

# ON THE THEORY OF FERMION DENSITY OPERATORS. I.\*

## THE DEFINITION OF THE ONE-PARTICLE STATES AND CLUSTER EXPANSIONS OF THE DENSITY OPERATORS

By

J. I. HORVÁTH and I. K. GYÉMÁNT

DEPARTMENT OF THEORETICAL PHYSICS, JÓZSEF ATTILA UNIVERSITY, SZEGED

(Received 13. I. 1969)

After the definitions of density operators (§2), the concept of single particle states is defined via the pure states of the first order reduced density operators (§3). Then the concepts of the NSO's and NSG's, as well as expansions in their terms are treated (§4). Furthermore, KIANG's variational approach is discussed and improved (§5). Finally, cluster expansions of the  $N$ -particle density operators are obtained in terms of the first order reduced density operators in various cases.

### § 1. Introduction

The independent particle model is the most familiar approximation for treating many-particle systems. It was originally suggested by its validity for perfect systems with completely separable Hamiltonian. However, for real many-particle systems where owing to the interactions of the particles the collective behaviour of the system is more dominant and characteristic it is clear that the independent particle model loses its validity. Nevertheless it can be accepted if the "bare" particles and the concept of the "bare particle states" are replaced by way of some kind of renormalization processes (such as those of Hartree—Fock or Brueckner) by the so-called "dressed" particles or "dressed particle states". But, in these very familiar cases too, it is a priori not quite evident that (a) individual or single particle states exist at all; (b) how they are related to the classical concept of particles; and (c) in which way the correlation problems of the particles have to be formulated.

Bearing in mind this antagonism between the fundamental ideas of the collective and independent particle models, the remarkable successes of the independent particle models mostly based on the methods of pseudo-potentials — more recently summarized and improved by Professor GOMBÁS in his excellent monograph [1] — suggest once more a reinvestigation of its theoretical background in terms of the new methods that have appeared recently in the theory of many-body (fermion) systems.

The methods mentioned — notably, the methods of density operators and cluster expansions including the most important information about the

\* Dedicated to Prof. P. GOMBÁS on his 60th birthday.

collective behaviours of the systems — are, strictly speaking, not new at all, but interest has again focused on them and they have helped in making remarkable progress in this important field.

It can be hoped that they will be of help also in replacing the a posteriori justification of the validity of the independent particle model by a direct one. Thus the aim of the present series of papers is to simplify the conceptual background of the problems investigated, to find a compromise in certain hotly discussed questions and to obtain a clear insight into the ideas involved. Improved mathematical tools are used which are related to simple and natural physical concepts and some relationships are brought out which may be useful in making further improvements.

In this first part after the definitions of the density operators and the brief summary of their fundamental properties needed in the following argumentation (§2), the concept of single particle states is defined via the pure states of the first order reduced density operator (§3). Then, the concepts of the natural spin orbitals and geminals, as well as expansions in their terms are treated (§4), furthermore KIANG's variational approach is discussed and improved (§5). Finally, cluster expansions of the  $N$ -particle density operator are obtained in terms of the first order reduced density operators in different cases.

## § 2. The definitions of density operators and their most fundamental properties

It seems that in looking for a consistent method of finding an approximation method in terms of particle states one has to use the method of density operators, where in the case of Hamiltonians with two-body interactions the expectation values of any important observable can be obtained in terms of the so-called one and two particle reduced density operators alone.

The *density* or as it is sometimes also called: *statistical operator* and in a certain representation mostly in co-ordinate representation the *density matrix*, respectively, were introduced by VON NEUMANN [2, 3] and by DIRAC [4] to describe statistical concepts in quantum physics. Their first version is more common in the case of statistical mechanics, i.e., in the case of many, practically infinite degrees of freedom; the second version rather in quantum chemistry, i.e., for atomic and molecular systems with limited degrees of freedom.

The theory of density operators and its applications has been investigated in detail from very different aspects by several authors. The existence of general references [5—8], and of more recent special investigations which have been focused on the problems: (a) how far and under which condition the wave function of the many particle systems can be replaced by the one and two particle density matrices alone [9—12]; (b) what kind of collective problems

of the system's behaviour can be explained [13—19]; (c) in what manner the usual variational method could be reformulated in terms of density matrices [20], etc., makes any extended discussion of the previous results unnecessary and we recall only the salient facts partly in terms of new arguments.

Having in mind atomic and molecular systems with limited degrees of freedom we start with DIRAC's definition of the density operator. Since in this case the number of electrons does not change during the discussion it may be specified implicitly and for a system of  $N$  particles in a state with the normalized wave function  $\Psi$ , the density matrix  $\mathbf{D}$  of the system and the  $p$ th order reduced density matrix  $\mathbf{D}_p$  — the so-called  $p$ -matrix —, respectively, may be regarded as an integral operator with kernels:

$$D(x_1, \dots, x_N; x'_1, \dots, x'_N) \equiv \Psi(x_1, \dots, x_N) \Psi^*(x'_1, \dots, x'_N) \quad (2.1)$$

and

$$\begin{aligned} D_p(x_1, \dots, x_p; x'_1, \dots, x'_p) = \\ = \int dx_{p+1} \dots dx_N \Psi(x_1, \dots, x_N) \Psi^*(x'_1, \dots, x'_p, x_{p+1}, \dots, x_N), \end{aligned} \quad (2.2)$$

where each co-ordinate  $x_i$  of the "configurational space" is a combination of the space co-ordinates  $\vec{r}_i$  and spin-coordinate  $s_i$  of the particles considered. The integration with respect to the Lebesgue—Stieltjes measure  $dx_{p+1} \dots dx_N$  indicates an integration over the co-ordinates  $\vec{r}_{p+1}, \dots, \vec{r}_N$  and a summation over the dichotomic spin-variables  $s_{p+1}, \dots, s_N$  in the case of spin-half particles (e.g., for systems of electrons).

Independently of any particular representation let us characterize a definite state of the system by the normalized  $|\Psi\rangle$  being an element of the abstract Hilbert space  $\mathcal{H}$ . This means that the state vector in coordinate representation introduced above is an element

$$\Psi(x_1, \dots, x_N) = \langle x_N, \dots, x_1 | \Psi \rangle \quad (2.3)$$

of the Hilbert space  $\tilde{\mathcal{H}}$  of the square integrable functions over the  $N$ -particle configuration space  $\{x_1, \dots, x_N\}$ .

In a definite state — i.e., using von Neumann's terms: in a pure state — of the system considered, the density operator  $\mathbf{D}$  is the projector of the corresponding subspace  $\mathcal{H}^{(N)}$  of the abstract Hilbert space  $\mathcal{H}$ , i.e.,

$$\mathbf{D} = |\Psi\rangle\langle\Psi| \quad (2.4)$$

being an idempotent operator

$$\mathbf{D}^2 = \mathbf{D}, \quad (2.5)$$

and the expectation value of any dynamical quantity  $\mathbf{A}$  can be obtained as

$$\langle \mathbf{A} \rangle = \text{tr} \{ \mathbf{A} \mathbf{D} \}, \quad (2.6)$$

where  $\text{tr} \mathbf{M}$  indicates the trace (i.e., the sum of the diagonal elements) of a matrix  $\mathbf{M}$ .

The most important properties of  $\mathbf{D}$  can be summarized as follows:

(1) The condition that  $\langle \mathbf{A} \rangle$  has to be real for every Hermitian operator  $\mathbf{A}$ , requires  $\mathbf{D}$  to be Hermitian too,

$$\mathbf{D} = \mathbf{D}^+. \quad (2.7)$$

(2) Keeping in mind that the unit operator  $\mathbf{1}$  has the mean value 1, requires

$$\text{tr} \{ \mathbf{D} \} = 1. \quad (2.8)$$

(3) The condition that every operator with non-negative spectrum has non-negative mean value, requires  $\mathbf{D}$  to be positive definite, i.e., every diagonal element  $\langle n | \mathbf{D} | n \rangle$  must be non-negative

$$\langle n | \mathbf{D} | n \rangle \geq 0. \quad (2.9)$$

(4) Owing to Eqs. (2.8) and (2.9) it is easy to prove that

$$\text{tr} \{ \mathbf{D}^2 \} \leq 1, \quad (2.10)$$

which limits the value of every single element of the density matrix. The equality holds only for pure states.

### § 3. The definition of single particle states

In order to find a natural definition of single particle states of an  $N$ -particle system we use the concept of pure states which are not only of importance in density matrix theory, but also are adequate to the classical ideas in the background of the independent particle model. We recall the argument which COLEMAN [11] used to prove that it is sufficient to deal with pure states to solve the  $N$ -representability problem for a  $p$ -matrix.

The set of all  $N$ -particle density matrices  $\{ \mathbf{D}_N \}$  is identical with the set  $\mathcal{S}_N$  of positive Hermitian operators of unit trace on the Hilbert space of anti-symmetric  $N$ -particle functions. The set  $\mathcal{S}_N$  is convex and its extreme elements are the pure states in the case of which  $\mathbf{D}_N^{(i)}$  is idempotent. The  $N$ -particle state introduced above indicated by a single state vector  $|\Psi\rangle$  is, of course, a

pure state and the corresponding  $N$ -particle density operator  $\mathbf{D}$  is idempotent. Therefore,  $\mathbf{D}$  is an extreme element of the set  $\mathcal{S}_N = \{\mathbf{D}_N\}$ .

For fermions, the set  $\mathcal{S}_N$  consists of all positive Hermitian operators of unit trace on the space of antisymmetric  $p$ -particle functions. Whereas, the set of all  $\mathbf{D}_N$  coincides with  $\mathcal{S}_N$ , the set of  $\{\mathbf{D}_p\}$  is a proper subset of  $\mathcal{S}_p$  which we denote by  $\mathcal{S}_p^{(N)}$ . It consists of those positive operators of unit trace on the Hilbert space of the antisymmetric  $p$ -particle functions which are  $p$ -matrices derived from the  $N$ -particle pure state with the state vector  $|\Psi\rangle$ . Of course,  $\mathcal{S}_p^{(N)}$  is a convex subset of  $\mathcal{S}_p$ , too, and its extreme elements are the  $p$ -matrices  $\mathbf{D}_p^{(i)}$  being also idempotent and they indicate pure states, as well. In accordance with Krein—Milman's theorem which asserts that a compact convex set is determined by its extreme elements, our  $p$ -matrix  $\mathbf{D}_p$  can be set up in terms of the pure states  $p$ -matrices  $\mathbf{D}_p^{(i)}$  in the form

$$\mathbf{D}_p = \sum_i w_i^p \mathbf{D}_p^{(i)}, \quad \left( \sum_i w_i^p = 1 \right) \quad (3.1)$$

where  $w_i^p$ -s are again the statistical weights of the pure states. This means that the  $\mathbf{D}_p$  is, in general, no longer in a pure state,  $\|\mathbf{D}_p^2\| \leq \|\mathbf{D}_p\|$ , but is in a mixed state being a superposition of pure states  $\mathbf{D}_p^{(i)}$ .

For if  $p = 1$ ,  $\mathbf{D}_1$  means the one-particle reduced density operator which is in a mixed state of the one-particle pure states

$$\mathbf{D}_1 = \sum_i \lambda_i \mathbf{D}_1^{(i)}, \quad (\sum \lambda_i = 1). \quad (3.2)$$

Bearing in mind that  $\mathbf{D}_1$  and consequently also  $\mathbf{D}_1^{(i)}$ -s corresponding to pure states, are deduced from the  $N$ -particle density operator  $\mathbf{D}$ , they include all the information which follows from the collective behaviour of the system considered. Equ. (3.2) is nothing else but the spectral resolution of the operator  $\mathbf{D}_1$  and the operators  $\mathbf{D}_1^{(i)}$  are the projectors of its eigenstates which are usually denoted as the *natural spin-orbitals*, NSO's [9].

The NSO's as the eigenstates of the one-particle reduced density matrix are connected, on the one hand, to a single particle degree of freedom of the  $N$ -particle systems; on the other, they are uniquely determined by Krein—Milman's theorem. In fact, they can be interpreted as the single particle states of the  $N$ -particle system looked for, including all information about the collective behaviour of the real system needed.

#### § 4. Natural expansions of the state vector

Suppose that we have an  $N$ -particle quantum system in a bound state  $|\Psi\rangle$ , with norm unity. If the system is imagined to consist of two parts each with  $p$  and  $N-p$  particles, having respectively  $\mathcal{H}_p$  and  $\mathcal{H}_q$  as their complete

state vector spaces, then the original abstract Hilbert space can be formed as a complete tensor product space,  $\mathcal{H} = \mathcal{H}_P \otimes \mathcal{H}_Q$ . I.e., if  $|P\rangle \in \mathcal{H}_P$  and  $|Q\rangle \in \mathcal{H}_Q$  are arbitrary unit vectors, and  $\{|P_i\rangle\}$  and  $\{|Q_j\rangle\}$  are complete orthonormal bases in  $\mathcal{H}_P$  and  $\mathcal{H}_Q$ , respectively,  $\{|P_i Q_j\rangle\}$  is a complete orthonormal basis of  $\mathcal{H}$  with  $|P_i Q_j\rangle \equiv |P_j\rangle |Q_i\rangle = |Q_j\rangle |P_i\rangle$ , so that, e.g.,

$$|\Psi\rangle = \sum_{ij} c[P_i; Q_j] |P_i Q_j\rangle \quad (c[P_i; Q_j] = \langle Q_j P_i | \Psi \rangle), \quad (4.1)$$

where it seems desirable to emphasize by the notation that the coefficients  $c[P_i; Q_j]$  are functionals of the state vectors  $|P_i\rangle$  and  $|Q_j\rangle$ , respectively.

Let us consider the mappings  $\mathcal{H}_Q \rightarrow \mathcal{H}_P$  and  $\mathcal{H}_P \rightarrow \mathcal{H}_Q$ , realized by

$$\langle Q_i | \Psi \rangle = \sum_j a[Q_i; P_j] |P_j\rangle, \quad (4.2)$$

$$\langle P_j | \Psi \rangle = \sum_i b[P_j; Q_i] |Q_i\rangle,$$

with

$$a[Q_i; P_j] = \langle Q_i P_j | \Psi \rangle, \quad b[P_j; Q_i] = \langle P_j Q_i | \Psi \rangle. \quad (4.3)$$

It is easy to check the theorems:

*Theorem 1.* The coefficients  $a[Q_i; P_j]$  and  $b[P_j; Q_i]$  generating the mappings (4.2)  $\mathcal{H}_Q$  into  $\mathcal{H}_P$  and  $\mathcal{H}_P$  into  $\mathcal{H}_Q$ , respectively, are

(a) symmetrical anti-linear functionals of  $|Q_i\rangle$  and  $|P_j\rangle$ :

$$a[Q_i; P_j] = a[P_j; Q_i]; \quad b[P_j; Q_i] = b[Q_i; P_j], \quad (4.4)$$

(b) they are equivalent and the relation

$$a[Q_i; P_j] = b[P_j; Q_i] \quad (4.5)$$

remains valid for any linear combination of the vectors  $|Q_i\rangle$  and  $|P_j\rangle$ , e.g.,

$$a[\alpha_1 |Q_1\rangle + \alpha_2 |Q_2\rangle; \beta_1 |P_1\rangle + \beta_2 |P_2\rangle] = b[\beta_1 |P_1\rangle + \beta_2 |P_2\rangle; \alpha_1 |Q_1\rangle + \alpha_2 |Q_2\rangle].$$

Of course, the relations

$$\sum_i |Q_i\rangle \langle Q_i| \equiv \mathbf{I}_Q, \quad \sum_j |P_j\rangle \langle P_j| \equiv \mathbf{I}_P \quad (4.6)$$

are the resolution of the unit operators in  $\mathcal{H}_Q$  and  $\mathcal{H}_P$ , respectively.

Let us introduce the reduced operators

$$\mathbf{D}_P \stackrel{\text{def}}{=} \sum_i \langle Q_i | \Psi \rangle \langle \Psi | Q_i \rangle = \sum_{j'j} |P_j\rangle A_{j'j}^{(P)} \langle P_{j'}| \quad (4.7)$$

with

$$A_{jj'}^{(P)} \equiv \sum_i a[Q_i; P_j] a^*[Q_i; P_{j'}]; \quad (4.8)$$

and

$$\mathbf{D}_Q \stackrel{\text{def}}{=} \sum_j \langle P_j | \Psi \rangle \langle \Psi | P_j \rangle = \sum_{ii'} |Q_i\rangle A_{ii'}^{(Q)} \langle Q_{i'}| \quad (4.9)$$

with

$$A_{ii'}^{(Q)} \equiv \sum_j b[P_j; Q_i] b^*[P_j; Q_{i'}] = \sum_j a[Q_i; P_j] a^*[Q_{i'}; P_j], \quad (4.10)$$

respectively, where the relations (4.2) and (4.5) were used. On the one hand, owing to the Hermitian character of the matrices  $A_{jj'}^{(P)}$  and  $A_{ii'}^{(Q)}$

$$A_{jj'}^{(P)*} = A_{jj'}^{(P)} \quad \text{and} \quad A_{ii'}^{(Q)*} = A_{ii'}^{(Q)}, \quad (4.11)$$

i.e., their diagonal elements are real. On the other hand owing to the fact that the norm of the state vector  $|\Psi\rangle$  is unity:

$$\langle \Psi | \Psi \rangle = \sum_i \langle \Psi | Q_i \rangle \langle Q_i | \Psi \rangle = \sum_{ij} |a[Q_i; P_j]|^2 = 1, \quad (4.12)$$

both Hermitian operators  $\mathbf{D}_P$  and  $\mathbf{D}_Q$  have unit traces:

$$\text{tr} \{ \mathbf{D}_P \} = 1 \quad \text{and} \quad \text{tr} \{ \mathbf{D}_Q \} = 1. \quad (4.13)$$

*Theorem 2.* There exist orthonormal basis systems,  $\{|q_i\rangle\}$  in  $\mathcal{H}_Q$  and  $\{|p_i\rangle\}$  in  $\mathcal{H}_P$ , respectively, such that

$$a[q_i; p_j] = c_i \delta_{ij} \quad (4.14)$$

and the mappings (4.2) may be replaced by

$$\begin{aligned} \langle q_i | \Psi \rangle &= c_i |p_i\rangle, \\ \langle p_i | \Psi \rangle &= c_i |q_i\rangle, \end{aligned} \quad \text{with } c_i = \langle q_i | p_i \rangle \langle p_i | \Psi \rangle. \quad (4.15)$$

Indeed, for an arbitrary orthonormal basis system  $\{|p_i\rangle\} \in \mathcal{H}_P$  the state vector  $|\Psi\rangle \in \mathcal{H}$  can be expanded in the form

$$|\Psi\rangle = \sum_{ij} a[p_i; Q_j] |p_i Q_j\rangle = \sum_i \left( \sum_j a[p_i; Q_j] |Q_j\rangle \right) |p_i\rangle \equiv \sum_i \tilde{c}_i |\tilde{q}_i\rangle |p_i\rangle.$$

The vectors  $|\tilde{q}_i\rangle$  of the set  $\{|\tilde{q}_i\rangle\}$  are independent and they can be normalized to unity, but they are not necessarily orthogonal. However, for an adequate

$\{|p_i\rangle\} \in \mathcal{H}_P$  the set  $\{|\tilde{q}_i\rangle\}$  can be replaced by means of the Gram—Schmidt procedure by an orthonormal one so that

$$|\Psi\rangle = \sum_i c_i |q_i p_i\rangle \quad (4.16)$$

and, thus, the statement (4.14) is proved.

The vectors  $|q_i\rangle$  are linear expressions of the vectors of the set  $\{|\tilde{q}_i\rangle\}$ , but, owing to Theorem 1/b., if according to (4.14)  $a[q_i; p_i]$  is replaced by  $c_i \delta_{ij}$  then  $b[p_j; q_i] = c_i \delta_{ij}$ , too, for the given orthonormal basis  $\{|p_i\rangle\} \in \mathcal{H}_P$ . Indeed,

$$\begin{aligned} \langle p_i | \Psi \rangle &= \sum_j |q_j\rangle \langle q_j | \langle p_i | \Psi \rangle = \sum_j |q_j\rangle \langle p_i | \langle q_j | \Psi \rangle = \\ &= \sum_j |q_j\rangle \langle p_i | p_j \rangle c_j = c_i |q_i\rangle. \end{aligned}$$

This means that there exist such orthonormal bases  $\{|p_i\rangle\}$  in  $\mathcal{H}_P$  and  $\{|q_i\rangle\}$  in  $\mathcal{H}_Q$  that the mappings (4.16) are fulfilled for  $i = 1, 2, \dots$  and, thus, the proof of the theorem is completed.

The orthonormal set of vectors  $\{|p_i\rangle\} \in \mathcal{H}_P$  is the set of eigenstates of the operator  $D_P$  i.e., the NSO's in  $\mathcal{H}_P$

$$D_P |p_i\rangle = \lambda_i |p_i\rangle \quad \text{with} \quad \lambda_i = |c_i|^2. \quad (4.17)$$

Then

**Theorem 3.** (Carlson and Keller) If the set of vectors  $\{|p_i\rangle\} \in \mathcal{H}_P$  are the NSO's of  $\mathcal{H}_P$ , i.e., the eigenstates of the  $p$ -matrix  $D_P$  corresponding to the eigenvalues  $\lambda_i = |c_i|^2$  then in  $\mathcal{H}_Q$  the eigenvalues of the  $q$ -matrix  $D_q$  are also  $\lambda_i$  and the corresponding eigenstates  $\{|q_i\rangle\}$  are the NSO's in  $\mathcal{H}_Q$ .

Indeed, by the definitions (4.7) and (4.9) and from Eqs. (4.15)

$$D_P = \sum_i \langle q_i | \Psi \rangle \langle \Psi | q_i \rangle = \sum_i |p_i\rangle \lambda_i \langle p_i|, \quad (4.18)$$

$$D_q = \sum_i \langle p_i | \Psi \rangle \langle \Psi | p_i \rangle = \sum_i |q_i\rangle \lambda_i \langle q_i|, \quad (4.19)$$

which are just the spectral resolutions of the operators  $D_P$  and  $D_q$ , respectively, with the elementary projectors  $|p_i\rangle \langle p_i|$  and  $|q_i\rangle \langle q_i|$ .

**Theorem 4.** There exists such a partially isometric operator  $S_{PQ} \equiv \sum_i |p_i\rangle \langle q_i|$  of  $\mathcal{H}$  that

$$S_{PQ}^\dagger S_{PQ} = I_P \quad \text{and} \quad S_{PQ} S_{PQ}^\dagger = I_Q$$

and, from this point of view,  $D_P$  and  $D_q$  are unitarily equivalent:

$$S_{PQ}^\dagger D_P S_{PQ} = D_q. \quad (4.20)$$



This statement can be proved easily and it is another formulation of Carlson—Keller's theorem mentioned previously by KIANG [20], although he did not go into the precise details.

It is easy to see that the operator  $D_p$  in co-ordinate representation is just the  $p$ -matrix  $D(x_1, \dots, x_p; x'_1, \dots, x'_p)$  defined by Equ. (2.2).

In order to simplify the writing let us introduce the notations  $x_p \equiv \{x_1, \dots, x_p\}$ ,  $x_q \equiv \{x_{p+1}, \dots, x_N\}$ ,  $\Psi(x_p, x_q) = \langle x_q x_p | \Psi \rangle$ ,  $p_i(x_p) = \langle x_p | p_i \rangle$  and  $q_i(x_q) = \langle x_q | q_i \rangle$ , then

$$\Psi(x_p, x_q) = \sum_i c_i \langle x_q x_p | p_i q_i \rangle = \sum_i c_i \langle x_p | p_i \rangle \langle x_q | q_i \rangle = \sum_i c_i p_i(x_p) q_i(x_q). \quad (4.21)$$

As COLEMAN [11] pointed out Carlson—Keller's theorem was previously discovered by Schmidt and formulated in the following way:

*Theorem 5.* (Schmidt) Given a square integrable function  $\psi(x_p, x_q)$  suppose that for  $u < v$ ,  $f_i(x_p)$  with  $1 \leq i \leq u$  and  $g_j(x_q)$  with  $1 \leq j \leq v$  are linearly independent square integrable functions, then the minimum

$$\|\Psi\|^2 - \sum_{i=1}^u |c_i|^2$$

of

$$\Delta \equiv \|\Psi(x_p, x_q) - \sum_{ij} A_{ij} f_i(x_p) g_j(x_q)\|^2,$$

where  $A_{ij}$  are arbitrary complex numbers, is obtained if we put

$$A_{ij} = \begin{cases} c_i \delta_{ij}, & j \leq u \\ 0, & j > u \end{cases}$$

and choose

$$f_i(x_p) = p_i(x_p), \quad g_i(x_q) = q_i(x_q),$$

where  $p_i(x_p)$  and  $q_i(x_q)$  indicate the first  $u$  NSO's.

The proof of this important theorem can also be found, e.g., in COLEMAN's paper [11].

In other words, the best least-square approximation as a sum of  $uv$  products of the form  $f_i(x_p)g_j(x_q)$  is  $\sum_i c_i p_i(x_p)q_i(x_q)$ .

So far the symmetry properties of  $\psi(x_p, x_q)$  have not been used. It is, however, well-known and on the basis of its definition it can be easily checked

that for bosons and fermions there is a unique  $p$ -matrix associated with a given system. We shall investigate the fermion case below.

From (4.12) and *Theorem 5* it follows that, except possibly on a set of measure zero, in accordance with (4.21), setting  $p = 1$  and  $q = N - 1$ , we have

$$\Psi(x_1, x_q) = \sum_i c_i p_i^{(1)}(x_1) q_i^{(N-1)}(x_q) \quad (4.22)$$

with

$$c_i q_i^{(N-1)}(x_q) = \int dx_1 p_i^{(1)}(x_1) \Psi(x_1, x_q). \quad (4.23)$$

*Theorem 6.* (Coleman) Any function  $\chi(x_1) \neq 0$  belonging to the zero space  $\tilde{\mathcal{H}}_0^{(1)}$  of the operator  $\mathbf{D}^{(1)}$  on  $\tilde{\mathcal{H}}^{(1)}$ , i.e., being orthogonal to all the  $\Psi$ -NSO's, is orthogonal to  $q_i^{(N-1)}(x_q)$ , too.

Indeed, by (4.22)

$$\begin{aligned} 0 &= \sum_i c_i q_i^{(N-1)}(x_q) \int dx_1 \chi^*(x_1) p_i^{(1)}(x_1) = \int dx_1 \chi^*(x_1) \Psi(x_1, x_2, x_3, \dots, x_N) = \\ &= - \int dx_1 \chi^*(x_1) \Psi(x_2, x_1, x_3, \dots, x_N) = - \\ &= - \sum_i c_i p_i^{(1)}(x_2) \int dx_1 \chi^*(x_1) q_i^{(N-1)}(x_1, x_3, \dots, x_N) \end{aligned}$$

for all  $c_i$  and  $p_i^{(1)}(x_2)$ , therefore

$$\int dx_1 \chi^*(x_1) q_i^{(N-1)}(x_1, x_3, \dots, x_N) = 0, \quad (4.24)$$

qu. e. d.

*Corollary.* Since Equ. (4.24) is valid for any fixed  $x_3, \dots, x_N$ ,  $q_i^{(N-1)}(x_2, x_3, \dots, x_N)$  can be expanded in terms of  $p_i^{(1)}(x_2)$ , i.e.,

$$c_i q_i^{(N-1)}(x_2, \dots, x_N) = \sum_j c_{ij} p_i^{(1)}(x_2) q_j^{(N-2)}(x_3, \dots, x_N).$$

Therefore, by induction it can immediately be obtained that

$$\Psi(x_1, \dots, x_N) = \sum_{k_1, k_2, \dots, k_N} c_{k_1, k_2, \dots, k_N} p_{k_1}^{(1)}(x_1) p_{k_2}^{(1)}(x_2) \dots p_{k_N}^{(1)}(x_N), \quad (4.25)$$

or in the language of the abstract Hilbert space formalism

$$|\Psi\rangle = \sum_{k_1, k_2, \dots, k_N} c_{k_1, k_2, \dots, k_N} |p_{k_1}^{(1)} p_{k_2}^{(2)} \dots p_{k_N}^{(N)}\rangle. \quad (4.26)$$

In the factor-space  $\mathcal{H}^{(r)}$  of the  $r$ th particle one has to define the one-particle density operator in the form

$$\mathbf{D}^{(r)} \equiv \sum_{k_r} |p_{k_r}^{(r)}\rangle \lambda_{k_r} \langle p_{k_r}^{(r)}| \quad (4.27)$$

with the NSO's  $|p_{k_r}^{(r)}\rangle$  or in co-ordinate representation the first order reduced density matrix

$$D_1(x_r; x'_r) = \int dx_1 \dots dx_{r-1} dx_{r+1} \dots dx_N \Psi(x_1, \dots, x_r, \dots, x_N) \Psi^*(x_1, \dots, x'_r, \dots, x_N)$$

with its eigenfunctions  $p_{k_r}^{(1)}(x_r)$ . Owing to the unitary equivalence of the operators  $\mathbf{D}^{(r)}$  and  $\mathbf{D}^{(s)}$  in respect of the partially isometric operator

$$\mathbf{S}_{(rs)} \equiv \sum_i |p_i^{(r)}\rangle \langle p_i^{(s)}|$$

i.e.,

$$\mathbf{S}_{(rs)}^+ \mathbf{D}^{(r)} \mathbf{S}_{(rs)} = \mathbf{D}^{(s)},$$

one does not have to distinguish the eigenvalues of  $\mathbf{D}^{(r)}$  for the different  $r = 1, 2, \dots, N$ .

It is remarkable that the first-order eigenvalues are non-negative and bounded above by  $1/N$ , i.e.,

$$0 \leq \lambda_{k_r} \leq \frac{1}{N}. \quad (4.28)$$

The proof is straightforward and can be found in [9] and in papers dealing with the problem of the  $N$ -representability (e.g. [10,11]).

The set of the NSO's  $\{|p_{k_r}^{(r)}\rangle\}$  is complete orthonormal set in  $\mathcal{H}^{(r)} \ominus \mathcal{H}_0^{(r)}$ , where  $\mathcal{H}_0^{(r)}$  is the zero-space of the operator  $\mathbf{D}^{(r)}$  defined on  $\mathcal{H}^{(r)}$ . This means, however, that if the state vector  $|\Psi\rangle$  considered is expanded in terms of the NSO's, as in Equ. (4.26), only the subspace  $\otimes_{r=1}^N \{\mathcal{H}^{(r)} \ominus \mathcal{H}_0^{(r)}\}$  of  $\mathcal{H}$  is needed. As a consequence, one has to take into account that, of course, for each state vector  $|\Psi\rangle$  of the system a special subspace of  $\mathcal{H}$  is given. In fact, one has to be careful if the usual perturbation problems of the system are investigated in terms of the density operator technique.

A selection of  $N$  indices  $k_1 k_2 \dots k_N$  will in the following be called a configuration and in order to simplify the writing it will be abbreviated by  $K \equiv \{k_1 k_2 \dots k_N\}$ . Similarly, the notation  $|p_K\rangle \equiv |p_{k_1}^{(1)} p_{k_2}^{(2)} \dots p_{k_N}^{(N)}\rangle$  will be introduced for the product of the NSO's. Finally, if the  $r$ th index is absent in the configuration it will be denoted by

$$K[r] \equiv \{k_1 \dots k_{r-1} k_{r+1} \dots k_N\}, \quad |p_{K[r]}\rangle \equiv |p_{k_1}^{(1)} \dots p_{k_{r-1}}^{(r-1)} p_{k_{r+1}}^{(r+1)} \dots p_{k_N}^{(N)}\rangle$$

and analogously  $K[rs] \equiv \{k_1 \dots k_{r-1} k_{r+1} \dots k_{s-1} k_{s+1} \dots k_N\}$  etc. Using this new notation (4.26) can be replaced by

$$|\Psi\rangle = \sum_K c_K |p_K\rangle. \quad (4.29)$$

The  $N$ -particle density operator is thus given by

$$\mathbf{D} = \sum_{MN} |p_M\rangle c_M c_N^* \langle p_N|. \quad (4.30)$$

Since, owing to the orthonormality of the  $|p_M\rangle$ -s

$$\langle p_M | p_N \rangle = \delta_{MN} \equiv \delta_{m_1 n_1} \delta_{m_2 n_2} \dots \delta_{m_N n_N}, \quad (4.31)$$

the square of  $\mathbf{D}$  can easily be calculated:

$$\mathbf{D}^2 = \sum_{MNRS} |p_M\rangle c_M c_N^* \langle p_N | p_R \rangle c_R c_S^* \langle p_S| = \sum_{MNS} |p_M\rangle c_M |c_N|^2 c_S^* \langle p_S|. \quad (4.32)$$

However, owing to the unit norm of  $|\Psi\rangle$  it holds that

$$\langle \Psi | \Psi \rangle = \sum_{MN} \langle p_M | c_M^* c_N | p_N \rangle = \sum_N |c_N|^2 = 1 \quad (4.32)$$

so, finally,

$$\mathbf{D}^2 = \sum_{MS} |p_M\rangle c_M c_S^* \langle p_S| = \mathbf{D} \quad (4.33)$$

is obtained as was expected. Similarly

$$\text{tr}\{\mathbf{D}\} = \sum_{RMN} \langle p_R | p_M \rangle c_M c_N^* \langle p_N | p_R \rangle = \sum_R |c_R|^2 = 1. \quad (4.34)$$

Furthermore, having its definition (4.7) in mind,

$$\begin{aligned} \mathbf{D}^{(r)} &\stackrel{\text{def}}{=} \text{tr}_{\neq r} \{\mathbf{D}\} \equiv \sum_{K[r]} \langle p_{K[r]} | \Psi \rangle \langle \Psi | p_{K[r]} \rangle = \\ &= \sum_{MNK[r]} \langle p_{K[r]} | p_{m_r}^{(r)} p_{M[r]} \rangle c_{m_r M[r]} c_{n_r N[r]}^* \langle p_{N[r]} p_{n_r}^{(r)} | p_{K[r]} \rangle = \sum_{m_r n_r} |p_{m_r}^{(r)}\rangle A_{m_r n_r}^{(1)} \langle p_{n_r}^{(r)}| \end{aligned} \quad (4.35)$$

with

$$A_{m_r n_r}^{(1)} \equiv \sum_{K[r]} c_{m_r K[r]} c_{n_r K[r]}^* = A_{n_r m_r}^{(1)*}, \quad (4.36)$$

where the abbreviation means  $c_{m_r K[r]} \equiv c_{k_1 \dots k_{r-1} m_r k_{r+1} \dots k_N}$ , etc. However, the set  $\{|p_i^{(r)}\rangle\}$  is the set of the eigenvectors of  $\mathbf{D}^{(r)}$ . Therefore,

$$\mathbf{D}^{(r)} |p_i^{(r)}\rangle = \lambda_i |p_i^{(r)}\rangle;$$

since

$$\mathbf{D}^{(r)} |p_i^{(r)}\rangle = \sum_{m_r n_r} |p_{m_r}^{(r)}\rangle A_{m_r n_r}^{(1)} \langle p_{n_r}^{(r)} | p_i^{(r)} \rangle = \sum_{m_r} A_{m_r i}^{(1)} |p_{m_r}^{(r)}\rangle = \lambda_i |p_i^{(r)}\rangle$$

and

$$\lambda_i = \sum_{m_r} A_{m_r i}^{(1)} \langle p_i^{(r)} | p_{m_r}^{(r)} \rangle = A_{i i}^{(1)} \equiv \sum_{K[r]} |c_{iK[r]}|^2, \quad (4.37)$$

and by (4.35) we have

$$A_{ij}^{(1)} = \langle p_j^{(r)} | \mathbf{D}^{(r)} | p_i^{(r)} \rangle = \lambda_i \langle p_j^{(r)} | p_i^{(r)} \rangle = \lambda_i \delta_{ij}; \quad (4.38)$$

the important relation

$$\sum_{K[r]} c_{iK[r]} c_{jK[r]}^* = \delta_{ij} \sum_{K[r]} |c_{iK[r]}|^2 \quad (4.39)$$

is obtained.

We observed that, indeed,

$$\text{tr}\{\mathbf{D}^{(r)}\} = \sum_i \lambda_i = \sum_K |c_K|^2 = 1, \quad (4.40)$$

but

$$\text{tr}\{\mathbf{D}^{(r)2}\} = \text{tr}\left\{ \sum_{ij} |p_i^{(r)}\rangle \lambda_i \langle p_i^{(r)}| p_j^{(r)}\rangle \lambda_j \langle p_j^{(r)}| \right\} = \sum_i \lambda_i^2 < 1 \quad (4.41)$$

as was expected. Namely, the one-particle state is a mixed one in the  $N$ -particle pure state.

Finally, it seems to be worth-while to set up the structural properties of the two-particle reduced density operator, the 2-operator. It is defined by

$$\begin{aligned} \mathbf{D}^{(rs)} &\stackrel{\text{def}}{=} \text{tr}_{\neq r,s} \{\mathbf{D}\} = \sum_{MNK[rs]} \langle p_{K[rs]} | p_M \rangle c_M c_N^* \langle p_N | p_{K[rs]} \rangle = \\ &= \sum_{m_r m_s n_r n_s} |p_{m_r}^{(r)} p_{m_s}^{(s)}\rangle A_{m_r m_s n_r n_s}^{(2)} \langle p_{n_s}^{(s)} p_{n_r}^{(r)}| \end{aligned} \quad (4.42)$$

with

$$A_{m_r m_s n_r n_s}^{(2)} = \sum_{K[rs]} c_{m_r m_s K[rs]} c_{n_r n_s K[rs]}^* = A_{n_r n_s m_r m_s}^{(2)*}. \quad (4.43)$$

The eigenstates of the 2-operator are usually called *natural spin-geminals* (in the following NSG's). Let them be denoted by  $|g_\nu^{(rs)}\rangle$  and the corresponding eigenvalues of  $\mathbf{D}^{(rs)}$  by  $\gamma_\nu$ , then the spectral resolution of  $\mathbf{D}^{(rs)}$  is given as

$$\mathbf{D}^{(rs)} = \sum_\nu |g_\nu^{(rs)}\rangle \gamma_\nu \langle g_\nu^{(rs)}|. \quad (4.44)$$

The NSG's  $|g_\nu^{(rs)}\rangle$  are defined in the complete tensor-product space  $\{\mathcal{H}^{(r)} \ominus \mathcal{H}_0^{(r)}\} \otimes \{\mathcal{H}^{(s)} \ominus \mathcal{H}_0^{(s)}\}$  and they can be expanded in terms of the basis  $\{|p_i^{(r)} p_j^{(s)}\rangle\}$  as follows

$$|g_\nu^{(rs)}\rangle = \sum_{ij} g_{ij}^\nu |p_i^{(r)} p_j^{(s)}\rangle. \quad (4.45)$$

By the definitions (4.43) and (4.44), the relation

$$\begin{aligned} \langle p_l^{(s)} p_k^{(r)} | \mathbf{D}^{(rs)} | p_k^{(r)} p_l^{(s)} \rangle &= \sum_{\nu} \langle p_l^{(s)} p_k^{(r)} | g_{\nu}^{(rs)} \rangle \gamma_{\nu} \langle g_{\nu}^{(rs)} | p_k^{(r)} p_l^{(s)} \rangle = \\ &= \sum_{\nu} g_{kl}^{\nu} \gamma_{\nu} g_{k'l'}^{\nu} = A_{kl,k'l'}^{(2)} \end{aligned} \quad (4.46)$$

and, owing to Eqs. (4.42) and (4.43),

$$\begin{aligned} \gamma_{\nu} &= \langle g_{\nu}^{(rs)} | \mathbf{D}^{(rs)} | g_{\nu}^{(rs)} \rangle = \sum_{klk'l'} \langle_{\nu}^{(rs)} | p_k^{(r)} p_l^{(s)} \rangle A_{kl,k'l'}^{(2)} \langle p_l^{(s)} p_k^{(r)} | g_{\nu}^{(rs)} \rangle = \\ &= \sum_{klk'l'} g_{kl}^{\nu*} A_{kl,k'l'}^{(2)} g_{k'l'}^{\nu} \end{aligned} \quad (4.47)$$

may be obtained, by which the connections between the eigenvalues  $\gamma_{\nu}$  and the eigenmatrix  $A_{kl,k'l'}^{(2)}$  are explicitly given.

### § 5. Remarks on Kiang's variational approach

Let us consider again our system of equations (4.15) getting a special mapping between  $\mathcal{H}_P$  and  $\mathcal{H}_Q$ . It was proved in *Theorem 2* that orthonormal basissystems  $\{|q_i\rangle\} \in \mathcal{H}_Q$  and  $\{|p_i\rangle\} \in \mathcal{H}_P$  exist which are solutions of Eqs. (4.15). Furthermore, it was shown by means of Carlson and Keller's *Theorem 3* that they are exactly the corresponding eigenstates of  $\mathbf{D}_q$  and  $\mathbf{D}_p$ , respectively.

Essentially, the same system of equations was obtained by KIANG [20] in the form

$$\begin{aligned} \langle q | \Psi \rangle &= c | p \rangle, \\ \langle p | \Psi \rangle &= c | q \rangle, \end{aligned} \quad (5.1)$$

based on the requirement that the functional

$$\langle qp | \Psi \rangle \langle \Psi | pq \rangle = |\langle qp | \Psi \rangle|^2 \quad (5.2)$$

has to be stationary.

This stationary condition may be denoted as the "principle of maximum overlap". Apparently, KIANG did not observe that these principles are solely a special case of Schmidt's *Theorem 5* for  $u = 1$ . Indeed, the condition  $|\langle qp | \Psi \rangle|^2 = \text{maximum}$  is equivalent to the condition  $\|\Psi - c | pq \rangle\|^2 = \text{minimum}$ .

In order to determine the eigenstates of  $\mathbf{D}_q$  and  $\mathbf{D}_p$  based on this variational principle KIANG assumed the existence of the solutions  $c_i$ ,  $|q_i\rangle$  and  $|p_i\rangle$  for  $i = 1, 2, \dots$ . As a corollary of *Theorem 2* the existence of such solutions is proved, as mentioned above.

In reverse: due to *Theorems 2, 3 and 5* the solutions of *Eqs. (4.15)* make the functional (5.2) stationary.

Another point should be emphasized, too. KIANG has not observed that the solutions  $\{|q_i\rangle\} \in \mathcal{H}_Q$  and  $\{|p_i\rangle\} \in \mathcal{H}_P$  are complete orthonormal basis systems only in the subspaces  $\mathcal{H}_Q \ominus \mathcal{H}_Q^{(0)}$  and  $\mathcal{H}_P \ominus \mathcal{H}_P^{(0)}$ , respectively. As a matter of fact, just this is the reason while the variational approach and the iteration method proposed by KIANG is only adequate to determine the highest NSO's in the case of a given  $|\Psi\rangle$ . However, this resolution of the system state vector in terms of the maximal NSO's is a very interesting and remarkable result obtained by KIANG.

In order to improve the above statements to a certain extent let us consider again the expansion (4.29) of the state vector in terms of NSO's:

$$|\Psi\rangle = \sum_K c_K |p_K\rangle. \quad (5.3)$$

In fact, in our case  $|\Psi\rangle$  is antisymmetric. This means that  $c_K$  is antisymmetric in its indices  $K = (k_1, \dots, k_N)$ . If one introduces the ordered configuration  $\kappa = \{k_1, \dots, k_N\}$  with  $k_1 < k_2 < \dots < k_N$  instead of  $K$ , *Equ. (5.3)* can be written in the form [9]

$$|\Psi\rangle = \sum_{\kappa} c_{\kappa} \sqrt{N!} \mathbf{A}_N |p_{k_1}^{(1)} \dots p_{k_N}^{(N)}\rangle, \quad (5.4)$$

where the operator  $\mathbf{A}_N$  denotes the antisymmetrizer

$$\mathbf{A}_N = \frac{1}{N!} \sum_P (-1)^P \quad (5.5)$$

with summation over all permutations of the particle indices bearing in mind the convention that odd permutations have to be taken with negative and even ones with positive sign. This means that *Equ. (5.4)* is the expansion of  $|\Psi\rangle$  in terms of the Slater determinants of the NSO's, and

$$c_{\kappa} = \langle p_{k_N}^{(N)} \dots p_{k_1}^{(1)} | \mathbf{A}_N \sqrt{N!} |\Psi\rangle. \quad (5.6)$$

PRIMAS [21] pointed out that, owing to the theorem of SCHMIDT—GOLOMB [23], if  $|c_{\kappa}|^2 = \text{maximum}$  and the orbitals fulfil the relations

$$\langle p_{k_N}^{(N)} \dots p_{k_{r+1}}^{(r+1)} p_{k_{r-1}}^{(r-1)} \dots p_{k_1}^{(1)} | \Psi\rangle = c_{\kappa} \sqrt{N!} |p_{k_r}^{(r)}\rangle, \quad (5.7)$$

then

$$|\Phi\rangle = \sqrt{N!} \mathbf{A}_N |p_{k_1}^{(1)} \dots p_{k_N}^{(N)}\rangle \quad (5.8)$$

is a uniquely determined optimal Slater-determinant, the so-called Brueckner determinant. It will be proved in the next paragraph that the first highest NSO's fulfil condition (5.7), i.e., they are exactly the Brueckner orbitals.

### § 6. Cluster expansions of the density operator

Now, let us investigate the resolution of  $\mathbf{D}$  in terms of the one-particle density operators, essentially, using the method of the cluster expansion suggested by PRIMAS [21].

Consider the idempotent operator

$$\begin{aligned} \mathbf{I} &\equiv \sum_{KL} \mathbf{P}_{KL} \equiv \sum_{KL} |p_K\rangle\langle p_L| = \sum_K |p_K\rangle\langle p_L| + \sum_{K \neq L} |p_K\rangle\langle p_L| \equiv \\ &\equiv \sum_K \mathbf{P}_K + \sum_{KL} \mathbf{P}_{K \neq L} \equiv \mathbf{I}_d + \mathbf{I}_{nd}, \end{aligned} \quad (6.1)$$

which is a unit super-operator\* in respect to  $\mathbf{D}$ . Indeed,

$$\hat{\mathbf{I}}\{\mathbf{D}\} \stackrel{\text{def}}{=} \sum_{KL} \hat{\mathbf{P}}_{KL}\{\mathbf{D}\} \equiv \sum_{KL} \text{tr}\{\mathbf{P}_{KL}^+ \mathbf{D}\} \mathbf{P}_{KL} = \mathbf{D}, \quad (6.2)$$

owing to the fact that

$$\text{tr}\{|p_L\rangle\langle p_K| \mathbf{D}\} = \sum_{RMN} \langle p_R | p_M \rangle c_M c_N^* \langle p_N | p_R \rangle = c_K c_L^*. \quad (6.3)$$

If we introduce the notation

$$\mathbf{D} = \sum_M |p_M\rangle\langle c_M|^2 \langle p_M| + \sum_{M \neq N} |p_M\rangle\langle c_M c_N^* \langle p_N| \equiv \mathbf{D}_d + \mathbf{D}_{nd}, \quad (6.4)$$

it can be checked easily that

$$\text{tr}\{\mathbf{P}_{K \neq L}^+ \mathbf{D}\} = 0 \quad \text{and} \quad \text{tr}\{\mathbf{P}_K \mathbf{D}_{nd}\} = 0. \quad (\mathbf{P}_K = \mathbf{P}_K^+) \quad (6.5)$$

Since, by (6.2) for

$$\mathbf{I}\{\mathbf{D}_d\} = \sum_K \mathbf{P}_K^+ \{\mathbf{D}_d\} = \sum_K \text{tr}\{\mathbf{P}_K \mathbf{D}\} \mathbf{P}_K = \sum_K |c_K|^2 \mathbf{P}_K = \mathbf{D}_d \quad (6.6)$$

\* A super-operator is a function with the operator algebra of all operators as its domain and range. Any one-electron super-operator can be represented by  $\hat{\mathbf{P}}\{\mathbf{X}\} = \text{tr}\{\mathbf{P}^+ \mathbf{X}\} \mathbf{P}$  for all operators  $\mathbf{X}$  where  $\mathbf{P}$  is a certain Hermitian one-electron operator of the dynamical system considered.



and, also, the identity

$$\mathbf{P}_K \equiv |p_K\rangle\langle p_K| \equiv \prod_{r=1}^N |p_{k_r}^{(r)}\rangle\langle p_{k_r}^{(r)}| \equiv \prod_{r=1}^N [\mathbf{D}^{(r)} + (|p_{k_r}^{(r)}\rangle\langle p_{k_r}^{(r)}| - \mathbf{D}^{(r)})] \quad (6.7)$$

holds, the remarkable resolution of  $\mathbf{D}_d$

$$\begin{aligned} \mathbf{D}_d = & \sum_K |c_K|^2 \left\{ \prod_{r=1}^N \mathbf{D}^{(r)} + \sum_{n=1}^N (|p_{k_n}^{(n)}\rangle\langle p_{k_n}^{(n)}| - \mathbf{D}^{(n)}) \prod_{r \neq n} \mathbf{D}^{(r)} + \right. \\ & \left. + \frac{1}{2!} \sum_{n \neq m} (|p_{k_n}^{(n)}\rangle\langle p_{k_n}^{(n)}| - \mathbf{D}^{(n)}) (|p_{k_m}^{(m)}\rangle\langle p_{k_m}^{(m)}| - \mathbf{D}^{(m)}) \prod_{r \neq n, m} \mathbf{D}^{(r)} + \dots \right\} \quad (6.8) \end{aligned}$$

can be obtained. But owing to the definitions (4.29) and (4.42) and to Equ. (4.40), we have the resolution of  $\mathbf{D}_d$  as follows:

$$\mathbf{D}_d = \prod_{r=1}^N \mathbf{D}^{(r)} + \frac{1}{2!} \sum_{n \neq m} (\mathbf{D}_d^{(nm)} - \mathbf{D}^{(n)} \mathbf{D}^{(m)}) \prod_{i \neq n, m} \mathbf{D}^{(i)} + \dots \quad (6.9)$$

It is straightforward, even if it is to a certain extent tedious, to prove that the super-operator  $\hat{\mathbf{P}}_{K \neq L} \{ \mathbf{D}_{nd} \}$  obtains the terms  $\mathbf{D}_{nd}^{(nm)}$ , etc. at the resolution of  $\mathbf{D}$ .

Owing to the Pauli principle the density operator has to be antisymmetric in the sense:

$$\mathbf{D} = \hat{\mathbf{A}}_N \{ \mathbf{D} \} = \mathbf{A}_N \mathbf{D} \mathbf{A}_N, \quad (6.10)$$

where  $\mathbf{A}_N$  is the antisymmetrizer in Equ. (5.5).

Thus, the resolution of  $\mathbf{D}$  in terms of the one-particle density operators can be obtained as follows

$$\mathbf{D} = \hat{\mathbf{A}}_N \left\{ \prod_{r=1}^N \mathbf{D}^{(r)} + \frac{1}{2!} \sum_{n \neq m} \mathbf{C}^{(nm)} \prod_{i \neq n, m} \mathbf{D}^{(i)} + \frac{1}{3!} \sum_{n \neq m, l} \mathbf{C}^{(nml)} \prod_{r \neq n, m, l} \mathbf{D}^{(r)} + \dots \right\} \quad (6.11)$$

with the cluster operators

$$\mathbf{C}^{(nm)} \stackrel{\text{def}}{=} \mathbf{D}^{(nm)} - \mathbf{D}^{(n)} \mathbf{D}^{(m)}, \quad (6.12)$$

where, e.g.,  $\hat{\mathbf{A}}_2 \{ \mathbf{C}^{(nm)} \}$  is related to the two-particle correlation operator of the electrons, which will be discussed in the next part of this investigation.

We can get another useful way of expanding the density operator in terms of one-particle density operators. Let us consider the first  $N$  highest eigenstates of the one- and two-particle density operators etc., and introduce

the set of truncated operators

$$\tilde{\mathbf{D}}^{(r)} = \sum_{\mu=1}^N |P_{\mu}^{(r)}\rangle \lambda_{\mu} \langle P_{\mu}^{(r)}|, \quad \tilde{\mathbf{D}}^{(rs)} = \sum_{\nu=1}^N |g_{\nu}^{(rs)}\rangle \gamma_{\nu} \langle g_{\nu}^{(rs)}|. \quad (6.13)$$

Then, taking into account that the summation over the configuration  $K = \{k_1, k_2, \dots, k_N\}$  is not truncated, we have, e.g.,

$$\begin{aligned} \mathbf{D}_d &= \sum_K |c_K|^2 \prod_{r=1}^N \{ \tilde{\mathbf{D}}^{(r)} + (|P_{k_r}^{(r)}\rangle \langle P_{k_r}^{(r)}| - \tilde{\mathbf{D}}^{(r)}) \} = \\ &= \prod_{r=1}^N \tilde{\mathbf{D}}^{(r)} + \sum_{n=1}^N (\mathbf{D}^{(n)} - \tilde{\mathbf{D}}^{(n)}) \prod_{r \neq n} \tilde{\mathbf{D}}^{(r)} + \\ &+ \frac{1}{2!} \sum_{m \neq n} \mathbf{D}^{(nm)} - \mathbf{D}^{(n)} \tilde{\mathbf{D}}^{(m)} - \tilde{\mathbf{D}}^{(n)} \mathbf{D}^{(m)} - \tilde{\mathbf{D}}^{(n)} \tilde{\mathbf{D}}^{(m)}. \prod_{r \neq n, m} \mathbf{D}^{(r)} + \dots \end{aligned} \quad (6.14)$$

If the notations

$$\mathbf{D}^{(n)} = \tilde{\mathbf{D}}^{(n)} + \mathbf{v}^{(n)}, \quad \mathbf{D}^{(nm)} = \tilde{\mathbf{D}}^{(nm)} + \mathbf{v}^{(nm)} \quad (6.15)$$

are introduced, one obtains easily that

$$\mathbf{D} = \hat{\mathbf{A}}_N \left\{ \prod_{r=1}^N \tilde{\mathbf{D}}^{(r)} + \frac{1}{2!} \sum_{n \neq m} \{ \tilde{\mathbf{C}}^{(nm)} + \mathbf{v}^{(nm)} \} \prod_{r \neq n, m} \mathbf{D}^{(r)} + \dots \right\} \quad (6.16)$$

where the cluster operators

$$\tilde{\mathbf{C}}^{(nm)} \equiv \tilde{\mathbf{D}}^{(nm)} - \tilde{\mathbf{D}}^{(n)} \tilde{\mathbf{D}}^{(m)} \quad (6.17)$$

are related to the correlation electrons in the ground states corresponding to the first highest NSO's and  $\mathbf{v}^{(nm)}$  determines the correlations via excited states.

It is remarkable that the first order cluster operators corresponding to the single particle excitations are absent in both cluster expansions (6.11) and (6.16); i.e.

$$\text{tr}_{\neq r} \{ \mathbf{P}_{k_r} \mathbf{D} \} = \lambda_{k_r} \mathbf{P}_{k_r} \quad (\mathbf{P}_{k_r} = |P_{k_r}^{(r)}\rangle \langle P_{k_r}^{(r)}|). \quad (6.18)$$

In this way the statement at the end of §5 that the NSO's are just the Brueckner orbitals is proved. This problem, as well as the problems connected with the correlation between the electrons in terms of the cluster operators will also be discussed in the next part of this investigation in more detail.

Finally, let us still mention that if the higher order cluster terms  $C^{(nm)}$ ,  $C^{(nmk)}$ , ... are absent, i.e., if the system of the  $N$  electrons is a perfect one, the well known result [9]:

$$\langle x_N \dots x_1 | D | x'_1 \dots x'_N \rangle = \begin{vmatrix} D(x_1; x'_1) \dots D(x_1; x'_N) \\ \vdots \\ D(x_N; x'_1) \dots D(x_N; x'_N) \end{vmatrix} \quad (6.19)$$

and a similar expression in the case of the truncated first order reduced density operators are obtained.

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#### О ТЕОРИИ ОПЕРАТОРОВ ПЛОТНОСТИ ФЕРМИОНОВ I.

##### ОПРЕДЕЛЕНИЕ ОДНОЧАСТИЧНЫХ СОСТОЯНИЙ И КЛАСТЕРНОЕ РАЗЛОЖЕНИЕ ОПЕРАТОРОВ ПЛОТНОСТИ

Я. И. ХОРВАТ и И. К. ДЪЕМАНТ

#### Резюме

После определения операторов плотности (§ 2) вырабатывается понятие простых частичных состояний на основе чистых состояний приведенных операторов плотности первого порядка (§ 3). Далее рассматривается понятие NSO и NSG и разложения по ним (§ 4). Дискутируется и развивается дальше вариационное приближение Кiangа (§ 5). Наконец в различных случаях даются кластерные разложения операторов плотности  $N$ -частиц по приведенным операторам плотности первого порядка.