Properties of Fermion Density Matrices*

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CONTENTS

I. Introduction . . . 690
II. Definitions and Notation . . . 690
III. Classical Results . . . 691
IV. Upper Bounds for Higher-Order Eigenvalues . . . 692
V. Difficulties in Higher-Order Problems . . . 692
VI. Reproduction Problems . . . 693
VII. Approximation by a Slater Determinant . . . 697
VIII. Optimal Number of Configurations . . . 699
IX. Perburbation of Eigenvalues . . . 699
X. Appendixes . . . 700
1. Expansion . . . 700
2. Schmidt's Orthonormalization . . . 700
3. Variational Theorems . . . 700
4. Generalized Schwartz's Inequality . . . 701
5. Scaling . . . 701
6. Norms of an Operator . . . 701
7. Wielandt's Inequality . . . 702

I. INTRODUCTION

THIS paper reports an investigation of basic properties of Fermion density matrices which, introduced by Dirac[1] and extensively studied by Löwdin,[2] have revealed ever growing importance in quantum chemistry. Though the second-order density matrices play the most important role in connection with energy determination of many electron systems, compared with the first-order ones, there is a great deal of difficulty to be overcome and no result of definite importance has yet been obtained. This paper contains an advanced study of properties of the first-order density matrices and the general properties of higher-order ones. As to physical interpretations, interested readers may consult ter Haar's monograph.[3] In preparing this paper, the author was greatly inspired by Coleman's excellent papers[4,5] to which about half of the results in this paper belong.

In Sec. II definitions and special notations used in what follows are collected. It should be remarked that our definitions of density matrices differ from those in Löwdin[2] by scalars. Section III contains some well-known properties of density matrices which make cornerstones for the later sections. Section IV gives upper bounds for higher-order eigenvalues. While the basic inequality (Theorem 5) was proved by Coleman,[5] we present another proof. Theorem 6 seems new. One of the interesting problems in density matrix theory, from mathematical standpoints, is the reproduction problem; that is, to ask, given a nonnegative definite kernel, under what conditions it can coincide with the pth-order density matrix of a normalized antisymmetric function of n particles. The complete solution to this problem has not yet been settled. Section V reveals some difficult aspects in the reproduction problem even in a modified form. Section VI is completely devoted to the solution of the reproduction problem under severe restriction on rank. An interesting property on degeneracy is stated in Theorem 11, which was proved in slightly incorrect form by Coleman[5] with tensor calculus. A correct formulation with a proof is given here. Theorem 12 seems new. Section VII has the aim of answering the question of the best approximation of an arbitrary function by a Slater determinant. The basic Theorem 13 is essentially due to Löwdin and Shull[6] and the generalized form presented here was announced by Coleman[5] without proof. Our proof is Hilbert-theoretic and is essentially the same as Mirsky's.[7] Theorems 14 and 15 are stated in this paper for the first time. Section VIII answers the question raised by Foldy[8] concerning the minimum number of configurations. Theorem 17 seems new. Section IX contains entirely new results concerning the estimate of the deviation of eigenvalues. Finally, in Section X, most inequalities used in the paper are given simple proofs. However, because of limitation of space, we can not produce all.

II. DEFINITIONS AND NOTATION

When Ψ is a normalized antisymmetric function of n particles, its pth-*order density matrix* is defined by

$$D_p(x';x) \equiv D_p(1',2',\cdots,p';1,2,\cdots,p) \equiv \int_{p+1,\cdots,n} \Psi^*(x',p+1,\cdots,n)\Psi(x,p+1,\cdots,n)\,, \tag{1}$$

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4 A. J. Coleman, Can. Math. Bull. **4**, 209 (1961).
5 A. J. Coleman, Tech. Note 80, Uppsala Quantum Chemistry Group, Uppsala, Sweden (unpublished).
6 P.-O. Löwdin and H. Shull, Phys. Rev. **101**, 1730 (1956).
7 L. Mirsky, Quart. J. Math. **11**, 50 (1960).
8 L. L. Foldy, J. Math. Phys. **3**, 531 (1962).

where i stands for the spin-orbital coordinate of the ith particle and x for $(1,2,\cdots,p)$. When special reference to Ψ is necessary, we write $D_{p,\Psi}$ instead of D_p. Sometimes D_1 is simply denoted by D. $D_p(x';x)$ can be regarded as the kernel of an integral operator, and its basic properties are deduced from the following: (*nonnegative definiteness*)

$$\int \varphi^* D_p \varphi \geqslant 0 \qquad \text{for every function } \varphi \text{ of } p \text{ particles,} \tag{2}$$

(*normalization*)

$$\int D_p(x;x) = 1\,, \tag{3}$$

(*antisymmetry*)

$$\mathbf{A}_p D_p = D_p \mathbf{A}_p = D_p\,, \tag{4}$$

where $\mathbf{A}_p$ is the projection operator on the antisymmetric part, i.e.,

$$\mathbf{A}_p \equiv (1/p!) \sum (-1)^P \mathbf{P}\,,$$

where $\mathbf{P}$ runs over all permutations of $1,2,\cdots,p$. D_p can be obtained from D_{p+1} by the formula

$$D_p(x';x) = \int_{p+1} D_{p+1}(x',p+1;x,p+1)\,. \tag{5}$$

If we denote by $\{\lambda_j\}$[9] the eigenvalues of D_p and by $\{\varphi_j\}$ the normalized eigenfunctions belonging to them, respectively, D_p can be represented in the form

$$D_p(x';x) = \sum_{j=1} \lambda_j \varphi_j^*(x') \varphi_j(x)\,. \tag{6}$$

$\{\lambda_j\}$ and $\{\varphi_j\}$ are called the pth *order eigenvalues* and the *natural p states of Ψ*, respectively. Natural 1 states are specially referred to as *natural orbitals*. The number of nonzero λ_j is called the *p rank of Ψ* and the 1 rank is simply referred to as its *rank*. The properties (2) and (3) are converted into the following:

$$\sum_{j=1} \lambda_j = 1 \text{ and } 0 \leqslant \lambda_j\,. \tag{7}$$

For two normalized functions φ,ψ of p particles, the values

$$\int \varphi^* D_p \varphi \quad \text{and} \quad \int \varphi^* D_p \psi$$

are called the *p density of Ψ on φ* and the *p bond of Ψ between φ and ψ*. The p density on the natural p state φ_j is clearly equal to the pth-order eigenvalue λ_j.

III. CLASSICAL RESULTS

Here we collect basic well-known results, without proof, which are used freely in the later development. Most proofs can be found in Löwdin.[2]

Ψ always denotes a normalized antisymmetric function of n particles.

Theorem 1. Given an arbitrary complete orthonormal system $\{\psi_j\}$ of orbitals,[10] Ψ can be expanded as an (infinite) linear combination of Slater determinants constructed from $\{\psi_j\}$. When the rank of Ψ is finite, say r, and $\{\varphi_j\}_1^r$ are its natural orbitals belonging to nonzero eigenvalues, Ψ can be expanded as a linear combination of Slater determinants constructed only from $\{\varphi_j\}_1^r$.

This is fairly well known and easily verified.

Theorem 2. For every Slater determinant φ of p particles,

$$\int \varphi^* D_p \varphi \leqslant \frac{p!(n-p)!}{n!}\,.$$

In particular, in case $p = 1$, any 1 density is not greater than $1/n$ and if it is equal to $1/n$ on some orbital ψ, then ψ is one of the natural orbitals and Ψ is written as a linear combination of Slater determinants all of which contain ψ as a component.

While this was explicitly mentioned by Löwdin,[2] the case $p = 1$ had been obtained by Watanabe.[11]

The only antisymmetric function whose natural states of all order can be easily determined is a Slater determinant.

Theorem 3. If Ψ is a Slater determinant with components $\varphi_1, \varphi_2, \cdots, \varphi_n$, then its natural p states consist of all Slater determinants of p particles with components $\varphi_{i_1}, \varphi_{i_2}, \cdots, \varphi_{i_p}$, where $1 \leqslant i_1 < i_2 < \cdots < i_p \leqslant n$, and the corresponding eigenvalues are all equal to $p!(n-p)!/n!$. In particular, in case $p = 1$, the natural orbitals consist of $\varphi_1, \varphi_2, \cdots, \varphi_n$ with the equal eigenvalue $1/n$.

The final result has been more or less known; however, in connection with density matrix theory it was first pointed out by Carlson and Keller[12] and by Coleman.[4] The proof is straightforward.

Theorem 4. For the natural p state φ_j belonging to a pth order-eigenvalue λ_j, the function Φ_j of $(n-p)$ particles defined by

$$\Phi_j(p+1,\cdots,n) = \int_{1,\cdots,p} \varphi_j^*(1,\cdots,p)\Psi(1,\cdots,p,p+1,\cdots,n)$$

is the (not necessarily normalized) natural $(n-p)$ state belonging to an $(n-p)$th-order eigenvalue equal to λ_j, and

$$\Psi = \sum_{j=1} \varphi_j \cdot \Phi_j\,.$$

[9] Unless the contrary is mentioned, $\{\lambda_j\}$ are always arranged in nonincreasing order, i.e., $\lambda_1 \geq \lambda_2 \geq \ldots$, repeated with their respective multiplicities.

[10] An *orbital* is a function of a single particle.

[11] S. Watanabe, Z. Physik **113**, 482 (1939).

[12] B. C. Carlson and J. M. Keller, Phys. Rev. **121**, 659 (1961).

IV. UPPER BOUNDS OF HIGHER-ORDER EIGENVALUES

From Theorem 2 combined with Theorem 4 with $p = 1$ it follows that every $(n-1)$th-order eigenvalue is not greater than $1/n$. Now let $\{\psi_j\}$ be the natural $(p+1)$ states of a normalized antisymmetric function Ψ of n particles, then by (5) and (6) the pth-order density matrix can be expressed

$$D_p(x';x) = \int_{p+1} D_{p+1}(x',p+1;x,p+1)$$
$$= \sum_{j=1} \mu_j \int_{p+1} \psi_j^*(x',p+1)\psi_j(x,p+1) ,$$

where $\{\mu_j\}$ are the $(p+1)$th order eigenvalues. Since each ψ_j is a normalized antisymmetric function of $(p+1)$ particles and

$$\int_{p+1} \psi_j^*(x',p+1)\psi_j(x,p+1)$$

is its pth-order density matrix, it follows from the above remark with $p+1$ instead of n that for every normalized function φ of p particles

$$\int_{x,x'}\int_{p+1} \varphi^*(x)\psi_j^*(x',p+1)\psi_j(x,p+1)\varphi(x') \leqslant \frac{1}{p+1} ;$$

hence

$$\int \varphi^* D_p \varphi$$
$$= \sum_{j=1} \mu_j \int \varphi^*(x)\psi_j^*(x',p+1)\psi_j(x,p+1)\varphi(x')$$
$$\leqslant \sum_{j=1} \frac{\mu_j}{p+1} = \frac{1}{p+1} ,$$

because $\sum_{j=1} \mu_j = 1$ by (7). This means that every p density of Ψ is not greater than $1/(p+1)$. On the other hand, by Theorem 4 each pth order eigenvalue is equal to one of the $(n-p)$th order eigenvalues which are not greater than $1/(n-p+1)$ for the same reason. Since the greatest p density is equal to the greatest pth-order eigenvalue by the variation principle (Sec. X3), we have

Theorem 5.[13] Every pth-order eigenvalue is not greater than

$$\min \{1/(p+1) , \quad 1/(n-p+1)\} .$$

When either Ψ or φ can be represented as a linear combination of relatively few Slater determinants, the upper bound for the p density of Ψ on φ is suitably improved.

Theorem 6. If either

$$\varphi(1,\cdots,p) = \sum_{j=1}^{k} \alpha_j\psi_j(1,\cdots,p)$$

or

$$\Psi(1,\cdots,p,\cdots,n) = \sum_{j=1}^{k} \beta_j\Psi_j(1,2,\cdots,n) ,$$

where $\{\psi_j\}_1^k$ and $\{\Psi_j\}_1^k$ are mutually orthogonal Slater determinants of p particles and n particles, respectively, then

$$\int \varphi^* D_p \varphi \leqslant k \times \frac{p!(n-p)!}{n!}$$

As the proofs to both cases are quite similar, we confine ourselves to the first case. Since the kernel D_p is nonnegative definite, by the generalized Schwartz's inequality (Sec. X4) and Theorem 2

$$\left| \int \psi_i^* D_p \psi_j \right| \leqslant \left\{ \int \psi_j^* D_p \psi_j \right\}^{\frac{1}{2}} \left\{ \int \psi_i^* D_p \psi_i \right\}^{\frac{1}{2}}$$
$$\leqslant \frac{p!(n-p)!}{n!} .$$

Hence

$$\int \varphi^* D_p \varphi \leqslant \frac{p!(n-p)!}{n!} \times \sum_{i,j=1}^{k} |\alpha_i|\cdot|\alpha_j|$$
$$\leqslant \frac{p!(n-p)!}{n!} \times \sum_{i,j=1}^{k} \frac{|\alpha_i|^2+|\alpha_j|^2}{2}$$
$$= \frac{p!(n-p)!}{n!} \times k \times \left(\sum_{j=1}^{k} |\alpha_j|^2\right)$$
$$= k \times \frac{p!(n-p)!}{n!} .$$

The last equality follows from normalization of φ and orthogonality of $\{\psi_j\}$; i.e.,

$$\sum_{j=1}^{k} |\alpha_j|^2 = \int |\varphi|^2 = 1 .$$

This estimate gives a better upper bound than that given in Theorem 5 only when $k \leqslant n!/(n-p+1)!p!$. In the case $p = 2$, this means $k \leqslant n/2$.

Finally, an estimate for p bonds is given. This also follows from the generalized Schwartz's inequality (Sec. X4) just as the above theorem.

Theorem 7.

$$\{p \text{ bond between } \varphi \text{ and } \psi\}$$
$$\leqslant \{p \text{ density on } \varphi\}^{\frac{1}{2}} \times \{p \text{ density on } \psi\}^{\frac{1}{2}}$$
$$\leqslant \min \{1/(p+1) , 1/(n-p+1)\} .$$

V. DIFFICULTIES IN HIGHER-ORDER PROBLEMS

Given a nonnegative definite kernel $\mathbf{E}(1';1)$ with eigenfunctions $\{\varphi_j\}$ belonging, respectively, to eigen-

[13] It can be proved that, except in the case $p = 1$ or $p = n-1$, this upper bound is never attained. See Coleman.[5] Recently F. Sasaki (unpublished communication) has obtained much better upper bounds.

values $\{\mu_j\}$ which satisfy the condition

$$\sum_{j=1} \mu_j = 1 \text{ and } 0 \leqslant \mu_j \leqslant 1/n \,, \qquad (8)$$

is there any normalized antisymmetric function Ψ of n particles whose first-order density matrix coincides with $\mathbf{E}$? Unfortunately, this is not always the case, as is seen in Sec. VI. If Ψ is represented, by Theorem 1, as a linear combination of Slater determinants constructed from $\{\varphi_j\}$, i.e.,

$$\Psi = \sum_K c_K \Psi_K \,,$$

this problem can be reduced to solving a system of simultaneous nonlinear equations

$$\sum_{j \in K} |c_K|^2 = \mu_j \qquad (j = 1,2,\cdots) \qquad (9)$$

and

$$\sum_{K-j=L-i} c_K^* c_L = 0 \qquad (i \neq j) \,, \qquad (10)$$

where $j \in K$ means that j is contained in the configuration K and $K - j$ means the $(n-1)$ configuration with j deleted. Thus, whether any Ψ in question exists or not depends only on the properties of $\{\mu_j\}$ but not on the eigenfunctions $\{\varphi_j\}$. Difficulties arise mostly from the condition (10) which requires that, when $\mathbf{E}$ is expanded by $\{\varphi_j\}$, the off-diagonal terms must vanish. If we neglect requirement (10) and only take into account the condition (9), putting $\rho_k = |C_k|^2$, the problem is reduced to finding *nonnegative* solutions of a system of linear equations

$$\sum_{j \in K} \rho_K = \mu_j \qquad (j = 1,2,\cdots) \,. \qquad (9')$$

This condition means that the 1 density of Ψ on each φ_j is equal to μ_j. Recently Kuhn[14] gave a positive answer to this modified problem, the proof of which is too difficult to reproduce here.

Theorem 8. Given a finite orthonormal system $\{\varphi_j\}_1^r$ of orbitals and a finite sequence $\{\mu_j\}_1^r$ with the property

$$\sum_{j=1}^{r} \mu_j = 1 \text{ and } 0 \leqslant \mu_j \leqslant \frac{1}{n} \,,$$

there exists a normalized antisymmetric function Ψ of n particles such that

$$\int \varphi_j^* D_\Psi \varphi_j = \mu_j \qquad (j = 1,2,\cdot\cdot, r) \,.$$

Can we extend this result to higher-order cases? Naturally, $1/n$ must be replaced by $1/(n-1)$ in the case $p = 2$ by Theorem 5. Given a finite orthonormal system $\{\psi_j\}_1^r$ of two particles and a finite sequence $\{\lambda_j\}_1^r$ with the property

$$\sum_{j=1} \lambda_j = 1 \text{ and } 0 \leqslant \lambda_j \leqslant 1/(n-1) \,,$$

is there any normalized antisymmetric function Ψ of n particles whose 2 density on ψ_j is equal to λ_j, i.e.,

$$\int \psi_j^* D_{2,\Psi} \psi_j = \lambda_j \,?$$

The answer, however, is negative. For example, if all ψ_j are Slater determinants of two particles, by Theorem 2, λ_j must be not greater than $2/n(n-1)$. On the other hand, it is pointed out by Coleman[5] that the estimate in Theorem 5 is the best possible.[15] This means that whether $\{\lambda_j\}$ can be a sequence of the 2 densities of a normalized antisymmetric function is not determined by $\{\lambda_j\}$ alone, but largely depends on the choice of the orthonormal system $\{\psi_j\}$. This makes the problem much more difficult.

VI. REPRODUCTION PROBLEMS

Given a nonnegative definite kernel $\mathbf{E}(1';1)$, under what conditions does there exist a normalized antisymmetric function of n particles whose first-order density matrix coincides with $\mathbf{E}$? This problem is called the *reproduction problem* of the first order. In this section the reproduction problem of the first order is given a complete solution for the kernel with rank[16] not greater than $n + 2$.

For this purpose let us begin with a more detailed study of the first-order eigenvalues. Let Ψ be a normalized function of n particles with the natural orbitals $\{\varphi_j\}$ belonging to the first-order eigenvalues $\{\lambda_j\}$, respectively. Then Ψ can be written in the form

$$\Psi(1,\cdots,n) = \mathbf{A}_n \varphi_1(1) \Phi_1(2,\cdots,n) + \Phi_2(1,2,\cdots,n) \,,$$

where Φ_1 and Φ_2 are antisymmetric functions of $(n-1)$ particles and of n particles, respectively. In fact, expanding Ψ as a linear combination of Slater determinants constructed from $\{\varphi_j\}$

$$\Psi = \sum c_K \Psi_K \,.$$

The functions Φ_1 and Φ_2 are given, respectively, by

$$\mathbf{A}_n \varphi_1(1) \Phi_1(2,\cdots,n) = \sum_{1 \in K} c_K \Psi_K$$

and

$$\Phi_2 = \sum_{1 \notin L} c_L \Psi_L \,,$$

[14] H. W. Kuhn, Proc. Symp. Appl. Math. **10**, 141 (1960).

[15] That is, the greatest pth-order eigenvalue can approach the upper bound, min $\{1/(p+1), 1/(n-p+1)\}$.

[16] The *rank* of the kernel is the number of its nonzero eigenvalues.

where $1 \notin L$ means that the configuration L does not contain 1. From this it is easily seen that φ_1 is *totally orthogonal*[17] to both Φ_1 and Φ_2. Then the first-order density matrix D is written in the form

$$D(1';1) = \int_x \{\mathbf{A}_n\varphi_1(1')\Phi_1(x)\}^*\{\mathbf{A}_n\varphi_1(1)\Phi_1(x)\}$$
$$+ \int_x \{\mathbf{A}_n\varphi_1(1)\Phi_1(x)\}^*\Phi_2(1,x)$$
$$+ \int_x \Phi_2^*(1',x)\{\mathbf{A}_n\varphi_1(1)\Phi_1(x)\}$$
$$+ \int_x \Phi_2^*(1',x)\Phi_2(1,x)$$

with the abbreviation $x = (2,\cdots,n)$. For every two permutations

$$P = \begin{pmatrix} i_1,\cdots,i_n \\ 1,\cdots,n \end{pmatrix} \quad \text{and} \quad Q = \begin{pmatrix} j_1,\cdots,j_n \\ 1,\cdots,n \end{pmatrix}$$

total orthogonality of φ_1 to Φ_1 implies

$$\int_{2,\cdots,n} \varphi_1^*(i_1)\Phi_1^*(i_2,\cdots,i_n)\varphi_1(j_1)\Phi_1(j_2,\cdots,j_n) = 0 \quad \text{when } i_1 \neq j_1 .$$

Hence, using antisymmetry of Φ_1, the first term can be calculated as follows:

$$\frac{1}{(n!)^2}\sum_{P,Q}(-1)^P(-1)^Q\int_{2,\cdots,n}\varphi_1^*(i_1)\Phi_1^*(i_2,\cdots,i_n)\varphi_1(j_1)$$
$$\times \Phi_1(j_2,\cdots,j_n) = \frac{\alpha}{n^2}\cdot\varphi_1^*(1')\varphi_1(1) + \frac{n-1}{n^2}$$
$$\times \int_y \Phi_1^*(1',y)\Phi_1(1,y) ,$$

where

$$y = (2,\cdots,n-1) \text{ and } \alpha = \int \Phi_1^*\Phi_1 .$$

The sum of the second and third terms is written in the form

$$\varphi_1^*(1')\Theta(1) + \Theta^*(1')\varphi_1(1) ,$$

where Θ can be expanded by $\{\varphi_j\}_2$ without φ_1, i.e.,

$$\Theta = \sum_{j=2}\beta_j\varphi_j .$$

Total orthogonality of φ_1 to Φ_2 implies that the last term can be expanded by products of $\{\varphi_j\}_2$ without φ_1, i.e.,

$$\int_x \Phi_2^*(1',x)\Phi_2(1,x) = \sum_{i,j=2}\gamma_{ij}\varphi_i^*(1')\varphi_j(1) .$$

[17] A function φ of p particles is said to be *totally orthogonal* to a function Ψ of q particles (with $p \leq q$), if

$$\int_{1,\cdots,p}\varphi^*(1,\ldots,p)\Psi(1,\ldots,p,\ldots,q) = 0 .$$

Since the φ_j are eigenfunctions of D, it follows that

$$\int \varphi_1^* D\varphi_1 = \lambda_1 \text{ and } \int \varphi_1^* D\varphi_j = 0 (j \neq 1) .$$

Substituting the decomposition, we obtain

$$\lambda_1 = \alpha/n^2 \text{ and } \Theta(1) \equiv 0 .$$

Normalizing Φ_1, i.e., putting $\Psi_1 \equiv \Phi_1/\alpha^{\frac{1}{2}}$, we obtain the result

$$D(1';1) = \lambda_1\varphi_1^*(1')\varphi_1(1) + (n-1)\lambda_1 D_{\Psi_1}(1';1) + \int_x \Phi_2^*(1',x)\Phi_2(1,x) .$$

Since by (2)

$$\int_1 D(1;1) = \int_1 D_{\Psi_1}(1;1) = 1 ,$$

it follows that

$$\lambda_1 + (n-1)\lambda_1 + \int \Phi_2^*\Phi_2 = 1 .$$

Hence normalizing Φ_2, i.e., putting

$$\Psi_2 \equiv (1 - n\lambda_1)^{-\frac{1}{2}}\Phi_2 \quad \text{when} \quad 1 - n\lambda_1 \neq 0$$

we attain a decomposition of D. Incidentally, notice that the condition $\Theta(1) \equiv 0$ is equivalent to total orthogonality of Ψ_1 to Ψ_2. Summarizing, we have

Lemma 1. The first-order density matrix D of Ψ can be decomposed into the following form:

$$D = \lambda_1\varphi_1^*\varphi_1 + (n-1)\lambda_1 D_{\Psi_1} + (1 - n\lambda_1)D_{\Psi_2} , \quad (11)$$

where Ψ_1 and Ψ_2 are normalized antisymmetric functions of $(n-1)$ particles and of n particles, respectively. Moreover, φ_1, Ψ_1, and Ψ_2 are totally orthogonal to one another.

This decomposition was first shown by Coleman[4,5] in a slightly different way. While he says that this gives a double induction algorithm for the reproduction problem of the first order, there is no way to determine Ψ_1 and Ψ_2 in terms of D alone, and so we can not agree with him.

We need another lemma in order to give effective applications of Lemma 1.

Lemma 2. In the decomposition (11), if D_{Ψ_1} has an eigenfunction φ belonging to the eigenvalue $1/(n-1)$, it is also a natural orbital of Ψ belonging to the eigenvalue λ_1, and is totally orthogonal to Ψ_2 when $1 - n\lambda_1 \neq 0$.

This can be seen as follows: since λ_1 is the greatest eigenvalue of D and the kernel $(1 - n\lambda_1)D_{\Psi_2}$ is non-negative definite,

$$\lambda_1 \geqslant \int \varphi^* D\varphi \geqslant \lambda_1 \left| \int \varphi_1^* \varphi \right|^2 + (n-1)\lambda_1 \int \varphi^* D_{\Psi_1} \varphi$$
$$+ (1 - n\lambda_1) \int \varphi^* D_{\Psi_2} \varphi \geqslant (n-1)\lambda_1 \int \varphi^* D_{\Psi_1} \varphi$$
$$= \lambda_1 ;$$

hence it follows that

$$\int \varphi^* D\varphi = \lambda_1 \text{ and } (1 - n\lambda_1) \int \varphi^* D_{\Psi_2} \varphi = 0 .$$

The former relation implies that φ is the eigenfunction of D belonging to the greatest eigenvalue λ_1 by the variation principle (Sec. X3), and the latter shows the total orthogonality of φ to Ψ_2.

Now we turn to the reproduction problem of the first order. Let a nonnegative definite kernal $\mathbf{E}(1';1)$ be given with the eigenfunctions $\{\psi_j\}$ belonging to the eigenvalues $\{\mu_j\}$. By Theorem 5 a standard necessary condition for the reproduction problem is

$$\sum_{j=1} \mu_j = 1 \text{ and } 0 \leqslant \mu_j \leqslant 1/n .$$

If, in addition to this, each μ_j is degenerate with multiplicity divisible by n, i.e.,

$$\mu_{(k-1)n+1} = \mu_{(k-1)n+2} = \cdots = \mu_{kn} (k = 1,2,\cdots) ,$$

then there exists a normalized antisymmetric function Ψ whose first-order density matrix coincides with $\mathbf{E}$. In fact, denoting by Ψ_k the Slater determinant constructed from $\psi_{(k-1)n+1}, \cdots, \psi_{kn}$ the function Ψ defined by

$$\Psi = \sum_{k=1} [n\mu_{(k-1)n+1}]^{\frac{1}{2}} \Psi_k$$

meets the requirement. It must be remarked that any function of the form

$$\sum_{k=1} \alpha_k [n\mu_{(k-1)n+1}]^{\frac{1}{2}} \Psi_k \text{ with } |\alpha_k| = 1$$

also meets the requirement. This means that, even in case the reproduction is possible, the solution is not always essentially unique.

In the case $n = 2$, the above degeneracy condition is also necessary. The following theorem is due to Coleman.[5]

Theorem 9. In the case $n = 2$, each first-order eigenvalue is evenly degenerate.

For in the decomposition (11) $n = 2$ implies that Ψ_1 is a function of a single particle, so D_{Ψ_1} is $\Psi_1^*\Psi_1$; hence by Lemma 2 λ_1 is, at least, doubly degenerate and Ψ_1 is totally orthogonal to Ψ_2. Then all eigenfunctions of D_{Ψ_2} are also eigenfunctions of D and we can proceed inductively with D_{Ψ_2} and so on.

This theorem shows that the rank of a function of two particles is always an even number, so the condition (8) alone is not sufficient for the reproduction problem.

The condition (8) implies that the rank of $\mathbf{E}$ is not smaller than n. Once it is equal to n, by Theorem 3 a solution, in fact an essentially unique solution, to the reproduction problem is given by the Slater determinant constructed from the eigenfunctions.

The next step is to study the case of rank $n + 1$, but, as is shown in the following theorem, this case can not occur. Theorem 10 was proved by Coleman[5] and by Foldy[8,18] and by others by a different method.

Theorem 10. The rank of any normalized antisymmetric function of n particles can not be equal to $n + 1$.

This can be proved by induction with respect to n. When $n = 1$, the assertion is quite trivial because the rank is always equal to 1. Assume that the assertion is valid for any normalized antisymmetric function of $(n - 1)$ particles. Let Ψ be a normalized antisymmetric function of n particles with rank $n + 1$. In the decomposition (11) of the first-order density matrix of Ψ, Ψ_1 is a normalized antisymmetric function of $(n - 1)$ particles with rank not greater than $(n + 1) - 1 = (n - 1) + 1$; so by the induction assumption for $n - 1$, its rank is equal to $n - 1$ and it is a Slater determinant constructed from orthonormal orbitals, say $\psi_2, \psi_3, \cdots, \psi_n$, each of which is totally orthogonal to Ψ_2 by Lemma 2 when $1 - n\lambda_1 \neq 0$. On the other hand, if $1 - n\lambda_1 \neq 0$, from the construction in the proof of Lemma 1 it is easily seen that the range[19] of Ψ_2 must be spanned by $\psi_2, \psi_3, \cdots, \psi_n$ and one more additional orbital, say ψ_{n+1}, leading to a contradiction to total orthogonality of Ψ_1 to Ψ_2 in case $n > 1$. Thus $1 - n\lambda_1$ must be equal to 0, and then, in turn, Ψ itself is a Slater determinant and has rank n, contradicting the assumption. This means that Ψ can never have rank $n + 1$.

The next simplest step is a study of functions with rank $n + 2$. This case is divided into two according to whether n is even or odd, as is seen in the following theorem which was proved by Coleman[5] in a slightly incorrect form.

Theorem 11. If the rank of Ψ is $n + 2$, then

(i) in the case where n is odd, $\lambda_1 = 1/n$ and each of the remaining eigenvalues is evenly degenerate,

(ii) in the case where n is even, each eigenvalue is evenly degenerate.

The assertion is obviously valid for $n = 1$ or $= 2$ by Theorem 9. Assume that the assertion is valid for all functions of particles less than n. For general n we start with the decomposition (11)

$$D = \lambda_1 \varphi_1^* \varphi_1 + (n-1)\lambda_1 D_{\Psi_1} + (1 - n\lambda_1) D_{\Psi_2} .$$

[18] Foldy's proof seems to be wrong.

[19] The *range* of Ψ_2 is the set of all linear combinations of its natural orbitals belonging to nonzero eigenvalues.

(I) The case $\lambda_1 = 1/n$, i.e., when the third term vanishes. Let $\psi_1, \cdots, \psi_{n+1}$ be the eigenfunctions of D_{Ψ_1} belonging to the eigenvalues $\{\rho_j\}$, respectively, then total orthogonality of φ_1 to Ψ_1 implies that each ψ_j is an eigenfunction of D belonging to the eigenvalue $\lambda_{j+1} = (n-1)\rho_j/n$. When n is odd, $n-1$ is even and Ψ_1 has rank not greater than $n+1$. Hence by induction assumption for $n-1$, each ρ_j, *a fortiori* λ_{j+1}, is evenly degenerate, and (i) follows. The proof for even n is similar.

(II) The case $\lambda_1 \neq 1/n$. Then by Theorem 10 Ψ_2 is a Slater determinant, because its rank is not greater than $n+1$. Let $\psi_1, \psi_2, \cdots, \psi_n$ be the eigenfunctions of D_{Ψ_2}, then

$$\Psi_2 = \frac{1}{n!^{\frac{1}{2}}} \sum_{j=1}^{n} (-1)^{j+1} \psi_j(1)$$
$$\times \operatorname{Det}\{\psi_1(2), \cdots, \psi_{j-1}(j), \psi_{j+1}(j+1) \cdots \psi_n(n)\} .$$

Since the range of Ψ_1 must be spanned by $\psi_1, \psi_2, \cdots, \psi_n$, and one more additional orbital, say ψ_{n+1}, Ψ_1 can be represented by a linear combination of Slater determinants constructed from all $(n-1)$ orbitals chosen from $\psi_1, \psi_2, \cdots, \psi_{n+1}$, that is,

$$\Psi_1(1, \cdots, n-1) = \sum \gamma_{i_1 \cdots i_{n-1}} \operatorname{Det}\{\psi_{i_1}, \cdots, \psi_{i_{n-1}}\} ,$$

where $1 \leqslant i_1 < \cdots < i_{n-1} \leqslant n+1$. Total orthogonality of Ψ_1 to Ψ_2 implies

$$\int_{2,\cdots,n} \Psi_1^*(2, \cdots, n) \Psi_2(1, 2, \cdots, n)$$
$$= n!^{\frac{1}{2}} \sum_{j=1}^{n} (-1)^{jH} \gamma_{1 \cdots j-1, j+1 \cdot n} \psi_j(1) \equiv 0 .$$

Since $\{\psi_j\}$ are linearly independent, this relation yields that all $\gamma_{1, \cdots, j-1, j+1, \cdot n}$ are equal to 0, hence

$$\Psi_1 = \sum{}' \gamma_{i_1 \cdot i_{n-1}} \operatorname{Det}\{\psi_{i_1}, \cdots, \psi_{i_{n-1}}\} ,$$

where $\sum'$ means the summation over all the configurations with $i_{n-1} = n+1$. Then, by Theorem 2, ψ_{n+1} is a natural orbital of D_{Ψ_1} belonging to the eigenvalue $1/(n-1)$ so by Lemma 2 it is also a natural orbital of Ψ itself belonging to λ_1. Thus λ_1 is, at least, doubly degenerate. Applying again the decomposition (11) to the density matrix D_{Ψ_1} of Ψ_1, with $\varphi_2 \equiv \psi_{n+1}$,

$$D_{\Psi_1} = (n-1)^{-1} \varphi_2^* \varphi_2 + [(n-2)/(n-1)] D_\Phi ,$$

where Φ is a normalized antisymmetric function of $(n-2)$ particles with rank n. If $\varphi_3, \varphi_4, \cdots, \varphi_{n+2}$ denote the eigenfunctions of D_Φ belonging to the eigenvalues $\{\rho_j\}_3^{n+2}$, respectively, $\{\psi_1, \cdots, \psi_n\}$ and $\{\varphi_3, \varphi_4, \cdots, \varphi_{n+2}\}$ span the same subspace, hence the density matrix D_{Ψ_2} can be written in the form

$$D_{\Psi_2} = \frac{1}{n} \sum_{j=3}^{n+2} \varphi_j^* \varphi_j .$$

Hence we can write

$$D = \lambda_1 \varphi_1^* \varphi_1 + \lambda_1 \varphi_2^* \varphi_2 + \sum_{j=3}^{n+2} \left\{ (n-2)\lambda_1 \rho_j + \frac{1 - n\lambda_1}{n} \right\} \varphi_j^* \varphi_j .$$

When n is even, $n-2$ is also even and, by induction assumption for $n-2$, each ρ_j is evenly degenerate. Consequently, each eigenvalue of D is evenly degenerate. When n is odd, $n-2$ is also odd. Hence, by induction assumption for $n-2$, the greatest ρ_3 is equal to $(n-2)^{-1}$. Then by a calculation it is seen that φ_3 is an eigenfunction belonging to the eigenvalue $\lambda_1 + [(1 - n\lambda_1)/n]$ which is strictly greater than λ_1, contradicting the maximality of λ_1. This shows that, in the case where n is odd, λ_1 must be equal to $1/n$.

The foregoing considerations culminate in the following reproduction theorem.

Theorem 12. In order that, given a nonnegative definite kernel $\mathbf{E}(1';1)$ with rank not greater than $n+2$, there exist a normalized antisymmetric function of n particles whose first-order density matrix coincides with $\mathbf{E}(1';1)$, it is necessary and sufficient that

$$\sum_{j=1} \mu_j = 1 \text{ and } 0 \leqslant \mu_j \leqslant 1/n ,$$

where $\{\mu_j\}$ are the eigenvalues of $\mathbf{E}$, and

(i) in the case where n is odd, the greatest eigenvalue is equal to $1/n$ and each of the remaining eigenvalue is evenly degenerate,

(ii) in the case where n is even, each eigenvalue is evenly degenerate.

The first condition implies that the rank is not smaller than n, and the condition on degeneracy excludes $n+1$. Thus, there only remains the proof of the sufficiency for rank $n+2$. When $n = 1$ or $= 2$, the assertion is obviously true. Assume that the assertion is valid for all the cases with functions of not more than $n-1$ particles. Let $\{\psi_j\}$ be the eigenfunctions of $\mathbf{E}$ belonging to the eigenvalues $\{\mu_j\}$ in non-increasing order, respectively.

(I) In the case where n is odd, by (i), $\mathbf{E}$ can be written in the form

$$\mathbf{E} = \frac{1}{n} \psi_1^* \psi_1 + \frac{n-1}{n} \sum_{j=1}^{n+1} \rho_j \psi_{j+1}^* \psi_{j+1} ,$$

where

$$\rho_j = \frac{n\mu_{j+1}}{n-1} .$$

Then

$$\rho_{2j-1} = \rho_{2j} \leqslant (n-1)^{-1} \text{ and } \sum_{j=1} \rho_j = 1 .$$

Thus $\{\rho_j\}$ satisfy the conditions in Theorem 12 for $n-1$; hence, by induction there exists a normalized antisymmetric function Φ_1 of $(n-1)$ particles whose first-order density matrix coincides with

$$\sum_{j=1}^{n+1} \rho_j \psi_{j+1}^* \psi_{j+1} .$$

Then, finally, the function Ψ of n particles defined by

$$\Psi = n^{\frac{1}{2}} \mathbf{A}_n \psi_1(1) \Phi_1(2,\cdots,n)$$

meets the requirement.

(II) In the case where n is even, $\mathbf{E}$ can be written in the form

$$\mathrm{E} = \mu_1 \psi_1^* \psi_1 + \mu_1 \psi_2^* \psi_2 + \sum_{j=1}^{n} \left\{ (n-2)\mu_1 \rho_j + \frac{1-n\mu_1}{n} \right\} \psi_{j+2}^* \cdot \psi_{j+2} ,$$

where

$$\mu_{j+2} = (n-2)\mu_1 \rho_j + [(1-n\mu_1)/n] \; j = 1,2,\cdots,n .$$

Since

$$n\mu_1 + 2\mu_{n+2} \geqslant \mu_1 + \mu_2 + \cdots + \mu_{n+2} = 1 ,$$

it follows that

$$\rho_n = [(n-2)\mu_1]^{-1} \left\{ \mu_1 + \mu_{n+2} - \frac{1}{n} \right\} \geqslant 0 .$$

Hence,

$$0 \leqslant \rho_j \leqslant (n-2)^{-1}$$

and, similarly,

$$\rho_{2j-1} = \rho_{2j} \text{ and } \sum_{j=1}^{n} \rho_j = 1 .$$

Thus $\{\rho_j\}_1^n$ satisfy all the conditions for $n-2$; hence, by induction there exists a normalized antisymmetric function Φ_1 of $(n-2)$ particles whose first-order density matrix coincides with

$$\sum_{j=1}^{n} \rho_j \psi_{j+2}^* \psi_{j+2} .$$

Denoting by Φ_2 the Slater determinant constructed from $\{\psi_j\}_3^{n+2}$, we can easily verify that the function Ψ of n particles defined by

$$\Psi = [\lambda_1 n(n-1)]^{\frac{1}{2}} \mathbf{A}_n \psi_1(1)\psi_2(2)\Phi_1(3,\cdots,n) + (1-n\mu_1)^{\frac{1}{2}} \Phi_2(1,\cdots,n)$$

meets the requirement.

VII. APPROXIMATION BY A SLATER DETERMINANT

Given a normalized antisymmetric function Ψ of n particles, to what degree can it be approximated by a Slater determinant or by a Hartree product? Since an exact evaluation cannot be given in a simple formula, in this section, a reasonable lower bound is given in terms of the first-order eigenvalues.

For this purpose let us begin with an important general theorem which was originally proved by Löwdin and Shull[6] in the case where $n = 2$ and by Coleman[5] in the general form. Our proof, however, differs from theirs.

Theorem 13.[20] Given p and k, when Φ varies over all the functions of the form

$$\Phi(1,\cdots,n) = \sum_{j=1}^{k} \psi_j(1,\cdots,p)\Psi_j(p+1,\cdots,n) ,$$

where $\{\psi_j\}_1^k$ and $\{\Psi_j\}_1^k$ are arbitrary functions of p particles and $(n-p)$ particles, respectively. Then

$$\min_{\Phi} \int |\Psi - \Phi|^2 = 1 - \sum_{j=1}^{k} \lambda_j ,$$

where $\lambda_1, \lambda_2, \cdots, \lambda_k$ are the k greatest pth-order eigenvalues. The minimum value is attained when each ψ_j is the natural p state belonging to λ_j and each Ψ_j is the (nonnormalized) natural $(n-p)$ state given by

$$\Psi_j(p+1,\cdots,n) = \int \psi_j^*(1,\cdots,p)\Psi(1,\cdots,p,\cdots,n) .$$

First of all, let $\{\varphi_j\}$ be the natural p states belonging to $\{\lambda_j\}$; then by Theorem 4

$$\Psi(x,y) = \sum_{j=1} \varphi_j(x)\Phi_j(y) ,$$

where

$$\Phi_j(y) = \int_x \varphi_j^*(x)\Psi(x,y)$$

with abbreviations $x = (1,2,\cdots,p)$ and $y = (p+1, \cdots, n)$. Hence,

$$\int |\Psi(x,y) - \sum_{j=1}^{k} \varphi_j(x)\Phi_j(y)|^2 = \int | \sum_{j=k+1} \varphi_j(x)\Phi_j(y)|^2 = \sum_{j=k+1} \int |\Phi_j|^2 = \sum_{k=k+1} \lambda_j = 1 - \sum_{j=1}^{k} \lambda_j .$$

This means that the minimum in question is not greater than

$$1 - \sum_{j=1}^{k} \lambda_j .$$

[20] A general theorem of this type was recently obtained by Mirsky.[7]

Now, let

$$\Phi(x,y) = \sum_{j=1}^{k} \psi_j(x)\Psi_j(y)$$

with arbitrary $\{\psi_j(x)\}$ and $\{\Psi_j(y)\}$. Then there exists an orthonormal system of p particles $\psi_{k+1}, \psi_{k+2}, \cdots$ such that they constitute a complete orthonormal system together with Schmidt's orthonormalization (Sec. X2) $\chi_1, \chi_2, \cdots, \chi_k$ of $\psi_1, \psi_2, \cdots, \psi_k$. Hence, in particular,

$$\int_x \psi_j^*(x)\psi_{k+i}(x) = 0 \qquad \begin{array}{l} j = 1,2,\cdots,k \\ i = 1,2,\cdots \end{array} .$$

Taking into account the fact that

$$\int_x \Phi(x,y)\psi_{k+i}^*(x)$$
$$= \sum_{j=1}^{k} \left\{ \int_x \psi_j(x)\psi_{k+i}^*(x) \right\} \Psi_j(y) \equiv 0 ,$$

by Schmidt's theorem (Sec. X6), we find that

$$\int |\Psi - \Phi|^2 = \sum_{j=1}^{k} \int_y | \int_x \{\Psi(x,y) - \Phi(x,y)\}\chi_j^*(x)|^2$$
$$+ \sum_{j=k+1} \int_y | \int_x \{\Psi(x,y) - \Phi(x,y)\}\psi_j^*(x)|^2$$
$$\geq \sum_{j=k+1} \int_y | \int \Psi(x,y)\psi_j^*(x)|^2 = \sum_{j=k+1} \int \psi_j^* D_p \psi_j .$$

On the other hand,

$$\sum_{j=1}^{k} \int \chi_j^* D_p \chi_j + \sum_{j=k+1} \int \psi_j^* D_p \psi_j = \int D_p(x;x) = 1 ;$$

hence by Fan Ky's theorem (Sec. X3)

$$\sum_{j=k+1} \int \psi_j^* D_p \psi_j = 1 - \sum_{j=1}^{k} \int \chi_j^* D_p \chi_j \geqslant 1 - \sum_{j=1}^{k} \lambda_j .$$

When combined with the preceding result, this yields that the minimum in question is equal to $1 - \sum_{j=1}^{k} \lambda_j$ and is attained by the optimal function $\sum_{j=1}^{k} \varphi_j(x) \times \Phi_j(y)$.

In general, denoting by Φ' the normalization of Φ in Theorem 13, it is easily seen from the scaling Lemma (Sec. X5) that

$$\min_{\Phi} \int |\Psi - \Phi|^2 = \min_{\Phi'} \min_{\alpha} \int |\Psi - \alpha\Phi'|^2$$
$$= \min_{\Phi'} \left\{ 1 - | \int \Psi^*\Phi'|^2 \right\} = 1 - \max_{\Phi'} | \int \Psi^*\Phi'|^2$$

and[21]

$$\int |\Psi - \Phi'|^2 = 2 - 2| \int \Psi^*\Phi| .$$

[21] Without loss of generality we may assume $\int \Psi^*\Phi = |\int \Psi^*\Phi|$.

Hence, it follows that

$$\min_{\Phi'} \int |\Psi - \Phi'|^2$$
$$= 2 \left\{ 1 - \left(1 - \min_{\Phi} \int |\Psi - \Phi|^2 \right)^{\frac{1}{2}} \right\}$$

and the minimum is attained at the normalization of the optimal function in Theorem 13. Summarizing, we have

Theorem 14. Given p and k, when Φ' varies over all *normalized* functions of the form

$$\Phi'(x,y) = \sum_{j=1}^{k} \psi_j(x)\Psi_j(y) ,$$

where $\{\psi_j\}$ and $\{\Psi_j\}$ are arbitrary functions of p particles and of $(n - p)$ particles, respectively. Then

$$\min_{\Phi'} \int |\Psi - \Phi'|^2 = 2 \left\{ 1 - \left(\sum_{j=1}^{k} \lambda_j \right)^{\frac{1}{2}} \right\}$$

and the minimum is attained when Φ' is the normalization of the optimal function in Theorem 10.

Now we turn to the promised approximation problem. Since a Slater determinant Φ' is written in the form

$$\Phi'(1,\cdots,n) = \sum_{j=1}^{n} \psi_j(1)\Psi_j(2,\cdots,n) ,$$

on taking $p = 1$ and $k = n$ in Theorems 13 and 14, we have

Theorem 15. For every Slater determinant Φ'

$$\int |\Psi - \Phi'|^2 \geqslant 2 \left\{ 1 - \left(\sum_{j=1}^{n} \lambda_j \right)^{\frac{1}{2}} \right\}$$

and for every (not necessarily normalized) Slater determinant Φ

$$\int |\Psi - \Phi|^2 \geqslant 1 - \sum_{j=1}^{n} \lambda_j .$$

Finally, we treat approximation by a Hartree product of the form $\psi_1(1)\psi_2(2)\cdots\psi_n(n)$, where ψ_j are normalized orbitals but not necessarily orthogonal. Let $\{\chi_j\}_1^n$ be the Schmidt's orthonormalization of $\{\psi_j\}_1^n$ (Sec. X2), then

$$\psi_i = \sum_{j=1}^{n} \alpha_{ij}\chi_j , \quad \sum_{j=1}^{n} |\alpha_{ij}|^2 = \int |\psi_j|^2 = 1 ,$$

and

$$\mathrm{Det}\,\{\psi_1,\psi_2,\cdots,\psi_n\} = \mathrm{Det}\,\{\alpha_{ij}\} \times \mathrm{Det}\,\{\chi_1,\cdots,\chi_n\} .$$

Then, by Hadamard's well-known inequality,

$$|\,\mathrm{Det}\,\{\alpha_{ij}\}|^2 \leqslant \prod_{i=1}^{n} \left\{ \sum_{j=1}^{n} |\alpha_{ij}|^2 \right\} = 1 .$$

Since Ψ is antisymmetric, i.e., $\mathbf{A}_n\Psi = \Psi$,

$$\int|\Psi - \psi_1(1)\psi_2(2)\cdots\psi_n(n)|^2 \geqslant 2 - 2 \times \left|\int\Psi^*(\psi_1(1)\psi_2(2)\cdots\psi_n(n))\right|$$

$$= 2 - 2\left|\int\Psi^*\cdot\mathbf{A}_n\psi_1(1)\cdots\psi_n(n)\right|$$

$$= 2 - \frac{2}{n!}\left|\int\Psi^*\cdot \text{Det}\,\{\psi_1,\psi_2,\cdots,\psi_n\}\right|$$

$$\geq 2 - \frac{2}{n!}\int\Psi^*\cdot \text{Det}\,\{\chi_1,\chi_2,\cdots,\chi_n\}\,,$$

where we have assumed that, with suitable choice of a phase factor,

$$\int\Psi^*\cdot \text{Det}\,\{\chi_1,\cdots,\chi_n\} = \left|\int\Psi^*\cdot \text{Det}\,\{\chi_1,\cdots,\chi_n\}\right|.$$

On the other hand, by Theorem 15

$$2 - \frac{2}{(n!)^{\frac{1}{2}}}\int\Psi^*\cdot \text{Det}\,\{\chi_1,\cdots,\chi_n\}$$

$$= \int|\Psi - (n!)^{-\frac{1}{2}}\,\text{Det}\,\{\chi_1,\cdots,\chi_n\}|^2$$

$$\geqslant 2\left\{1 - \left(\sum_{j=1}^{n}\lambda_j\right)^{\frac{1}{2}}\right\}.$$

Hence, combined with the above, it follows that

$$\int|\Psi - \psi_1\psi_2\cdots\psi_n|^2 \geqslant 2\left\{1 - \left(\sum_{j=1}^{n}\lambda_j/n!\right)^{\frac{1}{2}}\right\}.$$

We can treat nonnormalized Hartree products in quite a similar way.

Theorem 16. For every set of n *normalized* orbitals $\psi_1', \psi_2', \cdots, \psi_n'$,

$$\int|\Psi - \psi_1'\psi_2'\cdots\psi_n'|^2 \geqslant 2\left\{1 - \left(\sum_{j=1}^{n}\lambda_j/n!\right)^{\frac{1}{2}}\right\}$$

and for every (not necessarily normalized) set of n orbitals $\psi_1, \psi_2, \cdots, \psi_n$,

$$\int|\Psi - \psi_1\cdot\psi_2\cdots\psi_n|^2 \geqslant 1 - \left(\sum_{j=1}^{n}\lambda_j/n!\right).$$

VIII. OPTIMAL NUMBER OF CONFIGURATIONS

How many Slater determinants are necessary to represent a normalized antisymmetric function Ψ of n particles, when its rank is not greater than r? The problem of this type was proposed by Foldy[8] in connection with the fact that the rank of D can never be equal to $n + 1$. Obviously by Theorem 1, $\binom{r}{n}$ Slater determinants will do; however, in practice, neglecting orthogonality between Slater determinants, the optimal number will considerably decrease. Here we take up some simple cases.

Theorem 17. If the rank of Ψ is not greater than $n + 2$, it can be represented as a linear combination of, at most, k Slater determinants where

$$k = (n+1)/2 \quad \text{when } n \text{ is odd}$$

or

$$k = (n/2) + 1 \quad \text{when } n \text{ is even}\,.$$

Proof by induction. When $n = 1$, the assertion is obvious. Assume that the assertion is valid for the case of functions of not more than $n - 1$ particles. If the rank of Ψ is equal to $n + 2$ and n is odd, by Theorem 12 Ψ can be written in the form

$$\Psi = n^{\frac{1}{2}}\mathbf{A}_n\psi_1(1)\Phi_1(2,\cdots,n)\,,$$

where Φ_1 is a normalized antisymmetric function of $(n - 1)$ particles with rank $n + 1$; hence, by induction Φ_1 can be written as a linear combination of, at most, $(n - 1)/2 + 1$ Slater determinants of $(n - 1)$ particles. Consequently, Ψ itself can be represented as a linear combination of, at most, $(n + 1)/2$ Slater determinants. The proof for the case of even n is quite similar.

IX. PERTURBATION OF EIGENVALUES

Let Ψ and Φ be two normalized antisymmetric functions of n particles with their pth-order eigenvalues $\{\lambda_j\}$ and $\{\mu_j\}$, respectively. It is clear that, as Φ approaches Ψ, i.e., the quadratic deviation $\int|\Psi - \Phi|^2$ approaches 0, each μ_j approaches λ_j. In this section a reasonable estimate of degree of simultaneous convergence is given in terms of $\int|\Psi - \Phi|^2$. Let us start with an easier problem.

Theorem 18. Given an arbitrary complete orthonormal system $\{\Theta_j\}$ of p particles, with the abbreviation

$$\alpha_j = \int\Theta_j^*D_{p,\Psi}\Theta_j$$

$$\beta_j = \int\Theta_j^*D_{p,\Phi}\Theta_j$$

it follows that

$$\sum_{j=1}|\alpha_j - \beta_j| \leqslant 2\left\{\int|\Psi - \Phi|^2\right\}^{\frac{1}{2}}.$$

Consider the projection operator $\mathbf{P}_j$ defined by the kernel $\Theta_j^*(x')\Theta_j(x)$; then orthogonality of $\{\Theta_j\}$ implies that for any choice $\epsilon_j = 1$ or -1 and for any normalized function ψ of p particles

$$\int \Big| \sum_{j=1} \epsilon_j \mathbf{P}_j \psi \Big|^2 = \sum_{ij=1} \epsilon_i \epsilon_j \int (\mathbf{P}_i \psi)^* (\mathbf{P}_j \psi)$$
$$= \sum_{j=1} \Big| \int \Theta_j^* \cdot \psi \Big|^2 = \int |\psi|^2 = 1 .$$

The last equation follows from the Parseval relation (Sec. X1). Then by the variation principle (Sec. X3) combined with the definition of norm, this is equivalent to the statement that the operator norm[22] of $\sum_{j=1} \epsilon_j \mathbf{P}_j$ is not greater than 1. Now α_j and β_j can be written in terms of $\mathbf{P}_j$

$$\alpha_j = \text{Trace } (D_{p,\Psi} \cdot \mathbf{P}_j)$$
$$\beta_j = \text{Trace } (D_{p,\Phi} \cdot \mathbf{P}_j) .$$

Since both α_j and β_j are real, for some choice $\epsilon_j = 1$ or -1

$$|\alpha_j - \beta_j| = \epsilon_j \{ \text{Trace } (D_{p,\Psi} \cdot \mathbf{P}_j) - \text{Trace } (D_{p,\Phi} \cdot \mathbf{P}_j) \} .$$

hence,

$$\sum_{j=1} |\alpha_j - \beta_j| = \text{Trace} \left\{ (D_{p,\Psi} - D_{p,\Phi}) \cdot \left(\sum_{j=1} \epsilon_j \mathbf{P}_j \right) \right\} .$$

By an inequality (Sec. X6) the last term is bounded from above by the trace norm of $(D_{p,\Psi} - D_{p,\Phi})$, because the operator norm of $\sum_{j=1} \epsilon_j \mathbf{P}_j$ is not greater than 1 as shown above. Thus there remains the problem of estimating the trace norm of $(D_{p,\Psi} - D_{p,\Phi})$. Since

$$\text{trace norm } (D_{p,\Psi} - D_{p,\Phi}) \leqslant \text{trace norm } \Gamma_1 + \text{trace norm } \Gamma_2 ,$$

where

$$\Gamma_1(x';x) = \int_y \{ \Psi^*(x',y) - \Phi^*(x',y) \} \Psi(x,y)$$

and

$$\Gamma_2(x';x) = \int_y \Phi^*(x',y) \{ \Psi(x,y) - \Phi(x,y) \} ,$$

and by an inequality (Sec. X6)

$$\text{trace norm of } \Gamma_1 \leqslant \left\{ \int |\Psi^* - \Phi^*|^2 \right\}^{\frac{1}{2}} \left\{ \int |\Psi|^2 \right\}^{\frac{1}{2}} = \left\{ \int |\Psi - \Phi|^2 \right\}^{\frac{1}{2}} ,$$

and similarly

$$\text{trace norm of } \Gamma_2 \leqslant \left\{ \int |\Psi - \Phi|^2 \right\}^{\frac{1}{2}} ,$$

the assertion follows.

In the above theorem $\{\Theta_j\}$ are taken common in making both α_j and β_j. Now consider the deviation of pth-order eigenvalues of Φ from those of Ψ. Taking the natural p states $\{\varphi_j\}$ and $\{\psi_j\}$ of Ψ and Φ, respectively, we can write their pth-order eigenvalues in the form

$$\lambda_j = \int \varphi_j^* D_{p,\Psi} \varphi_j$$
$$\mu_j = \int \psi_j^* D_{p,\Phi} \psi_j .$$

In general, $\{\varphi_j\}$ differ from $\{\psi_j\}$, so we have to use another method in order to obtain the estimate.

Theorem 19. When $\{\lambda_j\}$ and $\{\mu_j\}$ are the pth-order eigenvalues of Ψ and Φ, respectively, then

$$\sum_{j=1} |\lambda_j - \mu_j| \leqslant 2 \left\{ \int |\Psi - \Phi|^2 \right\}^{\frac{1}{2}} .$$

Since the generalized Wielandt's theorem (Sec. X7) implies

$$\sum_{j=1} |\lambda_j - \mu_j| \leqslant \text{trace norm } (D_{p,\Psi} - D_{p,\Phi}) ,$$

the assertion follows just as in the preceding theorem.

X. APPENDIXES

1. Expansion

Given a complete orthonormal system $\{\psi_j(x)\}$, every function $\Psi(x)$ can be expanded

$$\Psi = \sum \alpha_j \psi_j ,$$

where

$$\alpha_j = \int_x \psi_j^*(x) \Psi(x)$$

and the following *Parseval relation* holds

$$\sum_{j=1} |\alpha_j|^2 = \int |\Psi|^2 .$$

If the system is not complete, *Bessel's inequality* takes the place of Parseval relation:

$$\sum_{j=1} |\alpha_j|^2 \leqslant \int |\Psi|^2 .$$

2. Schmidt's Orthonormalization

Given a linearly independent system $\varphi_1, \varphi_2, \cdots, \varphi_k$, there exists an orthonormal system $\chi_1, \chi_2, \cdots, \chi_k$ such that each φ_j is a linear combination of $\{\chi_j\}$ and conversely each χ_j is a linear combination of $\{\varphi_j\}$. The system $\{\chi_j\}$ is called Schmidt's *orthonormalization* of $\{\varphi_j\}$.

3. Variational Theorems

Let $\mathbf{E}(x';x)$ be a nonnegative definite kernel with the eigenvalues $\{\lambda_j\}$ in non-increasing order. The

[22] Various definitions in this section are found in Sec. X6.

most well-known variational theorem reads

$$\int \varphi^* \mathbf{E} \varphi \leqslant \lambda_1$$

for every normalized φ. Once the equality holds for some ψ, that Ψ is an eigenfunction belonging to λ_1.

Another important inequality of this type is due to Fan Ky.[23]

For every k orthonormal functions $\psi_1, \psi_2, \cdots, \psi_k$,

$$\sum_{j=1}^{k} \int \psi_j^* \mathbf{E} \psi_j \leqslant \sum_{j=1}^{k} \lambda_j .$$

The proof proceeds as follows. Expanding each ψ_i by the eigenfunctions $\{\varphi_j\}$ of $\mathbf{E}$

$$\psi_i = \sum_{j=1} \alpha_{ij} \varphi_j \text{ with } \alpha_{ij} = \int \varphi_j^* \psi_i ,$$

we have

$$\sum_{i=1}^{k} \int \psi_i^* \mathbf{E} \psi_i = \sum_{i=1}^{k} \sum_{j,l=1} \alpha_{ij}^* \alpha_{il} \int \varphi_j^* \mathbf{E} \varphi_l$$
$$= \sum_{i=1}^{k} \sum_{j,l=1} \alpha_{ij}^* \alpha_{il} \lambda_l \int \varphi_j^* \varphi_l = \sum_{i=1}^{k} \sum_{l=1} |\alpha_{il}|^2 \lambda_l$$

because φ_l is the eigenfunction of $\mathbf{E}$ belonging to λ_l and is orthogonal to φ_j when $j \neq l$. Since $\lambda_j \geqslant \lambda_k \geqslant \lambda_l$ as $j \leqslant k \leqslant l$, from the Parseval relation it follows that

$$\begin{aligned}
&\sum_{i=1}^{k} \int \psi_i^* \mathbf{E} \psi_i \\
&\leqslant \sum_{l=1}^{k-1} \sum_{i=1}^{k} |\alpha_{il}|^2 \lambda_l + \lambda_k \left\{ \sum_{l=k} \sum_{i=1}^{k} |\alpha_{il}|^2 \right\} \\
&= \sum_{l=1}^{k-1} \lambda_l \left\{ \sum_{i=1}^{k} |\alpha_{il}|^2 \right\} + \lambda_k \left\{ k - \sum_{l=1}^{k-1} \sum_{i=1}^{k} |\alpha_{il}|^2 \right\} \\
&= \sum_{l=1}^{k-1} (\lambda_l - \lambda_k) \left\{ \sum_{i=1}^{k} |\alpha_{il}|^2 \right\} + k\lambda_k \\
&\leqslant \sum_{l=1}^{k-1} (\lambda_l - \lambda_k) + k\lambda_k = \sum_{l=1}^{k} \lambda_l
\end{aligned}$$

because Bessel's inequality (Sec. X1) for the orthonormal system $\{\psi_j\}_1^k$ implies

$$\sum_{i=1}^{k} |\alpha_{il}|^2 \leqslant \int |\varphi_l|^2 = 1 .$$

4. Generalized Schwartz's Inequality

If an operator $\mathbf{H}$ is nonnegative definite, for every (not necessarily normalized) function φ and ψ

$$\left| \int \varphi^* \mathbf{H} \psi \right|^2 \leqslant \left\{ \int \varphi^* \mathbf{H} \varphi \right\} \left\{ \int \psi^* \mathbf{H} \psi \right\} .$$

In particular, when $\mathbf{H} = \mathbf{I}$ (the identity operator)

$$\left| \int \varphi^* \psi \right|^2 \leqslant \int |\varphi|^2 \cdot \int |\psi|^2 .$$

The proof proceeds as follows. On putting

$$A = \int \varphi^* \mathbf{H} \varphi , \quad B = \int \psi^* \mathbf{H} \psi , \quad C = \int \varphi^* \mathbf{H} \psi$$

and $\qquad \alpha = -C^*/B ,$

nonnegative definiteness implies

$$\int (\varphi + \alpha\psi)^* \mathbf{H} (\varphi + \alpha\psi) \geqslant 0 ,$$

that is,

$$A + |\alpha|^2 B + \alpha C + \alpha^* C^* \geqslant 0$$

and substitution of α yields

$$A \cdot B \geqslant |C|^2 .$$

5. Scaling

Given two normalized functions Ψ and Φ,

$$\min_{\alpha} \int |\Psi - \alpha\Phi|^2 = 1 - \left| \int \Psi^* \Phi \right|^2 ,$$

where α varies over all complex numbers.
In fact, since

$$\int |\Psi - \alpha\Phi|^2 = 1 + |\alpha|^2 - 2 \operatorname{Re} \left[\alpha \int \Psi^* \Phi \right] ,$$

with $\alpha = \beta e^{i\theta}$ and θ such that

$$e^{i\theta} \int \Psi^* \Phi = \left| \int \Psi^* \Phi \right| ,$$

it follows that

$$\int |\Psi - \alpha\Phi|^2 = 1 + |\beta|^2 - 2 \left| \int \Psi^* \Phi \right| \times \operatorname{Re} (\beta) .$$

Thus, to obtain the minimum in question, it suffices to make β vary over all real numbers; consequently, the problem is reduced to an elementary calculation of a real quadratic function, and the minimum is attained at $\beta = |\int \Psi^* \Phi|$.

6. Norms of an Operator[24]

It is sometimes convenient to introduce several kinds of norms for a linear operator. Let $\mathbf{G}(x';x)$ be a general integral kernel and let $\{\lambda_j\}$ be the eigenvalues of the (nonnegative definite) composite kernel

$$\mathbf{H}(x';x) = \int_y \mathbf{G}^*(x';y) \mathbf{G}(x;y) .$$

[23] Fan Ky, Proc. Natl. Acad. Sci. U. S. **37**, 760 (1951).

[24] For the detailed exposition, see R. Schatten, *Norm Ideals of Completely Continuous Operators*, Vol. 27, Chaps. II–III, in *Ergebnisse der Mathematisch* (Springer-Verlag, Berlin, 1960).

Then the norms of **G** are defined by the following formulas:

$$\text{Operator norm}: ||\mathbf{G}||_\infty = (\lambda_1)^{\frac{1}{2}}$$

$$\text{Schmidt norm}: ||\mathbf{G}||_2 = \left\{\sum_{j=1} \lambda_j\right\}^{\frac{1}{2}},$$

$$\text{Trace norm}: ||\mathbf{G}||_1 = \sum_{j=1} (\lambda_j)^{\frac{1}{2}}.$$

The inequalities used in this note are the following:
For every kernel **G**

$$|\text{trace } \mathbf{G}| \leqslant \text{trace norm } \mathbf{G}.$$

Given another kernel $\mathbf{F}(x;y)$, define the composite kernel

$$\mathbf{L}(x';x) = \int_y \mathbf{F}(x',y)\mathbf{G}(x,y);$$

then
$$||\mathbf{L}||_1 \leqslant ||\mathbf{F}||_2||\mathbf{G}||_2$$

$$||\mathbf{L}||_1 \leqslant ||\mathbf{F}||_\infty||\mathbf{G}||_1 \text{ and } ||\mathbf{L}||_1 \leqslant ||\mathbf{F}||_1||\mathbf{G}||_\infty .$$

The Schmidt norm is conveniently evaluated. In fact, it is easily seen that

$$\int_{x,x'} |\mathbf{G}(x;x')|^2 = \sum_{j=1} \lambda_j .$$

Moreover, for an arbitrary complete orthonormal system $\{\psi_j\}$, the following (Schmidt's theorem) is valid

$$\sum_{j=1} \int_x \left| \int_{x'} \mathbf{G}(x';x)\psi_j(x')\right|^2 = \int_{x,x'} |\mathbf{G}(x';x)|^2 .$$

This can be proved by expanding $\mathbf{G}(x';x)$, as a function of x', in terms of $\{\psi_j(x')\}$ and then applying the Parseval relation.

7. Wielandt's Inequality

Given two $N \times N$ Hermitian matrices **A** and **B** with eigenvalues $\{\lambda_j\}$ and $\{\mu_j\}$ in non-increasing order, respectively, Wielandt's theorem[25] reads

$$\sum_{j=1}^{N} |\lambda_j - \mu_j| \leqslant \sum_{j=1}^{N} |\rho_j| ,$$

where $\{\rho_j\}$ are the eigenvalues of $\mathbf{A} - \mathbf{B}$. This can be modified for the integral kernels.

Let **F** and **G** be two nonnegative definite kernels with the eigenvalues $\{\lambda_j\}$ and $\{\mu_j\}$, respectively; then

$$\sum_{j=1} |\lambda_j - \mu_j| \leqslant \text{trace norm } (\mathbf{F} - \mathbf{G}) .$$

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[25] H. Wielandt, Proc. Am. Math. Soc. 6, 106 (1955).

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Wave and Reaction Operators in the Quantum Theory of Many-Particle Systems*

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1. INTRODUCTION

THE basic problem in the current quantum theory of matter is the solution of the many-particle problem connected with the Schrödinger equation $\mathcal{H}\Psi = E\Psi$ for the stationary states. For atomic, molecular, and solid-state systems, the problem is simple in the sense that the Hamiltonian is assumed to be at least approximately known, whereas for nucleonic systems the interaction potentials are still not determined. Here we concentrate essentially on the general features of many-particle systems having a Hamiltonian of the form:

$$\mathcal{H}_{\text{op}} = \sum_i \mathcal{H}_i + \sum_{i<j} \mathcal{H}_{ij} + \sum_{i<j<k} \mathcal{H}_{ijk} + \cdots . \quad (1)$$

In the theoretical interpretation of the experimental data for electronic systems, the so-called "in-

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