^{-1} \) to diagonal form. Instead of the rather complicated Eq. (97), we have now obtained an approximate representation in the form of an eigenvalue problem

\[
\{ \Omega_i + V(\mathbf{x}_i) \} \chi_i(\mathbf{x}_i) = \omega_0 \chi_i(\mathbf{x}_i),
\]

where \( V(\mathbf{x}_i) \) is the "average potential" given by (103).

We are now ready to carry out a comparison with the extended Hartree-Fock equations intuitively proposed by Slater.\(^\text{17}\) Since we are then mainly interested in electronic systems, the basic Hamiltonian is of the specific form (11), with \( \Omega_{ij} = \delta_{ij} / r_{ij}, \Omega_{ik} = 0, \cdots, \) etc. According to (103), we get for the "average potential"

\[
V(\mathbf{x}_i) = 2 \epsilon_d \int \frac{\Gamma(x_1 x_2) / \gamma(x_1)}{r_{12}} dx_2,
\]

which is just the potential discussed by Slater. Our procedure, based on the minimization of (100), gives then a strict derivation of this potential for \( M \geq N \)

Hence we obtain also a new derivation of Slater's average exchange potential\(^\text{22}\) in the ordinary Hartree-Fock scheme with \( M = N \).

As Slater has pointed out, the approximate form (105) is much more convenient to handle numerically than the exact Eqs. (97) containing exchange operators and leading to coupled integro-differential equations of a rather complicated type. Since the approximation also seems to be very good, as shown, e.g., by Pratt\(^\text{23}\) for the case of \( M = N \), it seems feasible for most applications to use (105) instead of (97). However, for investigating the convergence problem, it is not necessary to solve neither (105) nor (97), since this problem is now simply treated by the diagonalization (74) of the first-order density matrix, leading automatically to the natural spin-orbitals.

6. CONCLUSIONS

In the case in which our basic set of one-particle functions is chosen infinite and complete, we have shown that, in principle, the fundamental problems in the many-particle theory may be solved in a simple way: the eigenfunctions to (65) may be determined by the method of configurational interaction, which leads to a system of linear equations (70) with a secular equation (71) for determining the eigenvalues, and the convergence problem may then be treated by the diagonalization (74) of the first-order density matrix and the introduction of natural spin-orbitals.

However, the discussion in the previous section shows that, if our basic set is only of a finite order \( M \), the circumstances are much more complicated. The conditions for determining the best choice of this set of order are nonlinear integro-differential equations of the type (92) or of the approximate form (105), which may be solved only numerically by successive approximations by using the method of "self-consistent-fields." In the case \( M = N \), i.e., in the ordinary Hartree-Fock scheme, it is certainly worthwhile to try to carry out this numerical procedure, since the corresponding solution has a physical simplicity and visuality of great importance. However, in the case \( M > N \), it can be discussed whether it is worth the trouble to solve the complicated nonlinear equations (92) even in their simplified form (105). Instead it seems better to try to introduce an orthonormal set of considerably higher order than \( M \), where the limitation is given only by the capacity of the electronic computer or mathematical machine available, and to solve the algebraic secular equation (71) and the linear system (70). Afterwards, by transformation to natural spin-orbitals, one may then try to diminish the order of the basic set by taking only those spin-orbitals into account which have occupation numbers essentially different from zero. The number \( M \) of essential spin-orbitals, found in this way, is characteristic for the system and may serve for defining "closed shells," etc., in a more exact theory.

Our discussion could give the impression that it would be entirely meaningless to use any form of extended Hartree-Fock equations in the method of configurational interaction. However, in a following paper, we will show that, in treating degenerate systems and correlation effects, it is possible to extend the ordinary Hartree-Fock scheme for \( M = N \) to include a specific form of "fixed" configurational interaction based on the use of projection operators. The total wave function is here defined as the "projection" of a single determinant, and the basic set in this determinant of order \( M = N \) is determined by an ordinary Hartree-Fock equation associated with a "composite" Hamiltonian, modified to take the degeneracy into proper

\(^{17}\) J. C. Slater, Phys. Rev. 81, 385 (1951).

account. This form of "fixed" configurational interaction has the advantage that it is possible to preserve some of the physical simplicity and visuality of the ordinary Hartree-Fock scheme.

APPENDIX I

An Integral Formula

Let $\Psi_0$ be an approximate (or exact) solution to the Schrödinger equation (21), which does not possess the correct symmetry property. Since $\Omega_\psi$ is symmetric in the coordinates, every function $P\Psi_0$ is then also a solution of the same type, and the linear combination

$$\Psi_{AS} = (N!)^{-1} \sum_{\rho} (-1)^p P\Psi_{\rho},$$

(107)

summed over all $N!$ permutations $P$ ($\rho$ being the parity), has the correct antisymmetry character. This new wave function is simple to deal with in calculations, for, if $\Phi$ is an arbitrary antisymmetric function obtained, e.g., by letting a symmetric operator work on an antisymmetric wave function, we obtain

$$\int \Psi_{AS}^{*}\Phi(dx) = (N!)^{-1} \sum_P (-1)^p \int P^{*}\Psi_{\rho}^{*}\Phi(dx)$$

$$= (N!)^{-1} \sum_P (-1)^p \int \Psi_{\rho}^{*}P^{*}\Phi(dx)$$

$$= (N!)\int \Psi_{\rho}^{*}\Phi(dx),$$

(108)

since the sum over all $P$ contains $N!$ identical terms. We get therefore the basic formula:

$$\int \Psi_{AS}^{*}\Phi(dx) = (N!)^{-1} \int \Psi_{\rho}^{*}\Phi(dx),$$

(109)

which is of value in treating wave functions $\Psi_0$ built on simpler elements, as one- or two-particle functions.