a/L is small, the steady state saturation voltage is proportional to the surface recombination velocity σ; when a/L is large, the saturation voltage is independent of σ 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 ν_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, $F_1' \gg F_2'$, 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.,[3] the dependence of the transient behavior on the specimen parameters appears to be too complicated to afford a method for their determination.

ACKNOWLEDGMENT

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 ψ_k, 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.

IN the nonrelativistic quantum theory of many-particle systems, the basic Schrödinger equation refers to a configuration space having a dimension proportional to the number of particles. Even if it is possible to find a solution with sufficient accuracy by aid of for instance modern electronic computers, this wave function is usually too complicated to provide a simple physical picture of the system. The aim of this paper is to give a discussion of the interpretation problem, and we will show that it is possible to define a series of density matrices, which have a simpler and more direct physical meaning than the wave function itself. Dirac[1] has previously introduced a density matrix for describing a system in the Hartree-Fock scheme, where the total wave function is approximated by a single Slater determinant, but the idea will here be essentially generalized in order to include the treatment of exact or approximate wave functions of arbitrary

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[1] P. A. M. Dirac, Proc. Cambridge Phil. Soc. **26**, 376 (1930); **27**, 240 (1931). See also J. E. Lennard-Jones, Proc. Cambridge Phil. Soc. **27**, 469 (1931), and V. Fock, Z. Physik **61**, 126 (1930).

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, $\cdots x_N$ 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 Ψ, which we assume to be normalized. It fulfills the antisymmetry condition

$$P\Psi(x_1,x_2,\cdots x_N)=(-1)^p\Psi(x_1,x_2,\cdots x_N), \quad (1)$$

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

$$(dx)=dx_1dx_2\cdots dx_N$$

indicate integration-summation over all coordinates, (dx_i') the same procedure over all coordinates except x_i, (dx_{ij}') the same over all coordinates except x_i and x_j, etc.

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

$$\Omega_{\text{op}}=\Omega_{(0)}+\sum_i \Omega_i+\frac{1}{2!}\sum_{ij}' \Omega_{ij}+\frac{1}{3!}\sum_{ijk}' \Omega_{ijk}+\cdots, \quad (2)$$

where each term is a zero-, one-, two-, three-, $\cdots$, 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 Ψ, we will now introduce a series of *density matrices* of various orders:

$$\gamma(x_1'|x_1)=N\int \Psi^*(1'23\cdots N)\Psi(123\cdots N)(dx_1'),$$

$$\Gamma(x_1'x_2'|x_1x_2)$$

$$=\binom{N}{2}\int \Psi^*(1'2'3\cdots N)\Psi(123\cdots N)(dx_{12}'),$$

. . . .

$$\Gamma^{(p)}(x_1'x_2'\cdots x_p'|x_1x_2\cdots x_p)$$

$$=\binom{N}{p}\int \Psi^*(1'2'3'\cdots p'\cdots N)$$
$$\times\Psi(123\cdots p\cdots N)(dx_{12}'\cdots p), \quad (3)$$

. . . .

$$\Gamma^{(N)}(x_1'x_2'\cdots x_N'|x_1x_2\cdots x_N)$$
$$=\Psi^*(1'2'3'\cdots N')\Psi(123\cdots N),$$

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

$$\Gamma(x_1x_2|x_1'x_2')=\Gamma^*(x_1'x_2'|x_1x_2),$$
$$\Gamma(x_2'x_1'|x_1x_2)=-\Gamma(x_1'x_2'|x_1x_2), \quad (4)$$

and they are further related by the formula,

$$\Gamma^{(p-1)}(x_1'x_2'\cdots x_{p-1}'|x_1x_2\cdots x_{p-1})$$

$$=\frac{p}{N+1-p}\int \Gamma^{(p)}(x_1'x_2'\cdots x_{p-1}'x_p|$$
$$x_1x_2\cdots x_{p-1}x_p)dx_p. \quad (5)$$

Of special importance are the diagonal elements:

$$\gamma(x_1)=\gamma(x_1|x_1),$$
$$\Gamma(x_1,x_2)=\Gamma(x_1x_2|x_1x_2), \quad (6)$$

. . . .

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: $\gamma(x_1)dv_1=$ number of particles $\times$ the probability for finding a particle within the volume dv_1 around the point r_1 having the spin s_1, etc., when all the other particles have arbitrary positions and spins; $\Gamma(x_1x_2)dv_1dv_2=$ number of pairs $\times$ the probability for finding one particle within the volume dv_1 around the point r_1 with the spin s_1, etc., and another within the volume dv_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

$$\int \gamma(x_1)dx_1=N, \quad \int \Gamma(x_1x_2)dx_1dx_2=N(N-1)/2,$$

$$\int \Gamma^{(p)}(x_1x_2\cdots x_p)dx_1dx_2\cdots dx_p=\binom{N}{p}. \quad (7)$$

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:

$$\Gamma(x_1,x_1)=0, \quad \Gamma^{(3)}(x_1,x_2,x_2)=0, \quad \cdots \quad (8)$$

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

[2] See, for instance, E. Wigner and F. Seitz, Phys. Rev. **43**, 804 (1933); and J. C. Slater, Phys. Rev. **81**, 385 (1951).

operator term in (2). By changing names of the integration variables and using the symmetry properties, we obtain

$$\int \Psi^*(\tfrac{1}{2}\sum_{ij}{}' \Omega_{ij})\Psi (dx)$$

$$=\tfrac{1}{2}N(N-1)\int \Psi^*\Omega_{12}\Psi (dx)$$

$$=\binom{N}{2}\int \{\Psi^*(1'2'3\cdots N)\Omega_{12} \qquad (9)$$

$$\times\Psi(123\cdots N)\}_{x_1'=x_1,\ x_2'=x_2}dx_1dx_2(dx_{12}')$$

$$=\int \{\Omega_{12}\Gamma(\mathbf{x}_1'\mathbf{x}_2'|\mathbf{x}_1\mathbf{x}_2)\}_{x_1'=x_1,\ x_2'=x_2}dx_1dx_2.$$

In treating the density matrices, we will introduce the convention that the operators Ω_{ij} will work only on the unprimed coordinates $\mathbf{x}_i$, $\mathbf{x}_j$, etc., but *not* on $\mathbf{x}_i'$, $\mathbf{x}_j'$, etc., and that, after the operations have been carried out, we have to put $\mathbf{x}_i'=\mathbf{x}_i$, $\mathbf{x}_j'=\mathbf{x}_j$, etc. 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

$$\langle\Omega_{\mathrm{op}}\rangle_{\mathrm{Av}}=\int \Psi^*\Omega_{\mathrm{op}}\Psi (dx)$$

$$=\Omega_{(0)}+\int \Omega_1\gamma(\mathbf{x}_1'|\mathbf{x}_1)dx_1$$

$$+\int \Omega_{12}\Gamma(\mathbf{x}_1'\mathbf{x}_2'|\mathbf{x}_1\mathbf{x}_2)dx_1dx_2$$

$$+\int \Omega_{123}\Gamma(\mathbf{x}_1'\mathbf{x}_2'\mathbf{x}_3'|\mathbf{x}_1\mathbf{x}_2\mathbf{x}_3)dx_1dx_2dx_3+\cdots. \quad (10)$$

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:

$$\mathfrak{IC}_{\mathrm{op}}=\frac{e^2}{2}\sum_{gh} Z_gZ_h/r_{gh}+\sum_i\left\{\frac{\mathbf{p}_i^2}{2m}-e^2\sum_g Z_g/r_{ig}\right\}$$

$$+\tfrac{1}{2}\sum_{ij}{}' e^2/r_{ij}, \quad (11)$$

where Z_g 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.

$$\langle\mathfrak{IC}_{\mathrm{op}}\rangle_{\mathrm{Av}}=\frac{e^2}{2}\sum_{gh} Z_gZ_h/r_{gh}+\frac{1}{2m}\int \mathbf{p}_1^2\gamma(x_1'|x_1)dx_1$$

$$-e^2\sum_g Z_g\int \frac{\gamma(x_1)}{r_{1g}}dx_1+e^2\int \frac{\Gamma(x_1,x_2)}{r_{12}}dx_1dx_2, \quad (12)$$

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 $\Gamma(\mathbf{x}_1'\mathbf{x}_2'|\mathbf{x}_1\mathbf{x}_2)$, 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 $\hbar$ of a system of N antisymmetric particles. According to Dirac,[3] we have

$$S^2=\sum_{ij}\mathbf{S}_i\cdot\mathbf{S}_j$$

$$=-N(N-4)/4+\sum_{ij}{}'(1+\mathbf{\sigma}_i\cdot\mathbf{\sigma}_j)/4 \quad (13)$$

$$=-N(N-4)/4+\tfrac{1}{2}\sum_{ij}{}' P_{ij}{}^\sigma,$$

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

$$\langle S^2\rangle_{\mathrm{Av}}=-N(N-4)/4$$

$$+\int \Gamma(\mathbf{r}_1s_1,\mathbf{r}_2s_2|\mathbf{r}_1s_2,\mathbf{r}_2s_1)dx_1dx_2, \quad (14)$$

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 $\mathbf{D}$,

$$\mathbf{D}=e\sum_i \mathbf{r}_i. \quad (15)$$

According to (10), its average value for a particular situation is given by the diagonal elements of the first-order density matrix:

$$\langle\mathbf{D}\rangle_{\mathrm{Av}}=e\int \mathbf{r}_1\gamma(\mathbf{x}_1)dx_1. \quad (16)$$

In this connection we observe that we shall sometimes need quantities which are related to the *transition* of the system between two orthogonal states, I and II, which are characterized by the normalized wave functions Ψ_{I} and Ψ_{II}. In analogy to (3), we will for this

[3] P. A. M. Dirac, Proc. Roy. Soc. (London) A123, 714 (1929).

purpose define the *transition matrices*:

$$\gamma_{\text{I II}}(\mathbf{x_1}'|\mathbf{x_1})$$

$$= N \int \Psi_{\text{I}}^*(1'23\cdots N)\Psi_{\text{II}}(123\cdots N)(dx_1'),$$

$$\Gamma_{\text{I II}}(\mathbf{x_1}'\mathbf{x_2}'|\mathbf{x_1}\mathbf{x_2})$$

$$= \binom{N}{2}\int \Psi_{\text{I}}^*(1'2'3\cdots N)\Psi_{\text{II}}(123\cdots N)(dx_{12}'),$$

(17)

$$\cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot$$

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

$$\langle\text{I}|\Omega_{\text{op}}|\text{II}\rangle = \int \Psi_{\text{I}}^*\Omega_{\text{op}}\Psi_{\text{II}}(dx)$$

$$= \int \Omega_1\gamma_{\text{I II}}(\mathbf{x_1}'|\mathbf{x_1})dx_1$$

(18)

$$+ \int \Omega_{12}\Gamma_{\text{I II}}(\mathbf{x_1}'\mathbf{x_2}'|\mathbf{x_1}\mathbf{x_2})dx_1dx_2 + \cdots.$$

For the transition moment, we obtain, in particular,

$$\langle\text{I}|D|\text{II}\rangle = e\int \mathbf{r_1}\gamma_{\text{I II}}(\mathbf{x_1})dx_1.$$

(19)

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

$$\langle\Omega_{\text{op}}\rangle_{\text{Av}}$$

$$= \frac{\int\left\{\Omega_{(0)}+N\Omega_1+\binom{N}{2}\Omega_{12}\right\}\Gamma(\mathbf{x_1}'\mathbf{x_2}'|\mathbf{x_1}\mathbf{x_2})dx_1dx_2}{\int\Gamma(\mathbf{x_1}\mathbf{x_2})dx_1dx_2},$$

(20)

where, in agreement with the convention introduced in connection with (9), we have to put $\mathbf{x_1}'=\mathbf{x_1}$ and $\mathbf{x_2}'=\mathbf{x_2}$ 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 Ψ 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,

$$\Omega_{\text{op}}\Psi = \mathcal{W}\Psi,$$

(21)

and may also be derived from the variation principle,

$$\delta\langle\Omega_{\text{op}}\rangle_{\text{Av}} = 0,$$

(22)

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 that, in the Hartree-Fock scheme where the total wave function is approximated by a single Slater determinant, the *first-order* density matrix $\gamma(\mathbf{x_1}'|\mathbf{x_1})$ 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 $\psi_k(\mathbf{x})$ ($k=1, 2, 3, \cdots$) of such a type that every normalizable function $\psi(\mathbf{x})$ of a single coordinate $\mathbf{x}$ may be expanded in the form

$$\psi(\mathbf{x}) = \sum_k \psi_k(\mathbf{x})c_k, \quad c_k = \int \psi(\mathbf{x_1})\psi_k^*(\mathbf{x_1})dx_1.$$

(23)

Following Slater,[5] we will here include all spin properties explicitly in the wave functions, and the one-particle functions $\psi_k(\mathbf{r},s)$ are therefore *spin-orbitals*, obtained by multiplying two complete orthonormal sets of orbitals (being functions only of $\mathbf{r}$) 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

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[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 $\psi_k(\mathbf{x}_i)$ for each coordinate $\mathbf{x}_i$ $(i=1, 2, \cdots N)$ and by successively applying (23), we may now expand every normalizable function Ψ in configuration space in the following form:

$$\Psi(\mathbf{x}_1,\mathbf{x}_2,\cdots\mathbf{x}_N)=\sum_{k_1 k_2\cdots k_N}\psi_{k1}(\mathbf{x}_1)\psi_{k2}(\mathbf{x}_2)\cdots$$
$$\times\psi_{kN}(\mathbf{x}_N)C(k_1, k_2, \cdots k_N),\quad (25)$$

$$C(k_1,k_2,\cdots k_N)=\int\Psi(12\cdots N)\psi_{k1}^*(1)$$
$$\times\psi_{k2}^*(2)\cdots\psi_{kN}^*(N)(dx).$$

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

$$PC(k_1,k_2,\cdots k_N)=(-1)^pC(k_1,k_2,\cdots k_N). \quad (26)$$

A selection of N indices k_1, k_2, $\cdots k_N$ 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 $C(k_1,k_2,\cdots k_N)$ may be considered as the representation of the *wave function* in the k-space, and we note that it fulfills the normalization condition

$$\sum_{k_1 k_2\cdots k_N}|C(k_1 k_2\cdots k_N)|^2=\int|\Psi|^2(dx). \quad (27)$$

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, $\cdots k_N$ 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

$$C_K=(N!)^{\frac{1}{2}}C(k_1,k_2,\cdots k_N), \quad (28)$$

for then the normalization condition (27) takes the form

$$\sum_K|C_K|^2=\int|\Psi|^2(dx), \quad (29)$$

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, $\cdots k_N$ and by using (26) and (28), we

may now rearrange this expansion in the following way:

$$\Psi(\mathbf{x}_1,\mathbf{x}_2,\cdots\mathbf{x}_N)$$
$$=(N!)^{-1}\sum_P P_k\sum_{k_1 k_2\cdots k_N}\psi_{k1}(\mathbf{x}_1)\psi_{k2}(\mathbf{x}_2)\cdots$$
$$\times\psi_{kN}(\mathbf{x}_N)C(k_1 k_2\cdots k_N)$$
$$=(N!)^{-1}\sum_{k_1 k_2\cdots k_N}C(k_1 k_2\cdots k_N)\sum_P(-1)^p P_k$$
$$\times\psi_{k1}(\mathbf{x}_1)\psi_{k2}(\mathbf{x}_2)\cdots\psi_{kN}(\mathbf{x}_N)$$
$$=\sum_{k_1<k_2<\cdots k_N}C(k_1 k_2\cdots k_N)\det\{\psi_{k1},\psi_{k2},\cdots\psi_{kN}\}$$
$$=\sum_K C_K\Psi_K(\mathbf{x}_1,\mathbf{x}_2,\cdots\mathbf{x}_N), \quad (30)$$

where

$$\Psi_K(\mathbf{x}_1,\mathbf{x}_2,\cdots\mathbf{x}_N)=(N!)^{-\frac{1}{2}}\det\{\psi_{k1},\psi_{k2},\cdots\psi_{kN}\} \quad (31)$$

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 $K=(k_1,k_2,\cdots k_N)$ and $L=(l_1,l_2,\cdots l_N)$ 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[6] that two Slater determinants Ψ_K and Ψ_L belonging to two different ordered configurations K and L are orthogonal, and hence we have

$$\int\Psi_K^*\Psi_L(dx)=\delta_{KL}. \quad (32)$$

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

$$C_K=\int\Psi(12\cdots N)\Psi_K^*(dx)$$
$$=(N!)^{\frac{1}{2}}\int\Psi(12\cdots N)\psi_{k1}^*(1)\psi_{k2}^*(2)\cdots$$
$$\times\psi_{kN}^*(N)(dx). \quad (33)$$

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

$$\gamma(\mathbf{x}_1'|\mathbf{x}_1)=\sum_{kl}\psi_k^*(\mathbf{x}_1')\psi_l(\mathbf{x}_1)\gamma(l|k), \quad (34)$$

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

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[6] See Eq. (39).

set of its indices, we obtain in general:

$$\Gamma^{(p)}(\mathbf{x_1}'\mathbf{x_2}'\cdots\mathbf{x}_p'|\mathbf{x_1}\mathbf{x_2}\cdots\mathbf{x}_p)=\sum_{\substack{k_1k_2\cdots k_p\\l_1l_2\cdots l_p}}\psi_{k1}^*(\mathbf{x_1}')\cdots\psi_{kp}^*(\mathbf{x}_p')\psi_{l1}(\mathbf{x_1})\cdots\psi_{lp}(\mathbf{x}_p)\Gamma^{(p)}(l_1l_2\cdots l_p|k_1k_2\cdots k_p)$$

$$=\sum_{\substack{k_1<k_2<\cdots k_p\\l_1<l_2<\cdots l_p}}\begin{vmatrix}\psi_{k1}^*(\mathbf{x_1}')&\cdots&\psi_{kp}^*(\mathbf{x_1}')\\ \cdot&\cdot\cdot\cdot&\cdot\\ \psi_{k1}^*(\mathbf{x}_p')&\cdots&\psi_{kp}^*(\mathbf{x}_p')\end{vmatrix}\cdot\begin{vmatrix}\psi_{l1}(\mathbf{x_1})&\cdots&\psi_{lp}(\mathbf{x_1})\\ \cdot&\cdot\cdot\cdot&\cdot\\ \psi_{l1}(\mathbf{x}_p)&\cdots&\psi_{lp}(\mathbf{x}_p)\end{vmatrix}\Gamma^{(p)}(l_1l_2\cdots l_p|k_1k_2\cdots k_p). \quad (35)$$

The expansion coefficients $\Gamma^{(p)}(l_1,l_2,\cdots l_p|k_1,k_2,\cdots k_p)$, which are Hermitean 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 $C(k_1,k_2,\cdots k_N)$, 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:

$$U=(N!)^{-\frac{1}{2}}\det\{u_1,u_2,\cdots u_N\},$$
$$V=(N!)^{-\frac{1}{2}}\det\{v_1,v_2,\cdots v_N\}, \quad (36)$$

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_l, and we will further assume that they have mutual "nonorthogonality" integrals

$$d_{uv}(kl)=\int u_k^*(\mathbf{x_1})v_l(\mathbf{x_1})dx_1, \quad (37)$$

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

$$\int U^*V(dx)=\int u_1^*(\mathbf{x_1})u_2^*(\mathbf{x_2})\cdots u_N^*(\mathbf{x}_N)$$
$$\times\det\{v_1,v_2,\cdots v_N\}(dx) \quad (38)$$
$$=\sum_P(-1)^pP_l d(1l_1)d(2l_2)\cdots d(Nl_N)$$
$$=\det\{d(kl)\},$$

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:

$$\int U^*V(dx)=D_{UV}=\det\{d_{uv}(kl)\}. \quad (39)$$

The determinant D_{UV} is of basic importance for the following discussion, and we need it as well as its *minors*

of various orders:

$$D_{UV}(k|l),\ D_{UV}(k_1k_2|l_1l_2),\ D_{UV}(k_1k_2k_3|l_1l_2l_3),\ \cdots. \quad (40)$$

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

$$\det_u(12\cdots p|k_1k_2\cdots k_p),\quad \det_v(12\cdots p|l_1l_2\cdots l_p). \quad (41)$$

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

$$[(N-p)!]^{-1}\int \det_u^*(12\cdots p|k_1k_2\cdots k_p)$$
$$\times\det_v(12\cdots p|l_1l_2\cdots l_p)(dx'_{12\cdots p})$$
$$=D_{UV}(k_1k_2\cdots k_p|l_1l_2\cdots l_p). \quad (42)$$

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:

$$U(\mathbf{x_1}\mathbf{x_2}\cdots\mathbf{x}_N)=(N!)^{-\frac{1}{2}}\sum_k u_k(\mathbf{x_1})\det_u(1|k),$$
$$V(\mathbf{x_1}\mathbf{x_2}\cdots\mathbf{x}_N)=(N!)^{-\frac{1}{2}}\sum_l v_l(\mathbf{x_1})\det_v(1|l). \quad (43)$$

By using (42), we then obtain

$$N\int U^*(\mathbf{x_1}'\mathbf{x_2}\cdots\mathbf{x}_N)V(\mathbf{x_1}\mathbf{x_2}\cdots\mathbf{x}_N)(dx_1')$$
$$=\sum_{kl}u_k^*(\mathbf{x_1}')v_l(\mathbf{x_1})[(N-1)!]^{-1}$$
$$\times\int \det_u^*(1|k)\det_v(1|l)(dx_1')$$
$$=\sum_{kl}u_k^*(\mathbf{x_1}')v_l(\mathbf{x_1})D_{UV}(k|l). \quad (44)$$

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

$$\gamma_{UV}(\mathbf{x_1}'|\mathbf{x_1})=(D_{UU}D_{VV})^{-\frac{1}{2}}\sum_{kl}u_k^*(\mathbf{x_1}')$$
$$\times v_l(\mathbf{x_1})D_{UV}(k|l). \quad (45)$$

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 p rows:

$$U(\mathbf{x}_1\mathbf{x}_2\cdots\mathbf{x}_N)=(N!)^{-\frac{1}{2}}\sum_{k_1<k_2<\cdots k_p}\begin{vmatrix}u_{k1}(\mathbf{x}_1)&\cdots&u_{kp}(\mathbf{x}_1)\\ \cdot&\cdot\cdot\cdot&\cdot\\ u_{k1}(\mathbf{x}_p)&\cdots&u_{kp}(\mathbf{x}_p)\end{vmatrix}\det{}_u(12\cdots p\,|\,k_1k_2\cdots k_p),$$

$$V(\mathbf{x}_1\mathbf{x}_2\cdots\mathbf{x}_N)=(N!)^{-\frac{1}{2}}\sum_{l_1<l_2<\cdots l_p}\begin{vmatrix}v_{l1}(\mathbf{x}_1)&\cdots&v_{lp}(\mathbf{x}_1)\\ \cdot&\cdot\cdot\cdot\cdot\cdot&\cdot\\ v_{l1}(\mathbf{x}_p)&\cdots&v_{lp}(\mathbf{x}_p)\end{vmatrix}\det{}_v(12\cdots p\,|\,l_1l_2\cdots l_p).$$

(46)

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

$$\binom{N}{p}\int U^*(\mathbf{x}_1{}'\mathbf{x}_2{}'\cdots\mathbf{x}_p{}'\mathbf{x}_{p+1}\cdots\mathbf{x}_N)V(\mathbf{x}_1\mathbf{x}_2\cdots\mathbf{x}_p\mathbf{x}_{p+1}\cdots\mathbf{x}_N)(dx_{12\ldots p'})$$

$$=(p!)^{-1}\sum_{\substack{k_1<k_2<\cdots k_p\\ l_1<l_2<\cdots l_p}}\begin{vmatrix}u_{k1}{}^*(\mathbf{x}_1{}')&\cdots&u_{kp}{}^*(\mathbf{x}_1{}')\\ \cdot&\cdot\cdot\cdot\cdot&\cdot\\ u_{k1}{}^*(\mathbf{x}_p{}')&\cdots&u_{kp}{}^*(\mathbf{x}_p{}')\end{vmatrix}\cdot\begin{vmatrix}v_{l1}(\mathbf{x}_1)&\cdots&v_{lp}(\mathbf{x}_1)\\ \cdot&\cdot\cdot\cdot\cdot&\cdot\\ v_{l1}(\mathbf{x}_p)&\cdots&v_{lp}(\mathbf{x}_p)\end{vmatrix}\cdot[(N-p)!]^{-1}$$

$$\times\int\det{}_u{}^*(12\cdots p\,|\,k_1k_2\cdots k_p)\det{}_v(12\cdots p\,|\,l_1l_2\cdots l_p)(dx_{12\ldots p'})$$

$$=(p!)^{-1}\sum_{\substack{k_1<k_2<\cdots k_p\\ l_1<l_2<\cdots l_p}}\begin{vmatrix}u_{k1}{}^*(\mathbf{x}_1{}')&\cdots&u_{kp}{}^*(\mathbf{x}_1{}')\\ \cdot&\cdot\cdot\cdot\cdot&\cdot\\ u_{k1}{}^*(\mathbf{x}_p{}')&\cdots&u_{kp}{}^*(\mathbf{x}_p{}')\end{vmatrix}\cdot\begin{vmatrix}v_{l1}(\mathbf{x}_1)&\cdots&v_{lp}(\mathbf{x}_1)\\ \cdot&\cdot\cdot\cdot\cdot&\cdot\\ v_{l1}(\mathbf{x}_p)&\cdots&v_{lp}(\mathbf{x}_p)\end{vmatrix}D_{UV}(k_1k_2\cdots k_p\,|\,l_1l_2\cdots l_p)$$

$$=(p!)^{-1}\sum_{\substack{k_1k_2\cdots k_p\\ l_1l_2\cdots l_p}}u_{k1}{}^*(\mathbf{x}_1{}')\cdots u_{kp}{}^*(\mathbf{x}_p{}')v_{l1}(\mathbf{x}_1)\cdots v_{lp}(\mathbf{x}_p)D_{UV}(k_1k_2\cdots k_p\,|\,l_1l_2\cdots l_p),$$

(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:

$$\Gamma_{UV}{}^{(p)}(l_1l_2\cdots l_p\,|\,k_1k_2\cdots k_p)$$
$$=(p!)^{-1}D_{UV}(k_1k_2\cdots k_p\,|\,l_1l_2\cdots l_p)(D_{UU}D_{VV})^{-\frac{1}{2}}. \quad (48)$$

According to (18), we are now able to find the matrix element of an operator Ω_{op} with respect to two Slater determinants:

$$\int U^*\Omega_{\mathrm{op}}V(dx)$$

$$=\Omega_{(0)}D_{UV}+\sum_{kl}\{k\,|\,\Omega_1\,|\,l\}D_{UV}(k\,|\,l)$$

$$+\frac{1}{2!}\sum_{\substack{k_1k_2\\ l_1l_2}}\{k_1k_2\,|\,\Omega_{12}\,|\,l_1l_2\}D_{UV}(k_1k_2\,|\,l_1l_2)$$

$$+\frac{1}{3!}\sum_{\substack{k_1k_2k_3\\ l_1l_2l_3}}\{k_1k_2k_3\,|\,\Omega_{123}\,|\,l_1l_2l_3\}$$

$$\times D_{UV}(k_1k_2k_3\,|\,l_1l_2l_3)+\cdots, \quad (49)$$

where we have used the matrix notations

$$\{k\,|\,\Omega_1\,|\,l\}=\int u_k{}^*(\mathbf{x}_1)\Omega_1 v_l(\mathbf{x}_1)dx_1,$$

(50)

$$\{k_1k_2\,|\,\Omega_{12}\,|\,l_1l_2\}=\int u_{k1}{}^*(\mathbf{x}_1)u_{k2}{}^*(\mathbf{x}_2)$$
$$\times\Omega_{12}v_{l1}(\mathbf{x}_1)v_{l2}(\mathbf{x}_2)dx_1dx_2,$$

$\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot$

This is the general formula[8] for *nonorthogonal* basic sets u_k and v_l. 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

[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).

[10] J. C. Slater, Phys. Rev. **35**, 509 (1930); J. E. Lennard-Jones, Proc. Cambridge Phil. Soc. **27**, 469 (1931), particularly p. 480; D. R. Inglis, Phys. Rev. **46**, 135 (1934); H. M. James, J. Chem. Phys. **2**, 794 (1934); J. H. Van Vleck, Phys. Rev. **49**, 232 (1936); R. Landshoff, Z. Physik **102**, 201 (1936); G. H. Wannier, Phys. Rev. **52**, 191 (1937); B. H. Chirgwin and C. A. Coulson, Proc. Roy. Soc. (London) **A201**, 196 (1950); W. J. Carr, Phys. Rev. **92**, 28 (1953).

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 $D_{UV}\neq0$, a considerable simplification may be introduced in (49), for, according to a well-known theorem in the theory of determinants,[7] we then have

$$D_{UV}(k_1k_2\cdots k_p\,|\,l_1l_2\cdots l_p)$$

$$=D_{UV}{}^{-p+1}\begin{vmatrix} D_{UV}(k_1|l_1) & \cdots & D_{UV}(k_1|l_p) \\ \cdot & \cdots & \cdot \\ D_{UV}(k_p|l_1) & \cdots & D_{UV}(k_p|l_p) \end{vmatrix}$$

$$=D_{UV}\begin{vmatrix} d^{-1}(l_1k_1) & \cdots & d^{-1}(l_pk_1) \\ \cdot & \cdots & \cdot \\ d^{-1}(l_1k_p) & \cdots & d^{-1}(l_pk_p) \end{vmatrix},\quad(51)$$

where $d^{-1}(lk)$ 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

$$\sum_{kl}u_k{}^*(x_1')v_l(x_1)d^{-1}(lk),\quad(52)$$

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_1k_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

$$\sum_K^K\sum_k=\sum_k\sum_K^{(k)},\quad \sum_K^K\sum_{k_1k_2}=\sum_{k_1k_2}\sum_K^{(k_1k_2)},\quad\cdots.\quad(53)$$

We will assume that our normalizable wave function Ψ may be expanded in a series of Slater determinants Ψ_K over all ordered configurations K:

$$\Psi=\sum_K\Psi_KC_K,\quad(54)$$

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

$$\gamma(x_1'|x_1)=\sum_{KL}C_K{}^*\gamma_{KL}(x_1'|x_1)C_L/\sum_K|C_K|^2$$

$$=\sum_{KL}C_K{}^*C_L\sum_k^K\sum_l^L\psi_k{}^*(x_1')\psi_l(x_1)$$
$$\times D_{KL}(k|l)/\sum_K|C_K|^2$$

$$=\sum_{kl}\psi_k{}^*(x_1')\psi_l(x_1)\sum_K^{(k)}\sum_L^{(l)}C_K{}^*$$
$$\times D_{KL}(k|l)C_L/\sum_K|C_K|^2,\quad(55)$$

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

$$\gamma(l|k)=\sum_K^{(k)}\sum_L^{(l)}C_K{}^*D_{KL}(k|l)C_L/\sum_K|C_K|^2.\quad(56)$$

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

$$\Gamma^{(p)}(x_1'x_2'\cdots x_p'|x_1x_2\cdots x_p)=\sum_{KL}C_K{}^*\Gamma_{KL}{}^{(p)}(x_1'x_2'\cdots x_p'|x_1x_2\cdots x_p)C_L/\sum_K|C_K|^2$$

$$=\sum_{\substack{k_1k_2\cdots k_p\\l_1l_2\cdots l_p}}\psi_{k1}{}^*(x_1')\cdots\psi_{kp}{}^*(x_p')\psi_{l1}(x_1)\cdots\psi_{lp}(x_p)\Gamma^{(p)}(l_1l_2\cdots l_p|k_1k_2\cdots k_p),\quad(57)$$

where

$$\Gamma^{(p)}(l_1l_2\cdots l_p|k_1k_2\cdots k_p)=(p!)^{-1}\sum_K^{(k_1k_2\cdots k_p)}\sum_L^{(l_1l_2\cdots l_p)}C_K{}^*D_{KL}(k_1k_2\cdots k_p|l_1l_2\cdots l_p)C_L/\sum_K|C_K|^2.\quad(58)$$

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

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

$$\sum_k\gamma(k|k)=N,$$

$$\sum_{k_1k_2\cdots k_p}\Gamma^{(p)}(k_1k_2\cdots k_p|k_1k_2\cdots k_p)=\binom{N}{p},\quad(59)$$

[11] P. O. Löwdin, Arkiv mat. astron. fysik **A35**, No. 9 (1947); "A Theoretical Investigation into Some Properties of Ionic Crystals" (thesis) (Almqvist & Wiksells, Uppsala, 1948); J. Chem. Phys. **18**, 365 (1950).

which shows that the normalization is correct. The diagonal elements

$$\gamma(k)=\gamma(k|k),\quad \Gamma(k_1,k_2)=\Gamma(k_1k_2|k_1k_2),\quad\cdots\quad(60)$$

may be interpreted analogously to the diagonal elements in x-space: $\gamma(k)=$ number of particles $\times$ the probability for finding a particle in the spin-orbital k when all the other particles occupy arbitrary spin-orbitals; $\Gamma(k_1,k_2)=$ number of pairs $\times$ the probability for finding one particle in the spin-orbital k_1 and another in the spin-orbital k_2, when all other particles may occupy arbitrary spin-orbitals; etc.

However, even the nondiagonal elements of the density matrices in k-space may have a physical meaning. Taking over a terminology from quantum

chemistry developed by Coulson and Longuet-Higgins,[12] we will call $\gamma(k|k)$ the *charge order* of the spin-orbital k and the coefficient $\gamma(l|k)$ 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 $\gamma(l|k)$ 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 $\Gamma(l_1 l_2|k_1 k_2)$ 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

$$\Gamma(k_1,k_1)=0, \quad \Gamma(k_1,k_2,k_2)=0, \quad \cdots \quad (61)$$

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 $\psi_k(x)$ of one-particle functions is assumed to be orthonormalized ($d_{kl}=\delta_{kl}$), 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 ($d_{kl}=1$). 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

$$D_{KL}(k_1 k_2 \cdots k_p | k_1 k_2 \cdots k_p)=\delta_{KL}. \quad (62)$$

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

$$\gamma(k)=\overset{(k)}{\underset{K}{\sum}} |C_K|^2 / \sum_K |C_K|^2,$$

$$\Gamma^{(p)}(k_1 k_2 \cdots k_p)=\overset{(k_1 k_2 \cdots k_p)}{\underset{K}{\sum}} |C_K|^2 / \sum_K |C_K|^2, \quad (63)$$

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 (64) lead to the inequalities

$$0 \leq \gamma(k) \leq 1, \quad 0 \leq \Gamma^{(p)}(k_1 k_2 \cdots k_p) \leq 1, \quad (64)$$

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 $(k_1,k_2,\cdots k_p)$ lies 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 Hermitean operators Ω_{op} corresponding to physical quantities, i.e., in solving the equation

$$\Omega_{op}\Psi=\mathcal{W}\Psi. \quad (65)$$

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

$$\Psi=\sum_K \Psi_K C_K,$$
$$\Psi_K=(N!)^{-\frac{1}{2}} \det\{\psi_{k1},\psi_{k2},\cdots \psi_{kN}\}. \quad (66)$$

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 Ψ may be expanded in the same way, and, for the average value of Ω_{op} with respect to such a wave function, we find therefore

$$\langle\Omega_{op}\rangle_{Av}=\int \Psi^*\Omega_{op}\Psi(dx) \Big/ \int \Psi^*\Psi(dx)$$
$$=\sum_{KL} C_K^*\langle K|\Omega_{op}|L\rangle C_L / \sum_{KL} C_K^*\delta_{KL}C_L, \quad (67)$$

[12] C. A. Coulson and H. C. Longuet-Higgins, Proc. Roy. Soc. (London) **A191**, 39; **192**, 16 (1947); **193**, 447, 456 (1948); **195**, 188 (1948).

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

$$\langle K|\Omega_{\text{op}}|L\rangle = \int \Psi_K^*\Omega_{\text{op}}\Psi_L(dx)$$

$$= \Omega_{(0)}D_{KL} + \sum_k^K \sum_l^L \{k|\Omega_1|l\}D_{KL}(k|l)$$

$$+(2!)^{-1}\sum_{k_1k_2}^K \sum_{l_1l_2}^L \{k_1k_2|\Omega_{12}|l_1l_2\}$$
$$\times D_{KL}(k_1k_2|l_1l_2)$$

$$+(3!)^{-1}\sum_{k_1k_2k_3}^K \sum_{l_1l_2l_3}^L \{k_1k_2k_3|\Omega_{123}|l_1l_2l_3\}$$

$$\times D_{KL}(k_1k_2k_3|l_1l_2l_3)+\cdots, \quad (68)$$

with the matrix notations

$$\{k|\Omega_1|l\} = \int \psi_k^*(x_1)\Omega_1\psi_l(x_1)dx_1,$$

$$\{k_1k_2|\Omega_{12}|l_1l_2\} = \int \psi_{k1}^*(x_1)\psi_{k2}^*(x_2)\Omega_{12}$$
$$\times \psi_{l1}(x_1)\psi_{l2}(x_2)dx_1dx_2, \quad (69)$$

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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

$$\sum_L\{\langle K|\Omega_{\text{op}}|L\rangle - \mathcal{W}\delta_{KL}\}C_L = 0. \quad (70)$$

The condition for solubility is given by the secular equation

$$\det\{\langle K|\Omega_{\text{op}}|L\rangle - \mathcal{W}\delta_{KL}\} = 0, \quad (71)$$

which determines the eigenvalues $\mathcal{W}$. 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[13] and Meckler[14] 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 $\gamma(x_1'|x_1)$, 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 $n_{kk} = n_k$:

$$U^\dagger\gamma U = n = \text{diagonal matrix.} \quad (72)$$

We have further, in matrix form, $\gamma = UnU^\dagger$, and, if we introduce a new set of spin-orbitals χ_k by the matrix relation $\chi = \psi U$, or

$$\chi_k = \sum_\alpha \psi_\alpha U_{\alpha k}, \quad (73)$$

we may rewrite the density matrix in the form

$$\gamma(x_1'|x_1) = \sum_k n_k\chi_k^*(x_1')\chi_k(x_1). \quad (74)$$

This form is characterized by the fact that all bond orders are vanishing, and the new spin-orbitals χ_k will therefore be called the *natural spin-orbitals* associated with the system and state under consideration. The corresponding charge orders n_k, which are the eigenvalues of the matrix $\gamma(l|k)$, will be interpreted as their *occupation numbers*, since they represent the average number of particles in each one of the natural spin-orbitals. We note that, if two or more charge orders are the same for spin-orbitals of the same spin type, the corresponding orbitals form a degenerate group, and $\gamma(x_1'|x_1)$ is then invariant against unitary transformations of the orbitals within such a group.

[13] S. F. Boys, Proc. Roy. Soc. (London) A200, 542 (1950); 201, 125 (1950); 206, 489 (1951); 207, 181, 197 (1951); etc.
[14] A. Meckler, J. Chem. Phys. 21, 1750 (1953).

According to (64) and (59), the occupation numbers fulfill the two conditions

$$0 \leq n_k \leq 1, \quad \sum_k n_k = N, \tag{75}$$

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

$$\gamma^2 = \gamma, \quad \mathrm{Tr}(\gamma) = N, \tag{76}$$

where $\mathrm{Tr}(\equiv \mathrm{trace})$ 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 Ψ 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 γ 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[15] 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 ψ_k 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 χ_l, we will now carry out the matrix transformation $\psi = \chi U^\dagger$, or

$$\psi_k = \sum_\alpha \chi_\alpha U_{\alpha k}{}^\dagger. \tag{77}$$

By using a theorem[7] for expanding a determinant of a matrix being a product of two rectangular matrices, we obtain the following transformation for the basic Slater determinants Ψ_K and X_L:

$$\Psi_K = \sum_L X_L A_{LK}, \quad X_L = (N!)^{-\frac{1}{2}} \det\{\chi_1, \chi_2, \cdots \chi_N\}, \tag{78}$$

where

$$A_{LK} = \begin{vmatrix} U^\dagger(l_1 k_1) & \cdots & U^\dagger(l_1 k_N) \\ \cdot & \cdot \cdot \cdot \cdot \cdot & \cdot \\ U^\dagger(l_N k_1) & \cdots & U^\dagger(l_N k_N) \end{vmatrix}. \tag{79}$$

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

$$\Psi = \sum_L X_L (\sum_K A_{LK} C_K). \tag{80}$$

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_k 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]

[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.

[17] J. C. Slater, Quarterly Progress Report of Solid-State and Molecular Theory Group at M.I.T., 6, January 15, 1953 (unpublished); Technical Report No. 3, 39, February 15, 1953 (unpublished); Phys. Rev. **91**, 528 (1953).

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 ψ_k to occur in the expansion of the total wave function Ψ. 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: $M!/N! (M-N)!$. 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 ψ_k 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 the quantity

$$\vartheta = (1/N) \sum_k \{1-\gamma(k)\}\gamma(k) = 1 - (1/N) \sum_k \{\gamma(k)\}^2,$$

which fulfills the inequality of $0 \leq \vartheta < 1$. In considering different basic sets $\psi_1, \psi_2, \psi_3, \cdots$ for the description of the same total wave function Ψ, it is clear that the natural spin-orbitals χ_k are characterized by having the *smallest ϑ value possible*. According to (72), we have $\gamma = \mathbf{U}\mathbf{n}\mathbf{U}^\dagger$ and $\gamma^2 = \mathbf{U}\mathbf{n}^2\mathbf{U}^\dagger$, leading to $\mathrm{Tr}(\gamma^2) = \mathrm{Tr}(\mathbf{n}^2)$ and

$$\sum_k \gamma_k{}^2 = \sum_k n_k{}^2 - \sum_{l \neq k} |\gamma_{kl}|^2 \leq \sum_k n_k{}^2,$$

with the final result

$$1 - (1/N) \sum_k n_k{}^2 \leq 1 - (1/N) \sum_k \gamma_k{}^2,$$

which proves our theorem. This means that the natural spin-orbitals are distinguished not only by having vanishing bond orders but also by giving the smallest number of essential charge orders possible. By investigating the quantity ϑ, one can therefore easily estimate how much improvement one can expect in the convergence of a given configurational interaction series by introducing the natural spin-orbitals.

The quantity ϑ_{nat} for the natural spin-orbitals themselves may also be expressed in the form

$$\vartheta_{\text{nat}} = (1/N) \, \mathrm{Tr}(\gamma - \gamma^2),$$

and we note that, provided the necessary existence and convergence conditions are fulfilled, the relation

$$\vartheta_{\text{nat}} = 0$$

is a necessary and sufficient condition for expressing an arbitrary antisymmetric wave function in the form of a single determinant. The necessity follows from Dirac's theorem (see reference 1) $\rho^2 = \rho$, and, in order to prove the sufficiency, we note that from $\vartheta_{\text{nat}} = 0$ it follows that $\sum_k n_k(1-n_k) = 0$ with $0 \leq n_k \leq 1$, and that, since this sum does not contain any negative terms, this relation can be fulfilled only if $n_k = 0$ or 1. Combined with the normalization condition $\mathrm{Tr}(\gamma) = N$, this means that exactly N natural spin-orbitals are fully occupied each by one electron, and, according to the first relation (63), the antisymmetric wave function must then be expressible as a single determinant built up from these spin-orbitals. The deviation from zero of the single number ϑ_{nat} tells us also how far our wave function Ψ is from the Hartree-Fock approximation. (Received January 24, 1955.)

By the transformation (77), even the higher-order densities may now be expressed in the natural spin-orbitals, but we note that, unlike the first-order density, they are usually not brought to diagonal form. As an example, we may consider the second-order density matrix in the limiting case, when exactly N spin-orbitals are fully occupied, i.e., the relation (76) is

fulfilled. According to (74) and (51), we obtain

$$\gamma(\mathbf{x}_1' | \mathbf{x}_1) = \sum_k \chi_k{}^*(\mathbf{x}_1')\chi_k(\mathbf{x}_1),$$

$$\Gamma(\mathbf{x}_1'\mathbf{x}_2' | \mathbf{x}_1\mathbf{x}_2) = \tfrac{1}{2} \begin{vmatrix} \gamma(\mathbf{x}_1' | \mathbf{x}_1) & \gamma(\mathbf{x}_1' | \mathbf{x}_2) \\ \gamma(\mathbf{x}_2' | \mathbf{x}_1) & \gamma(\mathbf{x}_2' | \mathbf{x}_2) \end{vmatrix}$$

$$= \tfrac{1}{2} \sum_{kl} \{\chi_k{}^*(\mathbf{x}_1')\chi_k(\mathbf{x}_1)\chi_l{}^*(\mathbf{x}_2')\chi_l(\mathbf{x}_2)$$

$$- \chi_k{}^*(\mathbf{x}_1')\chi_l(\mathbf{x}_1)\chi_l{}^*(\mathbf{x}_2')\chi_k(\mathbf{x}_2)\}. \quad (81)$$

In the last term in the expansion for Γ, there are cross products of the form $\chi_k{}^*(\mathbf{x}_1')\chi_l(\mathbf{x}_1)$ which, for $k \neq l$, lead to the existence of the well-known *exchange effects* associated with each pair of natural spin-orbitals χ_k and χ_l. 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 secondo-rder matrix have previously been used successfully by, among others, Lennard-Jones[18] in discussing correlation properties between electrons in atoms and molecules. In case of *symmetric* wave functions Ψ, they have also been used by London[19] for 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 ψ_k of one-particle functions is infinite and complete. An arbitrary normalizable function $F(\mathbf{x}_1' | \mathbf{x}_1)$ may then be expressed by the expansion

$$F(\mathbf{x}_1' | \mathbf{x}_1) = \sum_{k,l=1}^{\infty} \psi_k{}^*(\mathbf{x}_1')\psi_l(\mathbf{x}_1)F_{lk}. \quad (82)$$

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.[20]

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

$$\int \psi_k{}^* \psi_l \, dx = \delta_{kl}, \quad (83)$$

which imposes an orthogonality condition on the

[18] J. Lennard-Jones, J. Chem. Phys. **20**, 1024 (1952); J. Lennard-Jones and J. A. Pople, Phil. Mag. **43**, 581 (1952).
[19] F. London, J. Chem. Phys. **11**, 203 (1943).
[20] 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* ϱ defined by

$$\rho(\mathbf{x}_1, \mathbf{x}_2) = \sum_{k=1}^{M} \psi_k^*(\mathbf{x}_1)\psi_k(\mathbf{x}_2). \qquad (84)$$

We observe, that, since ϱ fulfills the relations

$$\int \rho(\mathbf{x}_1, \xi_1)\rho(\xi_1, \mathbf{x}_2)d\xi_1 = \rho(\mathbf{x}_1, \mathbf{x}_2), \qquad \int \rho(\mathbf{x}_1, \mathbf{x}_1)dx_1 = M,$$

or

$$\varrho^2 = \varrho, \quad \mathrm{Tr}(\varrho) = M, \qquad (85)$$

it has really the character of a *projection operator.*[21] In the case $M = N$, it is identical with Dirac's density matrix,[1] 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 $F(\mathbf{x}_1'|\mathbf{x}_1)$, we have to be satisfied with the approximate form

$$f(\mathbf{x}_1'|\mathbf{x}_1) \equiv \sum_{k=1}^{M} \psi_k^*(\mathbf{x}_1')\psi_l(\mathbf{x}_1)F_{lk}. \qquad (86)$$

The function $f(\mathbf{x}_1'|\mathbf{x}_1)$, defined by this interrupted expansion, is said to represent the *orthogonal projection* of the function $F(\mathbf{x}_1'|\mathbf{x}_1)$ on the subspace of the general Hilbert space, defined by the basic set ψ_k $(k=1, 2, \cdots M)$. We note the validity of the matrix relation

$$\mathbf{f} = \varrho\mathbf{F}\varrho, \qquad (87)$$

which shows the use of the projection operator ϱ. For every function $f(\mathbf{x}_1'|\mathbf{x}_1)$ which is expansible in the basic set ψ_k, i.e., which belongs to the subspace defined by this set, we have further

$$\mathbf{f} = \varrho\mathbf{f} = \mathbf{f}\varrho = \varrho\mathbf{f}\varrho. \qquad (88)$$

Let us now again study the eigenvalue problem (65). In expansion (66) of the solution Ψ, both the coefficients C_K and the basic spin-orbitals ψ_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

$$\langle \Omega_{\mathrm{op}} \rangle_{\mathrm{Av}} = \Omega_{(0)} + \sum_{kl}\{k|\Omega_1|l\}\gamma(l|k)$$

$$+ \sum_{\substack{k_1k_2 \\ l_1l_2}}\{k_1k_2|\Omega_{12}|l_1l_2\}\Gamma(l_1l_2|k_1k_2)$$

$$+ \sum_{\substack{k_1k_2k_3 \\ l_1l_2l_3}}\{k_1k_2k_3|\Omega_{123}|l_1l_2l_3\}$$

$$\times \Gamma^{(3)}(l_1l_2l_3|k_1k_2k_3) + \cdots, \qquad (89)$$

where the matrix elements are defined by (69). Varia-

[21] J. v. Neumann, *Math. Grundlagen der Quantenmechanik* (Dover Publications, New York, 1943), p. 41.

tion of the coefficients C_K leads to Eqs. (70) and (71), and variation of the basic set ψ_k leads to extended Hartree-Fock equations of the form

$$\sum_l \Omega_l\psi_l(\mathbf{x}_1)\gamma(l|k)$$

$$+ 2\sum_l \sum_{k_2l_2} \int \psi_{k_2}^*(2)\Omega_{12}\psi_{l2}(2)dx_2\psi_l(\mathbf{x}_1)\Gamma(ll_2|kk_2)$$

$$+ 3\sum_l \sum_{\substack{k_2k_3 \\ l_2l_3}} \int \psi_{k_2}^*(2)\psi_{k_3}^*(3)\Omega_{123}\psi_{l2}(2)\psi_{l3}(3)dx_2dx_3$$

$$\times \psi_l(\mathbf{x}_1)\Gamma^{(3)}(ll_2l_3|kk_2k_3) + \cdots = \sum_l \psi_l(\mathbf{x}_1)\lambda(l|k). \quad (90)$$

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

$$\sum_{kl} \lambda(l|k)\delta \int \psi_k^*\psi_l dx \qquad (91)$$

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

$$\Omega_1\gamma(\xi_1'|\mathbf{x}_1) + 2\int \Omega_{12}\Gamma(\xi_1'\mathbf{x}_2'|\mathbf{x}_1\mathbf{x}_2)dx_2$$

$$+ 3\int \Omega_{123}\Gamma^{(3)}(\xi_1'\mathbf{x}_2'\mathbf{x}_3'|\mathbf{x}_1\mathbf{x}_2\mathbf{x}_3)dx_2dx_3$$

$$+ \cdots = \lambda(\xi_1'|\mathbf{x}_1), \quad (92)$$

where we have assumed that the operators Ω_1, Ω_{12}, Ω_{123}, $\cdots$ etc. do not work on the variables ξ_1', $\mathbf{x}_2'$, $\mathbf{x}_3' \cdots$. After the operations in the integrands have been carried out, we shall as before put all $\mathbf{x}_i' = \mathbf{x}_i$, whereas ξ_1' may have an arbitrary value. The function $\lambda(\xi_1'|\mathbf{x}_1)$ in the right-hand member is here given by the Lagrangian multipliers:

$$\lambda(\xi_1'|\mathbf{x}_1) = \sum_{k,l=1}^{M} \psi_k^*(\xi_1')\psi_l(\mathbf{x}_1)\lambda(l|k). \qquad (93)$$

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 $\Lambda(\xi_1'|\mathbf{x}_1)$ on the subspace defined by the basic set of. order M:

$$\lambda = \varrho\Lambda\varrho. \qquad (94)$$

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

$$\lim_{M \to \infty} \rho(\mathbf{x}_1, \mathbf{x}_2) = \delta(\mathbf{x}_1 - \mathbf{x}_2), \qquad (95)$$

and relation (94) is then changed into the identity $\mathbf{\Lambda} \equiv \mathbf{\Lambda}$. This means that, in the limiting case, the extended Hartree-Fock equations (92) loose their meaning as a restraining condition on the basic set ψ_k, 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 $\gamma(\xi_1' | \mathbf{x}_1)$ and $\lambda(\xi_1' | \mathbf{x}_1)$ in (92) are quadratic forms with Hermitean coefficients, and the question is whether we can bring them to diagonal forms. In the case when $M = N$, the first-order density $\gamma(\xi_1' | \mathbf{x}_1)$ 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 $\lambda(\xi_1' | \mathbf{x}_1)$ to diagonal form. This is a conventional procedure in the ordinary Hartree-Fock scheme, and the eigenvalues of the matrix $\lambda(l | k)$ are called the *orbital energies* of the basic spin-orbitals ψ_k. However, if $M > N$, the first order density matrix $\gamma(\xi_1' | \mathbf{x}_1)$ may be brought to diagonal form (74) first by introducing the natural spin-orbitals χ_k, and, only if several occupation numbers n_k are the same with a corresponding degeneracy in the spin-orbitals χ_k, we have any additional transformations free for changing the form of $\lambda(\xi_1' | \mathbf{x}_1)$, too. In general, we cannot therefore expect that it should always be possible to bring $\gamma(\xi_1' | \mathbf{x}_1)$ and $\lambda(\xi_1' | \mathbf{x}_1)$ *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

$$\int \psi_k(\xi_1') \Omega_1 \gamma(\xi_1' | \mathbf{x}_1) d\xi_1'$$

$$+ 2 \int \psi_k(\xi_1') \Omega_{12} \Gamma(\xi_1' \mathbf{x}_2' | \mathbf{x}_1 \mathbf{x}_2) d\xi_1' dx_2$$

$$+ 3 \int \psi_k(\xi_1') \Omega_{123} \Gamma^{(3)}(\xi_1' \mathbf{x}_2' \mathbf{x}_3' | \mathbf{x}_1 \mathbf{x}_2 \mathbf{x}_3) d\xi_1' dx_2 dx_3 + \cdots$$

$$= \int \psi_k(\xi_1') \lambda(\xi_1' | \mathbf{x}_1) d\xi_1'. \quad (96)$$

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

$$\Omega_1 \chi_k(\mathbf{x}_1) + 2 n_k^{-1} \int \chi_k(\xi_1') \Omega_{12} \Gamma(\xi_1' \mathbf{x}_2' | \mathbf{x}_1 \mathbf{x}_2) d\xi_1' dx_2$$

$$+ 3 n_k^{-1} \int \chi_k(\xi_1') \Omega_{123} \Gamma^{(3)}(\xi_1' \mathbf{x}_2' \mathbf{x}_3' | \mathbf{x}_1 \mathbf{x}_2 \mathbf{x}_3)$$

$$\times d\xi_1' dx_2 dx_3 + \cdots = \sum_{l=1}^{M} \chi_l(\mathbf{x}_1) \lambda'(l | k) n_k^{-1}, \quad (97)$$

where $\lambda' = \mathbf{U}^\dagger \lambda \mathbf{U}$. This is the exact integro-differential equation satisfied by the natural spin-orbitals, which previously are shown to lead to the most rapid convergency 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[17] 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

$$\{\Omega_1 + V_{\mathrm{op}}(1)\} \chi_k(1) = \sum_{l=1}^{M} \chi_l(1) \lambda'(l | k) n_k^{-1}, \qquad (98)$$

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 $\mathbf{x}$, 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 $\mathbf{x}$-space:

$$V_{\mathrm{op}} \chi_k(\mathbf{x}_1) \approx V(\mathbf{x}_1) \chi_k(\mathbf{x}_1), \quad k = 1, 2, \cdots M \qquad (99)$$

which may be defined by the condition that the sum

$$\sum_{k=1}^{M} \kappa_k | V_{\mathrm{op}} \chi_k(\mathbf{x}_1) - V(\mathbf{x}_1) \chi_k(\mathbf{x}_1) |^2, \qquad (100)$$

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

$$V(\mathbf{x}_1) = \frac{\sum_k n_k \chi_k^*(\mathbf{x}_1) V_{\mathrm{op}} \chi_k(\mathbf{x}_1)}{\sum_k n_k \chi_k^*(\mathbf{x}_1) \chi_k(\mathbf{x}_1)}. \qquad (101)$$

According to (74), the quantity in the denominator is just the first-order density $\gamma(\mathbf{x}_1 | \mathbf{x}_1)$. Using (97) and (98), and observing the validity of the relations

$$\int \rho(\mathbf{x}_1, \xi_1') \Gamma(\xi_1' \mathbf{x}_2' | \mathbf{x}_1 \mathbf{x}_2) d\xi_1' = \Gamma(\mathbf{x}_1 \mathbf{x}_2' | \mathbf{x}_1 \mathbf{x}_2),$$

$$(102)$$

$$\int \rho(\mathbf{x}_1, \xi_1') \Gamma(\xi_1' \mathbf{x}_2' \mathbf{x}_3' | \mathbf{x}_1 \mathbf{x}_2 \mathbf{x}_3) d\xi_1' = \Gamma(\mathbf{x}_1 \mathbf{x}_2' \mathbf{x}_3' | \mathbf{x}_1 \mathbf{x}_2 \mathbf{x}_3),$$

we get finally for the "average potential" $V(\mathbf{x}_1)$:

$$V(\mathbf{x}_1) = 2 \int \Omega_{12} \Gamma(\mathbf{x}_1'\mathbf{x}_2' | \mathbf{x}_1\mathbf{x}_2) dx_2 / \gamma(\mathbf{x}_1)$$

$$+ 3 \int \Omega_{123} \Gamma(\mathbf{x}_1'\mathbf{x}_2'\mathbf{x}_3' | \mathbf{x}_1\mathbf{x}_2\mathbf{x}_3) dx_2 dx_3 / \gamma(\mathbf{x}_1) + \cdots. \quad (103)$$

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

$$\{\Omega_1 + V(\mathbf{x}_1)\}\chi_k(\mathbf{x}_1) = \sum_{l=1}^{M} \chi_l(\mathbf{x}_1) \lambda'(l | k) n_k^{-1}. \quad (104)$$

Since the operator $(H_1 + V_1)$ is Hermitean, the same must hold also for the matrix $\lambda'(l|k)n_k^{-1}$ in the right-hand member, which implies that, in this approximation, there can be λ'-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 $\lambda'(l|k)n_k^{-1}$ to diagonal form. Instead of the rather complicated Eq. (97), we have now obtained an approximate representation in the form of an eigenvalue problem

$$\{\Omega_1 + V(x_1)\}\chi_k(x_1) = \omega_k \chi_k(x_1), \quad (105)$$

where $V(x_1)$ 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.[17] Since we are then mainly interested in electronic systems, the basic Hamiltonian is of the specific form (11), with $\Omega_{ij} = e^2/r_{ij}$, $\Omega_{ijk} = 0$, $\cdots$, etc. According to (103), we get for the "average potential"

$$V(x_1) = 2e^2 \int \frac{\Gamma(x_1 x_2)/\gamma(x_1)}{r_{12}} dx_2, \quad (106)$$

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[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[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 this 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 $M \geq N$, 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 a 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

[22] J. C. Slater, Phys. Rev. **81**, 385 (1951).
[23] G. W. Pratt, Jr., Phys. Rev. **88**, 1217 (1952).

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 Ψ_0 be an approximate (or exact) solution to the Schrödinger equation (21), which does not possess the correct symmetry property. Since Ω_{op} is symmetric in the coordinates, every function $P\Psi_0$ is then also a solution of the same type, and the linear combination

$$\Psi_{AS} = (N!)^{-\frac{1}{2}} \sum_P (-1)^p P\Psi_0, \qquad (107)$$

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

metric wave function, we obtain

$$\int \Psi_{AS}^* \Phi(dx) = (N!)^{-\frac{1}{2}} \sum_P (-1)^p \int P^* \Psi_0^* \Phi(dx)$$

$$= (N!)^{-\frac{1}{2}} \sum_P (-1)^p \int \Psi_0^* P^\dagger \Phi(dx)$$

$$= (N!)^{\frac{1}{2}} \int \Psi_0^* \Phi(dx), \qquad (108)$$

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

$$\int \Psi_{AS}^* \Phi(dx) = (N!)^{-\frac{1}{2}} \int \Psi_0^* \Phi(dx), \qquad (109)$$

which is of value in treating wave functions Ψ_0 built on simpler elements, as one- or two-particle functions.